Mineralogy

Native silver crystals

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Written by Dexter Perkins, University of North Dakota (2020); minor edits subsequently.

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Contributors
This book was a team effort. In addition to the principal author, significant contributions came from Miranda Shanks, Elizabeth Perkins, Douglas Perkins, Kevin Henke, Alyssa Schultz, Paige Tibke, Hunter Morris, and Josh Crowell.

Companion Book

If you find this book of value, you may wish to check out the companion Open Petrology text.

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The visuals, especially the photos, are one of the things that make this book what it is. As of September 2020, the book contains 1,028 figures; almost all are full color and most are photographs. And, the majority of the photos came from Wikimedia Commons or others websites where selfless individuals have made their material available under a Creative Commons license for educational purposes. We have put figure credits at the end of every chapter. But, a number of individuals deserve special recognition for all the terrific photos they have shared: James St. John, Didier Descouens, Robert M. Lavinsky, Géry Parent, Marie Lan Taÿ Pamart, Siim Sepp, Andrew Silver, Eurico Zimbres, Amcyrus2012, Alex Strekeisen, Chmee2, Kevin Walsh, Teravolt, Acroterion, Amotoki, Bereket Haileab, Brocken Inaglory, Daniel Mayer, Graeme Churchard, Jan Helebrant, John Krygier, Kelly Nash, Leon Hupperichs, Mike Norton, R. Weller, Raike, Roy Goldberg, Walter Siegmund, and Woudloper. Unbeknownst to them, every one of these individuals contributed multiple photos to this project.

Ongoing Project

The nature of this kind of book means that it is always an ongoing project. If you see need for changes or additions of any sort, please email the main author at: dexter[dot]perkins[at]und[dot]edu. If we make any major changes, we will describe them here on the title page.

Web Browsers

Different web browsers have different quirks. For the best and most consistent results, we recommend using Chrome and recommend against using Firefox when viewing this book. But, sometimes Chrome does not show the same sharp images that Firefox does. So, the bottom line is that you should try several browsers and use the one that works best for you. They will NOT be the same. Additionally, we warn that many tables will not render well on small screens, and not at all on cell phones.

1 Introduction

1.1 Blue cavansite (a calcium-vanadium silicate) on top of silvery heulandite (calcium-sodium aluminosilicate)

1 Introduction

KEY CONCEPTS

- Minerals make up just about everything on our planet and are important for our daily lives.
- Minerals in rocks or sediment make up the material we walk on and form the foundations for buildings and other structures.
- Mineral resources have long been used by people; today they are keys to modern agriculture and industry.
- The knowledge gained by studying minerals has wide ranging applications.

- Most minerals are naturally occurring homogeneous geological substances that are stable at Earth-surface conditions.
- Minerals are inorganic compounds and are crystalline solids.
- Non-crystalline materials, synthetic minerals, biological minerals, and anthropogenic minerals are not, in general, considered to be true materials.
- We generally classify minerals based on their chemical compositions and atomic arrangements.

1.1 The Importance of Minerals

1.2 Bedrock on the California coast with the Golden Gate Bridge in the background

Minerals are our planet. They form the Earth and the bedrock that we live on, making up all of Earth’s rocks and sediments, and they are important components in soils. So, they literally are the foundations for our lives. Perhaps because they are ubiquitous, most people don’t even notice them or consider that all rock is made of minerals. But, engineers do because building a bridge or other structure on unstable material, or using poor ingredients for construction of all sorts, would lead to disasters. And, farmers care about minerals because healthy soils produce great crops. Petrologists who study rocks of all sorts need to know about minerals. And others who use resources in manufacturing need minerals. So, the world’s people rely on minerals. And, minerals, mineral production, and the study of minerals are absolutely essential to maintain our lifestyles.

1.3 Bronze Age spearheads and ferrules

The use and processing of minerals goes back more than 4,000 years. In fact, archaeologists and anthropologists define major periods of early human civilization based on mineral resources that were used. The late Stone Age, also called the Neolithic Age, was followed by the Chalcolithic Age from 4,500 to 3,500 BCE (Before Common Era) when people started using native copper to make tools and other artifacts. The Bronze Age that followed the Chalcolithic Age began in the Mesopotamian civilization of Sumeria and lasted from 4,200 to 1,000 BCE. During this time people combined mineralogical tin and copper and the result was bronze – a metal alloy that was stronger and more durable than copper. Some early cultures progressed to the Chalcolithic and Bronze Ages before others;

even today, some Stone Age cultures still exist. Figure 1.3 shows some Bronze Age artifacts.

The Iron Age followed the Bronze Age, beginning around 1,500 BCE, when the Hittite society of ancient Anatolia (modern day Turkey) discovered how to smelt iron. The iron came from native iron in meteorites that also contained small amounts of nickel. Fortuitously, the nickel produced an alloy superior to pure iron. So, copper, tin, iron, and nickel were all important during the early ages of humans. They are equally important today. These metals – and many others – are key parts of a seemingly infinite number of products we use every day. The metals come from minerals.

Ask most people today why minerals are important, and they will probably mention diamonds and other gems, or perhaps precious metals such as gold or silver. Gems and gold are important, but other minerals resources are equally, or substantially more, important. Highways and buildings, fertilizers, cars, jewelry, computers and other electronic devices, kitchenware, salt, magazines, vitamins and medicines, and just about everything that supports modern living require mineral resources for production. We are addicted to minerals and related commodities.

1.1.1 Mineral Commodities

The table below, from the United States Geological Survey, lists some mineral commodities deemed essential for modern living, and the amounts that a typical person consumes in their lifetime. The list includes both metals derived from minerals (some minerals are listed in the right-hand column) and rock materials, such as stone or sand, that are made of minerals.

Metallic Commodities		
metal	lifetime needs	primary ore mineral

aluminum (bauxite)	5,677 pounds	bauxite
cement	65,480 pounds	calcite in limestone or related rocks
clay minerals	19,245 pounds	clays in sedimentary deposits
copper	1,309 pounds	copper sulfide minerals
gold	1,576 ounces	native gold in hard rock or sediments
iron	29,608 pounds	magnetite and hematite
lead	928 pounds	galena
phosphate rock	19,815 pounds	apatite
stone, sand, and gravel	1.61 million pounds	mineral mixtures in sedimentary deposits
zinc	671 pounds	sphalerite

Overall, modern society uses stone, sand, gravel and other construction materials more than other mineral commodities. Construction materials are generally mixtures of different minerals and are prized for their overall properties, not the properties of the individual mineral components. We also use large amounts of what are termed industrial minerals – resources valued for their mineralogical properties. Industrial minerals include limestone, clays, bentonite, silica, barite, gypsum, and talc.

1.1.2 Ore Minerals

Ore Minerals
aluminum bauxite (mix of Al-hydroxides)

copper	bornite	Cu_5FeS_4
	chalcocite	Cu_2S
	chalcopyrite	$CuFeS_2$
	malachite	$Cu_2CO_3(OH)_2$
chrome	chromite	$(Fe,Mg)Cr_2O_4$
lead	galena	PbS
iron	hematite	Fe_2O_3
	ilmenite	$FeTiO_3$
	magnetite	Fe_3O_4
molybdenum	molybdenite	MoS_2
manganese	pyrolusite	MnO_2
tungsten	scheelite	$CaWO_4$
	wolframite	$(Fe,Mn)WO_4$
zinc	sphalerite	ZnS

Ore minerals are especially significant to our daily lives. These are minerals that are mined and processed for the elements they contain. Some of the most important elements include iron, aluminum, copper, zinc, and other metals associated with steel making and modern industry. The table to the right lists common ore minerals for a number of important metals. These minerals are prized because they contain a large amount of the desired metal and because processing to remove the metal is relatively easy.

1.4 Malachite (green) and azurite (blue) from Morenci, Arizona. Both minerals are hydrated copper carbonates.

This photo (Figure 1.4) shows a rock containing the ore minerals azurite (blue) and malachite (green). The specimen comes from the Morenci Mine, the most productive of about a dozen copper mines in Arizona. Arizona produces more copper than any other U.S. state. Although copper is mined around the world, Chile is the biggest producer by far.

People produce and use huge amounts of copper, iron, aluminum, and some other metals, but production statistics do not reflect the true importance of some mining operations. Small amounts of rare elements, for example gallium, indium, and selenium, derived from equally rare minerals, and only produced in small quantities, are keys to fast computers, smart phones, and other cutting edge devices. Minerals are produced, bought, and sold on a world market. And, mineral resources are not everywhere. So, today, the United States does not produce gallium, indium, selenium, and some other metals in sufficient amounts to meet our needs. We are entirely dependent on imports for about 20 important mineral commodities.

1.1.3 The Importance of Crystallography

So, we prize mineral commodities and ore minerals because they provide resources that support our lifestyles. But, the science of mineralogy is important in other ways. In particular, crystallography, the branch of mineralogy that deals with the formation and properties of crystals, plays a huge role in our daily lives. Knowledge of crystals and their properties, and the technology that comes from them, are fundamental to electronics, and to modern living.


1.5 Silicon video chip in circuit board

For example, the silicon chips in electronic devices (Figure 1.5), semiconductors and microchips of many sorts, and the LCD (liquid crystal display) screen on a smart phone are all crystalline. Light emitting diodes (LEDs) are commonplace in TV screens, light bulbs, and other devices. LEDs are crystalline. Electronic clocks in devices of many sorts, microphones and telephones, pickups for guitars, and ultrasound devices in hospitals are based on the piezoelectric effect of a quartz crystal. And roof-top photovoltaic systems use crystalline materials to generate electricity.

It is, perhaps, a stretch for mineralogists to claim credit for modern electronic devises. After all, most of the crystalline materials used in modern electronic applications today are synthetic. Yet they all have natural analogs. And, in large part, it was the study of those analogs and other investigations of mineral crystals that were the start that led to today’s industries based on crystal technology.

1.2 Definition of a Mineral

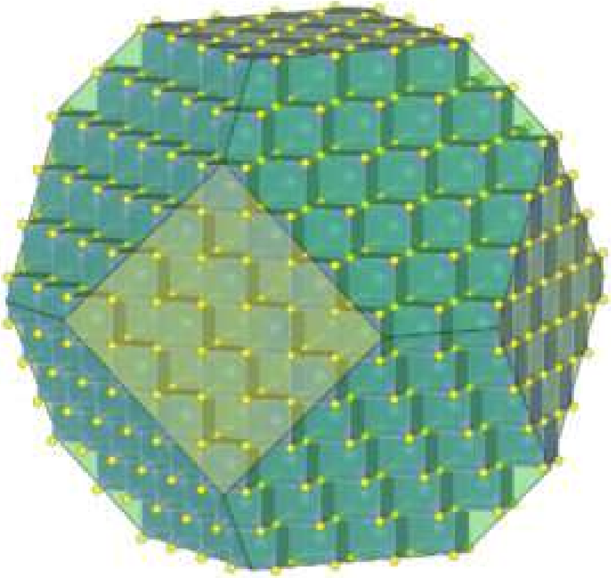
The word *mineral* means different things to different people. In ancient times, people divided all things on Earth into the animal, vegetable, or mineral kingdoms, so a mineral was any natural inorganic substance. Today, dieticians use the term to refer to nutritional elements such as calcium, iron, or sodium, while miners often use it for anything they can take out of the ground—including coal, sand, or gravel. Mineralogists have their own definition.

1.2.1 Traditional Definition

James D. Dana (1813-1895), who developed the first widely used mineral classification system (which forms the basis of the one used today), defined a mineral as “. . . a naturally occurring solid chemical substance formed through biogeochemical processes, having characteristic chemical composition, highly ordered atomic structure, and specific physical properties.”

Dana’s definition was arguably the first, but more recent definitions have been quite similar. Some sticking points today are whether minerals can be wholly or partly *anthropogenic* (created by human activity, such as crystalline compounds in coal ash), whether minerals may have biological origins, and whether some mineral-like, non-crystalline materials can be considered minerals.

The International Mineralogical Association (IMA) is the most widely recognized authority on mineral names and nomenclature. The IMA has developed specific criteria that must apply for a substance to be considered a mineral. Today, the IMA list of approved minerals contains 6,000-7,000 entries (http://cnmnc.main.jp/). Many of the names, however, were “grandfathered-in.” They were approved for historical reasons but do not meet the current IMA criteria. And other names, such as *olivine* and *biotite*, that are commonly used to refer to minerals, are not on the list because they do not have specific compositions. Olivine is a general name given to minerals that are primarily solutions of fayalite and forsterite, and biotite refers to micas with compositions between annite and phlogopite.



1.6 Ions in a fluorite crystal

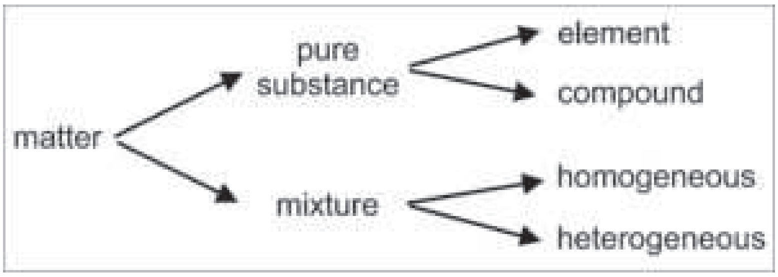
The requirement that minerals have highly ordered structures means that they must be crystalline – which is a key thing that separates minerals from many other solid materials. The drawing in Figure 1.6 shows calcium and fluorine ions in a crystal of fluorite. The fluorine ions (small and yellow) are at the corners of cubes called *unit cells*; the calcium ions (larger and lighter colored) are in the centers of the unit cells.

The model crystal in Figure 1.6 contains a few hundred unit cells and the crystal faces have “steps” in them. A real fluorite crystal, if large enough to see, will contain more than 10^{20} unit cells. If the crystal contains no defects, the unit cells stack together in an orderly and repetitive way – as in this model drawing – but cells are so small that crystal faces are smooth.

For more discussion about what constitutes a mineral, try this video:

▶ Video 1-1: What is a mineral? (9 minutes)

1.2.2 Matter and Minerals



1.7 Different kinds of matter

All matter can be classified as being either an *essentially pure substance* or a *mixture* (Figure 1.7). Mixtures, in contrast with pure substances, are made of two or more substances that can differ in composition or properties, and that can be separated from each other. Some mixtures are *homogeneous* (like a drink in which gin and tonic are completely mixed) and some are *heterogeneous* (like a gin and tonic with ice cubes floating in it), but they can always be separated into individual and different substances using some sort of physical process. Most rocks are examples of mixtures – they can be separated into individual mineral components that have different properties.

1.8 Quartz crystals

Minerals and other pure substances have invariant compositions and distinctive properties. This means that although we can often divide a pure substance into portions, all portions are equivalent and have the same overall composition and properties. For example, we can take a large piece of quartz, perhaps any of the quartz crystals in Figure 1.8, and break it into smaller pieces – the pieces will all still be quartz, the atoms in every piece will all be arranged the same way, and all pieces will have the same hardness and other properties.

Pure substances, including minerals, may be made of a single element, for example argon gas (Ar) or the mineral copper (Cu). Or, they may be compounds made of two or more elements in fixed proportions. Quartz (SiO_2), consisting of two elements (silicon and oxygen), is a very common natural compound. Other minerals may consist of more than two elements, and some contain many elements.

1.9 Sand from South Point, Hawaii

Some sand is made of a single mineral, perhaps quartz or gypsum, but most sand is a mix of materials. The sand seen in Figure 1.9 is a good example of a geological mixture. Most sand is made predominantly of quartz, sometimes also containing heavy minerals such as magnetite. This sand is different. It contains several minerals (1 mm sized green olivine grains are most dominant), some black volcanic glass, and two kinds of shell fragments (one white and one with pinkish stripes). We can, in principle, separate all the different components from each other. (Although it would probably be quite tedious.) Note that, except for the shell fragments, all the grains in this sand are very well rounded. This is because they were abraded while being transported before deposition.

● Box 1-1 The Standard Definition of a Mineral

Minerals are:

- naturally occurring
- crystalline solids
- formed by geological processes
- elements or compounds
- homogeneous
- characterized by a well-defined composition that can be described by a formula

So, although the definition of a mineral is sometimes debated today, for most purposes it is sufficient to say that minerals are natural crystalline solids that generally form by geological processes. They must also be elements or compounds with a well-defined chemical composition that can be described by a chemical formula. The few exceptions to these criteria are dealt with on a case-by-case basis by the International Mineralogical Association (IMA) and others who are tasked with keeping track of all approved minerals.

1.2.3 Minerals and Mineral Varieties

1.10 Dogtooth spar is named after the crystal shape

1.11 Iceland spar is a clear variety of calcite

An individual mineral species, such as calcite, is defined by its unique chemical and physical properties. All calcite is mostly $CaCO_3$, with atoms arranged in the same way, no matter the size or shape of the sample. However, calcite, like many other minerals, has more than one named *variety*, based on crystal shape, composition, color, occurrence, or other things. *Dogtooth spar* – an example is in Figure 1.10 – is a distinctive variety of calcite found in some caves, and *Iceland spar* (Figure 1.11) is a clear variety typically in cleavable rhomb shapes.

Gemologists often name mineral varieties based on color. Three varieties of beryl are shown below in Figures 1.12, 1.13, and 1.14. Beryl is called *aquamarine* if it has a light blue color, *emerald* if it is green, and *morganite* if it is pink. The different colors stem from very small compositional differences; all beryl is essentially $Be_3Al_2Si_6O_{18}$. Aquamarine, however, contains small amounts of Fe^{2+}, emerald contains small amounts of chromium (Cr^{3+}) and vanadium (V^{3+}), and morganite contains Mn^{2+}. Even small amounts of these transition metal ions can give minerals strong coloration.

1.12 Aquamarine (beryl)

1.13 Emerald (beryl)

1.14 Morganite (beryl)

1.2.4 Synthetic Minerals and Simulants

1.15 Synthetic zeolite

According to the definition given above, minerals must form by natural geological processes. However, synthetic minerals are commonly synthesized for industrial or commercial use. For example, zeolites sold as health products, such as the product shown here, are generally synthetic. And, because zeolites are natural sieves and sorbents, synthetic zeolites are used in water softeners, and in chemical manufacturing processes. The synthetic zeolites are fundamentally the same as naturally occurring minerals – they share many of the same properties – but are prized for engineering and industry because they have purer compositions and more consistent physical properties.

Gem	Mineral
ruby	corundum
sapphire	corundum
diamond	diamond
emerald	beryl
aquamarine	beryl
amethyst	quartz
citrine	quartz
alexandrite	chrysoberyl
moonstone	K-feldspar
topaz	topaz
zircon	zircon
opal	opal

And, we make many synthetic gems, too, today; we have been doing so for almost 150 years. Some of these “fake” gems are beautiful and valuable. Common ones include ruby, sapphire, diamond, emerald, amethyst, citrine, and alexandrite. The table lists these gemstones and others that may be synthesized, along with and their mineral equivalents. Some of the gems have the same name as their mineral equals; but many do not. Ruby and sapphire are both varieties of corundum, amethyst and citrine are varieties of quartz, emerald is a variety of beryl, and alexandrite is a variety of chrysoberyl.

Manufacturers also make other gem-like synthetic crystalline materials that have no natural mineral analogs. They are commonly called *simulants* and include, among others, forms of cubic zirconia, titanium oxide and strontium titanate that look something like diamonds. Synthetic gemstones and simulants are often of high quality and mimic natural minerals well – they may be unflawed and more perfectly formed than natural gems. It is sometimes difficult to tell synthetics from the real thing. For this reason, some people do not distinguish between synthetic and natural minerals.

1.16 Natural corundum

1.17 Synthetic rubies

The two photos of red stones (left) are natural corundum from Tanzania and synthetic corundum grown in a laboratory. The synthetic corundum was faceted (ground) to give it flat faces and sparkle. We call red varieties of corundum, like the corundum shown, *ruby*. Corundum of any other color is called *sapphire*. Blue sapphires are most common, but pink, yellow, and other colors exist.

1.19 Natural topaz crystal

1.18 Synthetic topaz

The blue stone in Figure 1.19 is natural topaz from Sri Lanka. Strong aquamarine blue is a rare color for topaz, which is typically clear or light colored. So, most commercial blue topaz is treated to enhance its blue color. The faceted stones in Figure 1.18 are natural topaz that has been treated. Note that the natural topaz, and the natural corundum above, contain crystal faces that formed as the mineral crystallized. The compositions and crystallinity of synthetic corundum and other synthetic minerals are nearly identical to natural specimens, but the synthetics are not considered true minerals.

1.2.4 Crystalline and Non-Crystalline Mineral Materials

Later chapters will discuss crystals and crystallinity in more detail. For now, it is sufficient to know that crystalline means “having an orderly and repetitive atomic structure.” The definition of a mineral given above includes all crystalline materials made by geological processes. Because minerals are crystalline, they must be solids. However, the International Mineralogical Association (IMA) has granted a special exception to mercury.

1.20 Cinnabar with native mercury

Mercury, although liquid under Earth-surface conditions, is considered a mineral because it is a naturally occurring native element like copper, gold, silver, and several others (that are solids except at high temperature). Figure 1.20 shows red, partially cubic crystals of the mineral *cinnabar* (mercury sulfide) from a famous mineral locale near Almaden, south of Madrid in Spain. Also seen are shiny droplets of silver-colored liquid mercury. Both cinnabar and mercury are minerals. Note that water, the most common natural liquid at Earth’s surface is not a mineral, but ice – crystalline H_2O – meets every requirement of the definition and is.

1.21 Obsidian and other volcanic debris in Iceland

Some natural geological substances appear a lot like minerals but are not crystalline. Instead, they are *amorphous* solids, meaning they contain a random arrangement of atoms. With a few exceptions (*e.g.*, the copper carbonate *georgeite*), such materials are not accepted as minerals by the IMA and are generally called *mineraloids*. Examples of mineraloids include obsidian and several other varieties of natural volcanic glass. This photo shows black obsidian in Iceland. The material surrounding the obsidian is made of scoria and other volcanic debris. Obsidian and other volcanic glasses form when lava cools so quickly that atoms do not have time to arrange themselves in an orderly and repetitive way.

1.22 Opal

Opal contains silicon and oxygen. It has about the same composition as quartz but contains up to 10% water. On an atomic scale, opal is not crystalline; it comprises spheres of silica (SiO_2), 150-300 nanometers in diameter, arranged in a random pattern. The spheres cause light refraction and give some opal a beautiful appearance with rainbow-like colors. If the colors change when the sample is viewed at different angles, we call the property a *play of colors*. The sample in Figure 1.22, from Ethiopia, displays a beautiful example of play of colors. Because of its play of colors, and because it is very hard, opal is often a much-prized gemstone. The most common kind of opal is like the opal shown, with a rainbow of pastel hues. Black opal is darker colored in blue, gray and green. Fire opals contain brilliant sparks of red, yellow and orange. Like mercury, the IMA has granted opal the right to be called a mineral even if it is not crystalline.

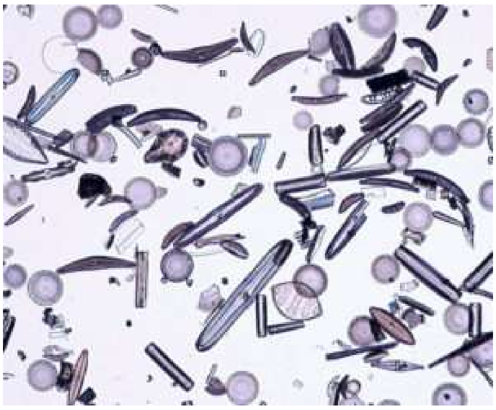
Agate and *chalcedony*, two varieties of microcrystalline silica (SiO_2) related to opal, have the same composition as quartz, but strictly speaking are not minerals because they are not crystalline. They also, typically, consist of more than one mineral. Some mineralogists, however consider agate and chalcedony to simply be textural varieties of quartz.

1.2.5 Biominerals

Some living organisms produce crystalline materials through a process called *biomineralization*. The result may be shells or skeletal parts or simply the hardening of soft tissues. Mineralogists have identified more than 60 different biominerals created by animals, plants, fungi, and smaller organisms; three examples are shown below in Figures 1.23 through 1.25.


1.23 Clamshell


1.24 Teeth


1.25 Diatoms

Organisms that produce biominerals in shells, teeth, skeletons, or bones have existed for nearly 600 million years. Their hard parts are typically composed of organic equivalents of the minerals calcite (calcium carbonate – that makes up the shell shown) and apatite (calcium phosphate – that makes up the teeth shown).

Biogenic processes produce other mineral equivalents too. For example, diatoms (like those seen in Figure 1.25), algae and sponges create structures made of various forms of silica – which is sometimes crystalline (and sometimes amorphous). And, bacteria deposit iron, copper and gold minerals, including iron oxides/hydroxides such as magnetite, goethite, and limonite. Some marine organisms produce aragonite, which is normally only stable under high pressures deep within Earth.

The IMA definition says that a substance is not considered a mineral if it was formed entirely by an organic process. Sometimes, however it is difficult to make this distinction. In some limestones, for example, it is impossible to determine whether a mineral grain precipitated from water (inorganic) or is a biomineral (organic). And, today, some people consider biominerals to be the same as any other minerals. They note the many different kinds of crystalline biogenic substances that, in many cases, are nearly identical to naturally occurring minerals. Additionally, the IMA makes exceptions for some substances formed from organic material by geological processes, such as minerals that crystallize from organic matter in shales.

1.2.6 Anthropogenic Minerals

1.26 Simonkolleite, a hydrated zinc chloride

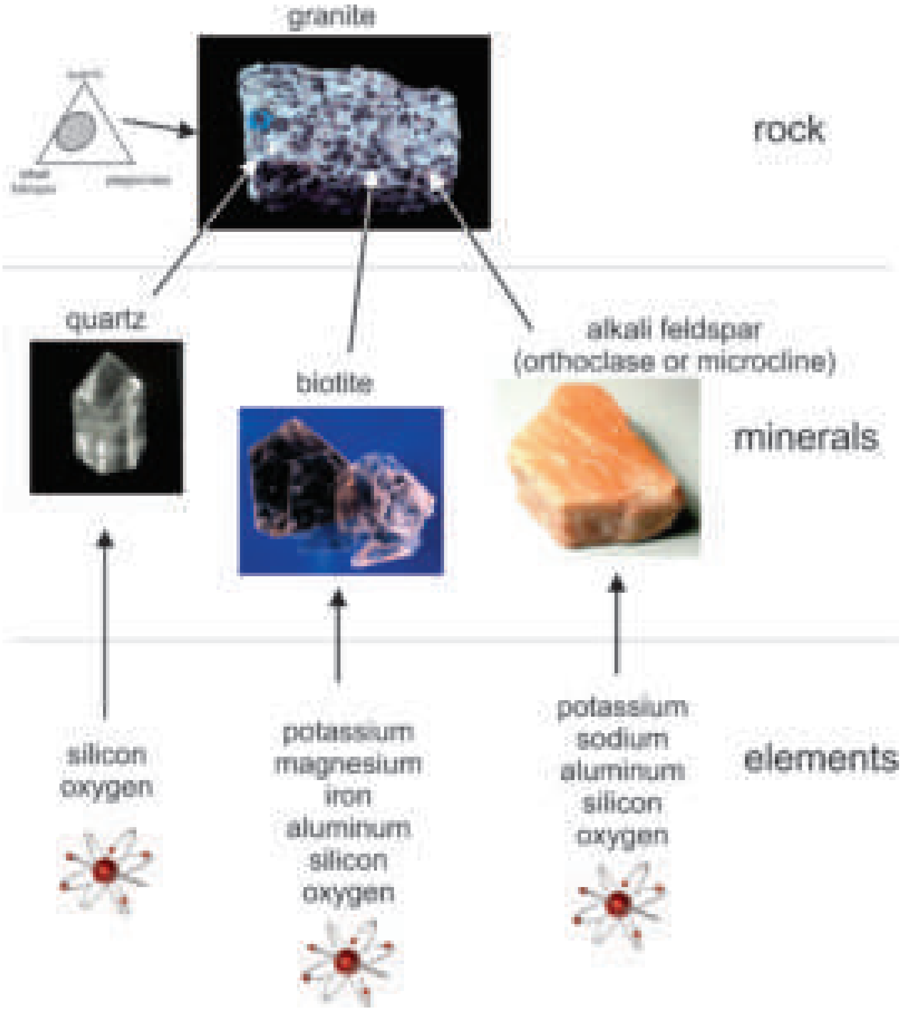
Crystalline materials that derive from human-produced materials or actions, but meet the definition of a mineral in other ways, are sometimes considered minerals — but generally not. For example, the rust that forms on our cars is not considered a mineral (although the mineral *goethite* has nearly the same composition and properties). And *simonkolleite*, a hydrated zinc chloride mineral (Figure 1.26), has been found in some smelter slag but nowhere else.

In 2017 Robert Hazen identified 208 distinct mineral species – all approved by the IMA – that only exist because of human activities and materials. There are no natural analogs. Most of the 208 derive from mining activities – perhaps as scaling on mine walls, as new compounds created in mine dumps, or as precipitates at high temperature in smelters or at low temperature from mine waters. A few developed by alteration of human materials, for example due to weathering of ancient lead or bronze artifacts. In 1998, the IMA decided that, going forward, no substances derived from human-created materials or activities could be called a mineral. But, they have made a few special exceptions since then and have “grandfathered in” many previously identified mineral species.

1.27 Martyite, an anthropogenic mineral containing zinc and vanadium

The photo seen in Figure 1.27 shows red-orange *martyite*, a zinc-vanadium hydrated mineral that precipitated from mine waters flowing from the Blue Cap Mine near Moab, Utah. This mineral would not exist if it were not for mine waste waters flowing through tailings piles. It was officially approved as a mineral in 2007 and retains that honor today.

1.3 Elements, Minerals, and Rocks



1.28 Elements, minerals, and rocks

This figure (1.28) shows the relationships between elements (bottom), minerals (center), and rocks (top). Elements, singly or in combination, make up minerals. For example, some of the most common elements in Earth’s crust make up the minerals quartz, alkali-feldspar, and biotite. Minerals, singly or in combination, make up rocks. For example, subequal amounts of quartz and alkali-feldspar, sometimes with biotite and plagioclase, make up granite, a common crustal igneous rock (triangular diagram at the top of the figure).

All minerals, like all materials, consist of one or more elements, the building blocks of all matter. Some minerals, diamond for example, contain a single element (carbon). Others contain many elements. Some minerals have compositions that vary little in nature. Quartz for example is always close to 100% silicon and oxygen in the atomic ratio 1:2. Other minerals incorporate elemental substitutions, so their compositions may vary a great deal from sample to sample. Biotite, for example, always contains potassium, magnesium, iron, aluminum, silicon, and oxygen. It generally also contains lesser amounts of manganese, sodium, titanium, and many other elements, so natural biotite compositions are quite variable.

Rocks are aggregates of one or more minerals, mineraloids, and organic components. Rocks may form when minerals grow (*crystallize*) together, forming a *crystalline rock*, such as the granite shown above. They also can form when loose grains are cemented together, forming a *clastic rock*, such as sandstone. Crystalline rocks may form from a magma (*e.g.*, granite), may form by metamorphism (*e.g.*, gneiss), or may form by precipitation from water (*e.g.*, gypsum). Most clastic rocks form from consolidated sediments, but some form by volcanic processes.

1.29 Dunite

Some rocks contain only one kind of mineral. Limestone (rock), for example, is often pure calcite (mineral). Anorthosite (rock) is made mostly or entirely of plagioclase (mineral). Quartzite (rock) may be made only of quartz (mineral). Dunite (Figure 1.29), an igneous rock that crystallizes from magma, is often nearly 100% olivine (mineral). The dunite shown in the photo also contains a few dark grains of chromite. (Other rocks contain virtually no minerals, such as pumice, which is almost entirely volcanic glass, and coal, which is mostly organic materials.)

1.4 Classifying Minerals

Chemical formulas form the basis for the standard mineral classification system used today. It is generally called the *Dana System of Mineralogy* and was created in the mid-19th century by an American mineralogist, James Dwight Dana. The system has been modified and fine-tuned several times since its inception and large classes have been subdivided. But the fundamental classes have not changed. The beauty of this system is that it is relatively straightforward for most minerals and requires no information other than chemical formula. A small number of minerals belong to more than one class, but for the most part classification is unambiguous.

At the largest scale, we divide minerals into classes. The table below lists the most important classes and key characteristics of their formulas. For example, all silicate minerals contain Si and O. Halides contain Cl, F, Br , or I. Hydroxides contain OH, carbonates contain CO_3, and so forth. Oxide minerals are those that contain oxygen but do not belong to one of the other classes. The column on the right gives a sample mineral (and formula) for each class.

Mineral Classes		
class	**key elements or molecules**	**example mineral**
silicates	Si and O	quartz – SiO_2
halides	Cl, F, Br , I	halite – NaCl
hydroxides	(OH)	gibbsite – $Al(OH)_3$

carbonates	(CO_3)	calcite – $CaCO_3$
nitrates	(NO_3)	nitratite – $NaNO_3$
borates	(BO_3) or (BO_4)	sinhalite – $MgAlBO_4$
sulfates	(SO_4)	gypsum – $CaSO_4 \bullet 2H_2O$
chromates	(CrO_4)	crocoite – $PbCrO_4$
tungstates	(WO_4)	scheelite – $CaWO_4$
molybdates	(MoO_4)	wulfenite – $PbMoO_4$
phosphates	(PO_4)	apatite – $Ca_5(PO_4)_3(OH,F,Cl)$
arsenates	(AsO_4)	scorodite – $FeAsO_4 \bullet 4H_2O$
vanadate	(VO_4)	vanadinite – $Pb_5(VO_4)_3Cl$
oxides	O	corundum – Al_2O_3
native elements	single elements	copper – Cu
sulfides	S	pyrite – FeS_2
sulfosalts	As, Sb	niccolite – NiAs

1.30 Siderite (a carbonate) “roses”

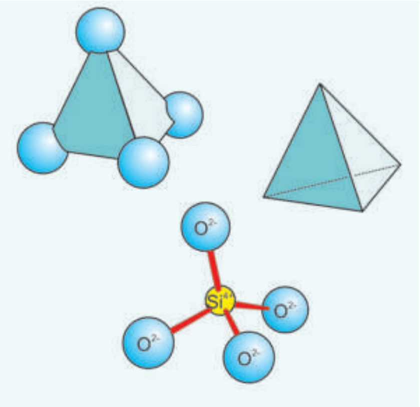
1.31 Pyrite (a sulfide) cubes

Dividing minerals into classes this way is convenient because we can determine class from chemical formula. Furthermore, minerals within a single class are often found together. Besides being convenient, however, this classification scheme makes sense in other ways. Within each class, the type of structure and bonding are somewhat similar. This means that minerals within a class often have similar physical properties, making the classes useful in mineral identification. Such would not be the case if we divided minerals into groups based on Fe or other transition metals. For example, the carbonate mineral siderite ($FeCO_3$) and the sulfide mineral pyrite (FeS_2), pictured here, both contain Fe, but have few properties in common. The siderite (Figure 1.30) is in the form of “roses” and is on top of quartz and chalcopyrite. The pyrite (Figure 1.31) is in golden cubes surrounded by quartz grains in sandstone.

The IMA officially recognizes more than 5,500 minerals (5,650 as of December, 2020). About half are named after people, the rest mostly have names that refer to discovery locations, chemical compositions, or to mineral properties. Most common minerals belong to the silicate, oxide, hydroxide, or sulfide and sulfosalt classes. Oxides and hydroxides together account for about 500 species. Sulfides and sulfosalts also account for about 500 species. The silicate class contains the largest number of minerals, with more than 800 known. In contrast, the native element class contains just a handful of members.

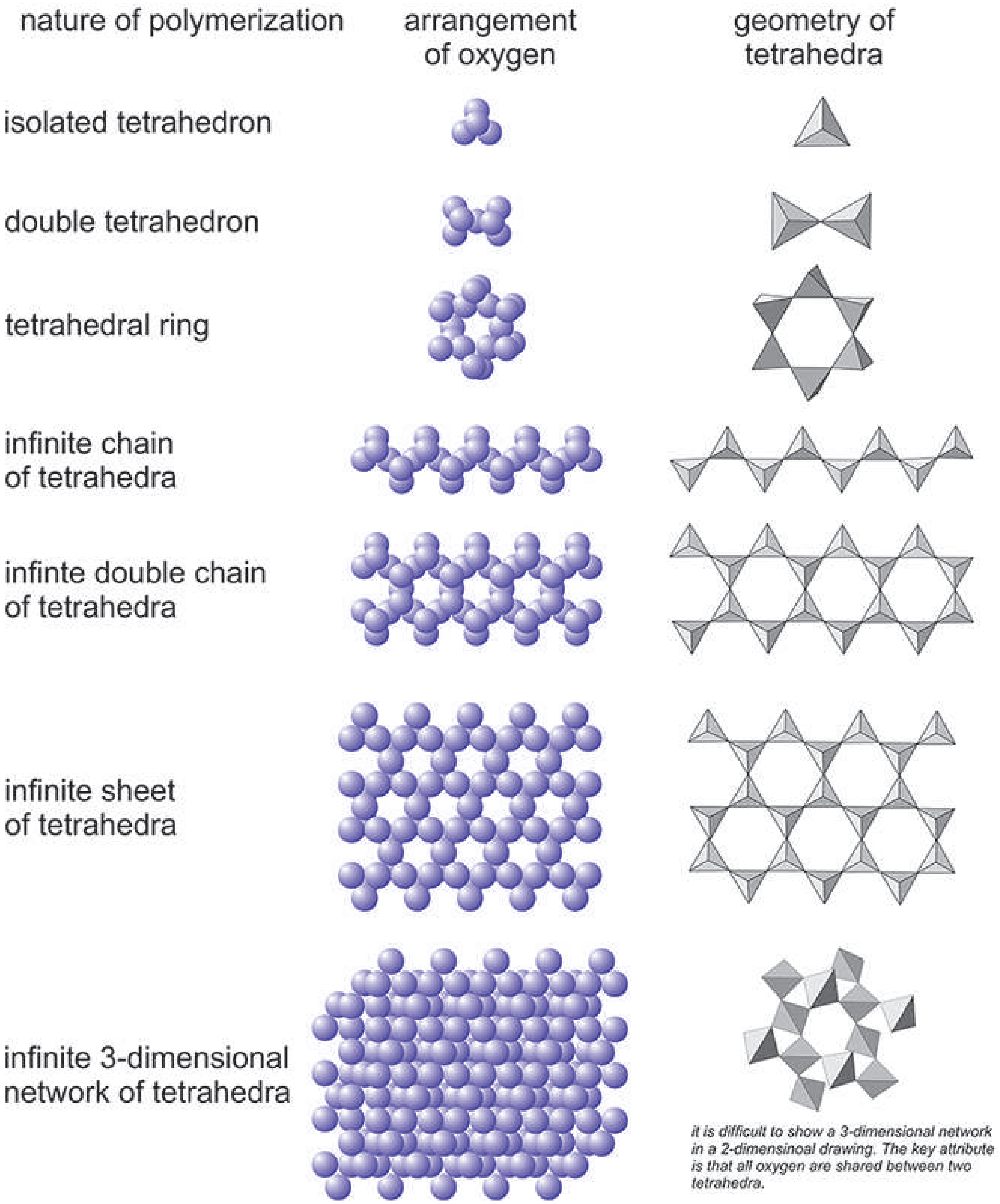
1.4.1 Subclasses, Groups, and Smaller Divisions

The mineral classes listed above are often subdivided into subclasses, groups, series or subgroups until finally reaching individual species. For example, consider minerals of the silicate class. Silicates make up more than 99% of the minerals found in igneous rocks and account for more than 90% of the Earth’s crust and mantle. Because the silicate class contains many important minerals, we divide it into subclasses.



1.32 Three views of a silicon tetrahedron

In silicates, except for very rare high-pressure minerals, all silicon atoms are surrounded by four oxygen atoms – arranged in the form of a tetrahedron, a pyramid shape with four identical faces. It can be depicted in several ways, some examples are shown in Figure 1.32. In mineral structures, these tetrahedra may share oxygen atoms to form chains, sheets, or three-dimensional networks. The linking forms atomic structures called *polymers*. We name the silicate subclasses according to how silicon tetrahedra are linked (polymerized). Figure 1.33 below shows the possibilities.

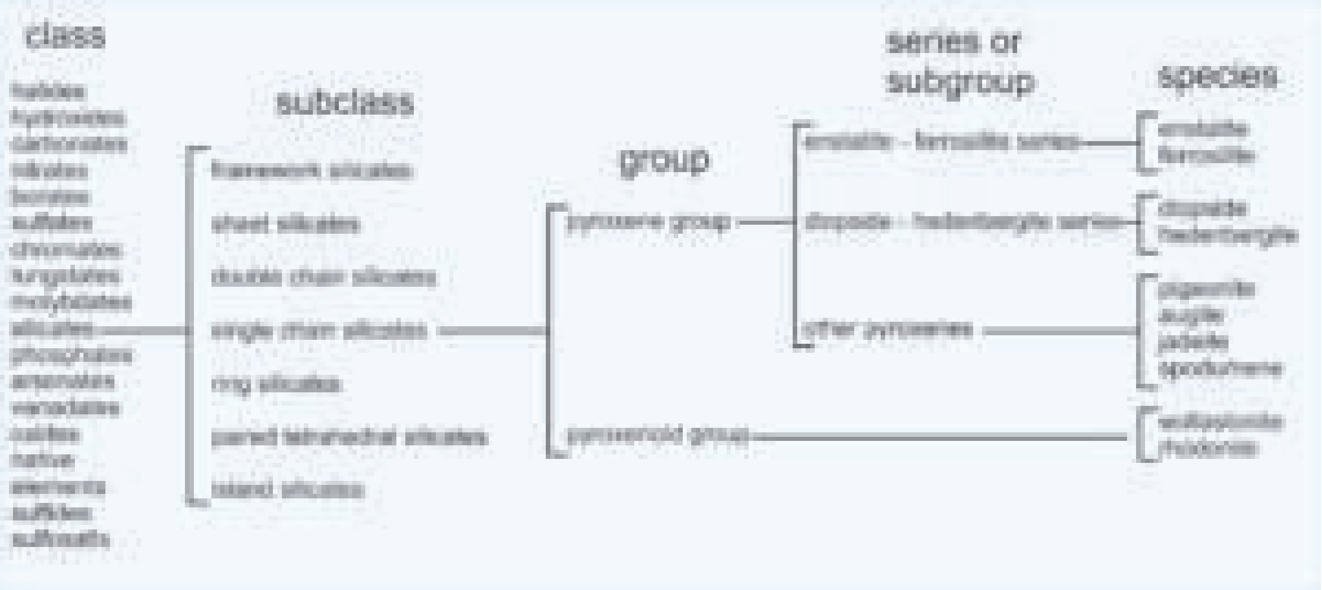


1.33 Polymerization in silicate minerals

1.4.2 An Example: Pyroxenes

Let’s consider the *pyroxene group* of minerals. All pyroxenes have the general formula ABT_2O_6. The A and B atoms may be the same or different but are typically Fe, Mg, Ca, Mn, and sometimes Na. T atoms are mostly Si but sometimes up to half

Al. The chart below shows how pyroxenes are classified into class, subclass, group, series or subgroup, and species.



1.34 Classification of pyroxene and pyroxenoid group minerals

1.35 Diopside, garnet, and clinochlore

As seen in the chart, pyroxenes belong to the *silicate class* and *single chain silicate subclass*. Single chain silicates include minerals of the *pyroxene group* and minerals of the *pyroxenoid group*. The groups contain specific species such as *enstatite* ($Mg_2Si_2O_6$), *ferrosilite* ($Fe_2Si_2O_6$), *diopside* ($CaMgSi_2O_6$), *hedenbergite* ($CaFeSi_2O_6$), and others listed in the far right column of the chart above.

The pyroxene group also contains series, for example the *diopside-hedenbergite series*, and the *enstatite-ferrosilite series*. Series define a range of possible mineral compositions between two mineral species. Thus, from general to specific, pyroxenes are classified into classes, groups, series, and species. These relationships hold true for other mineral groups as well. The photo in Figure 1.35 shows green diopside (a pyroxene) with red garnet and dark purple clinochlore in the background.

1.36 Chrome diopside

And, although not shown in the chart above, the individual mineral species may be divided into varieties based on any specific characteristics such as color or crystal shapes. For example, varieties of *diopside* include *chrome-diopside* (the emerald green chrome containing variety seen in Figure 1.36), *dekalbite* (diopside that contains no impurities at all), *malacolite* (a light colored or white variety that is usually fluorescent).

● Box 1-2 Chemical Formulas of Minerals

Throughout this book, we follow standard chemical conventions when we write mineral formulas. We list elements with subscripts to indicate the relative numbers of atoms present. We list cations (positively charged ions) before anions (negatively charged ions) and molecular anionic species, with the largest cations coming first. The following are some examples of formulas following these rules:

- marialite $Na_4(AlSi_3O_8)_3Cl$
- skutterudite $(Co,Ni)As_3$
- clinohumite $Mg_9(SiO_4)_4(OH,F)_2$
- olivine $(Mg,Fe)_2SiO_4$
- natrolite $Na_2Al_2Si_3O_{10}•2H_2O$
- montmorillonite $(Na,Ca)(Al,Mg)_2(Si_4O_{10})(OH)_2•nH_2O$

Subscripts outside parentheses apply to everything within if no commas are present. The formula unit of marialite, for example, indicates that 4 Na, 3 Al, 9 Si, 24 O, and 1 Cl are in one formula of marialite. Commas show an either-or situation. In one formula of clinohumite, for example, there are two atoms of OH or of F, or of the two combined. If we had omitted the comma, it would indicate that there were both 2 OH and 2 F per formula. Elements separated by commas, then, can be thought of as substituting for each other. For example, montmorillonite may contain either Al or Mg, or both; olivine may contain either Fe or Mg, or both. Parentheses surround complexes such as (SiO_4) or (CO_3) when it helps with clarity. In clinohumite, parentheses around (SiO_4) emphasize clinohumite’s chemical similarity to forsterite and other olivines, all of which have (SiO_4) in their formulas. In montmorillonite, the (Si_4O_{10}) is in parentheses to emphasize that the structure is that of a sheet silicate, many of which have (Si_4O_{10}) in their formula. Loosely bonded interstitial components (such as Cl in marialite, or OH and F in clinohumite) are on the right in the formulas. We indicate loosely bonded H_2O, often called nonstructural water, by a dot preceding nH_2O at the far right in a formula. The n (instead of an integer) in the formula for “clay” indicates that an unknown or variable amount of nonstructural water is present. Natrolite, a zeolite, has H_2O in holes in its structure. When completely hydrated, there are two moles of H_2O for each $Na_2Al_2Si_3O_{10}$ formula unit. When useful, we use superscripts to indicate ionic charge: $(OH)^-$ indicates the hydroxyl radical, which has a charge of -1. Similarly $(SiO_4)^{4-}$ indicates an Si atom bonded to 4 O, with a net charge of -4. Sometimes showing coordination (the number of bonds) of an atom is useful. We do this with superscript roman numerals; they are discussed later.

●Figure Credits

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Video 1-1 What is a Mineral? Keith Purtirka, YouTube

2 Mineral Chemistry

2.1 Carrollite has the formula $Cu(Co,Ni)_2S_4$

2 Mineral Chemistry

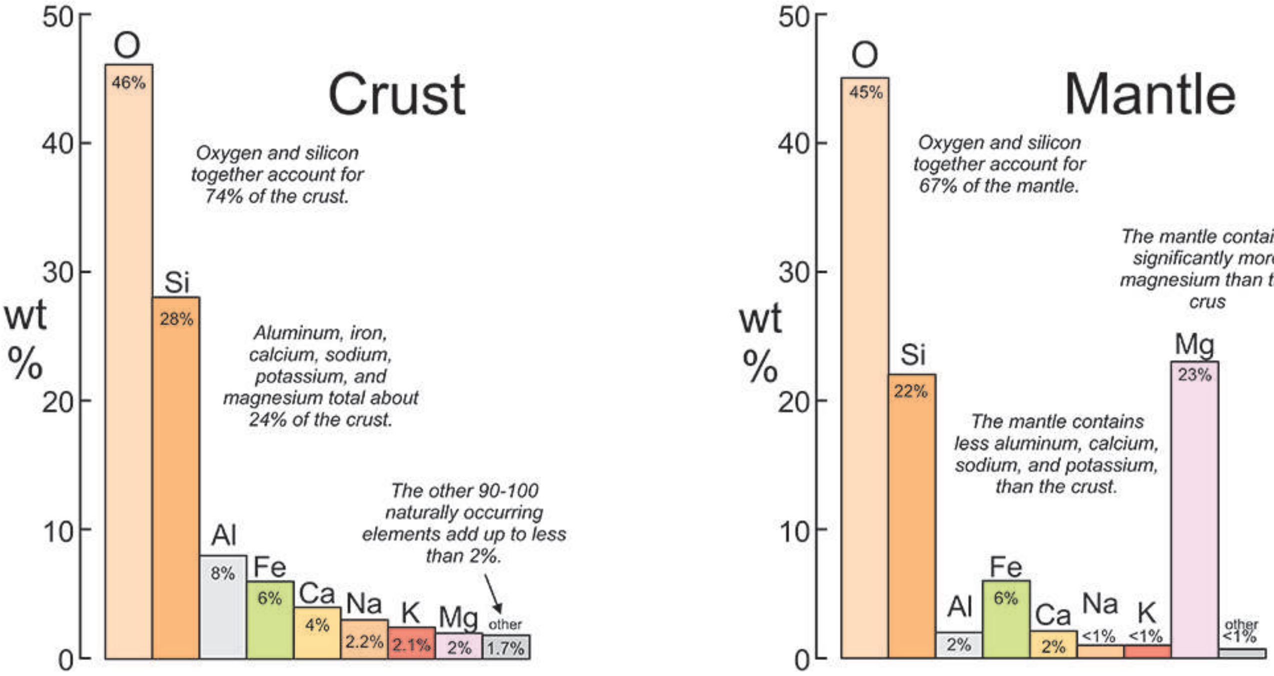
KEY CONCEPTS

- All matter, including mineral matter, is made of elements.
- 8 to 10 elements account for most of Earth’s mass but the elements are distributed unevenly.
- The Periodic Chart of the Elements orders elements by their atomic number and groups elements with similar

properties.
- Elements with similar properties may substitute for each other in minerals and many minerals have variable compositions.
- Ionic, covalent, or metallic bonding are most common in minerals.
- The kind of bonding affects mineral properties.
- We describe mineral compositions by giving weight %s of the elements or oxides present.
- Weight % values can be normalized to give chemical formulas.
- Although 1000s of minerals are known, only a small number are common.

2.1 Elements and Minerals

All matter is made of atoms of individual elements. For example, the matter of the Milky Way, our galaxy, is mostly hydrogen and helium – the same elements that make up >99% of our sun. Earth, however, is dominated by other elements, and 8 to 10 elements account for most of Earth’s mass. Although Earth’s crust and mantle contain the same major elements, the proportions are not the same (see histograms below). And, the core is completely different from the crust and mantle – it is mostly iron with perhaps 20% nickel and lesser amounts of other elements.



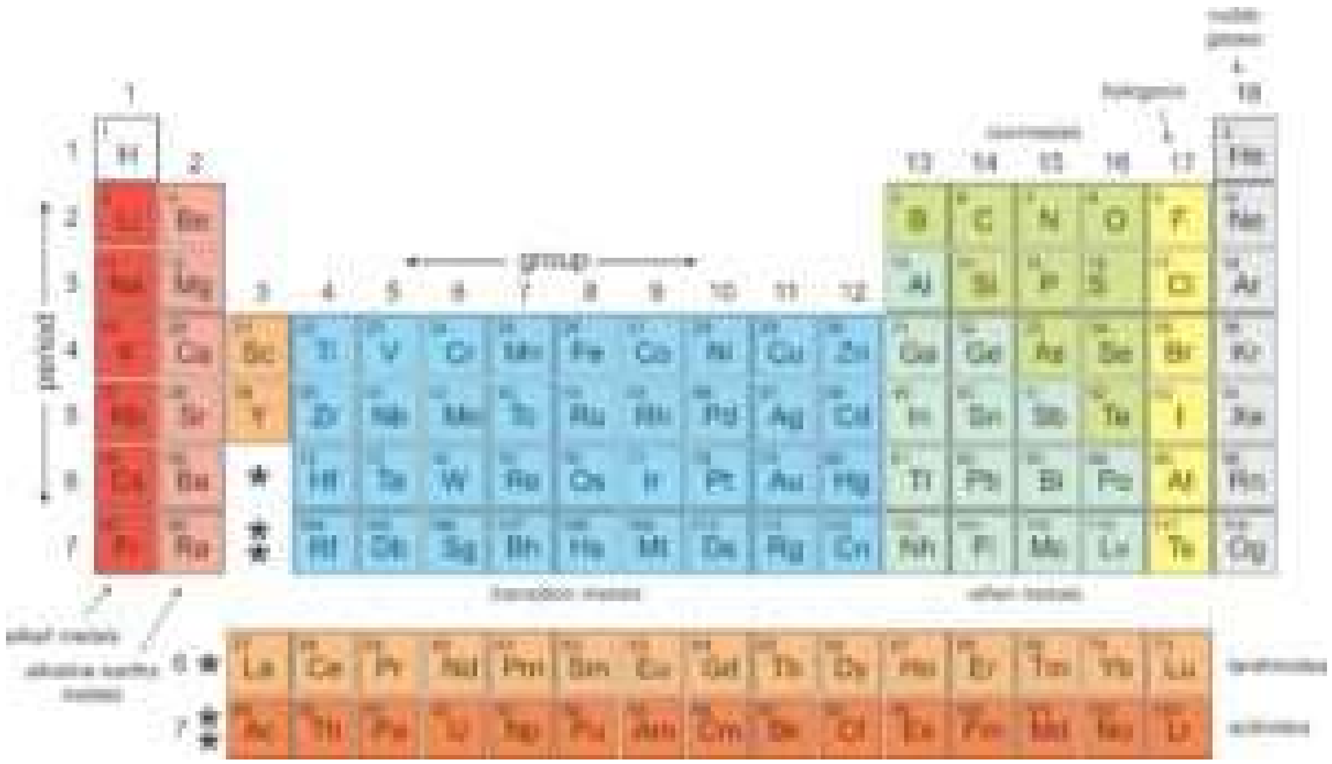
2.2 Elements in the crust and mantle

Most of the minerals and other geological materials we see derive from the crust, but some come from the uppermost part of the mantle. In both places, oxygen and silicon are the dominant elements (Figures 2.2 and 2.3). Together these two elements make up about three quarters of the crust, and two thirds of the mantle. Other quite abundant elements in both the crust and mantle include aluminum, iron, calcium, sodium, potassium, and magnesium. However, the mantle contains much more magnesium and iron, and less silicon, than the crust. Hydrogen (0.15 wt%) and carbon (0.18 wt%) are overall minor elements in the crust but are key components in some minerals. And other generally rare elements are sometimes concentrated by geological process to make exotic minerals.

The compositions of Earth’s outer layers vary somewhat laterally and vertically. For example, the oceanic crust is not the same composition as the continental crust. And, the composition of the shallow crust is somewhat different from the deep crust. Nonetheless, in most settings, we can expect common minerals to be made of the elements shown in the histograms above.

Some elements are common in many different minerals. Oxygen and silicon are perhaps the best examples. Many sedimentary rocks and nearly all igneous and metamorphic rocks are composed of multiple minerals containing these two elements. In contrast, because of their properties, some other elements tend to be found in only a few distinct minerals. For example, titanium (Ti) may occur as a minor component in biotite, amphibole, or other minerals. In many rocks, however, Ti is concentrated in Ti-rich minerals such as rutile (TiO_2), titanite ($CaTiSiO_5$), and ilmenite ($FeTiO_3$). Rocks rich in Ti always contain one of these latter three minerals. Similarly, rocks containing significant amounts of phosphorous usually contain apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, or monazite, $(Ce,La,Th,Y)PO_4$.

2.2 Elements and the Periodic Table



2.3 The Periodic Table

Here (Figure 2.3) we see the *Periodic Table of the Elements*. Elements are ordered by increasing atomic number (the number of protons in their atom nucleus), which correlates with atomic weight and size. The first element is *hydrogen* (atomic number 1) and the last is *oganesson* (atomic number 118). Oganesson is an obscure synthetic radioactive element that has only been produced a few times and in minute amounts. In this table, elements are in numbered *period*s (rows) and *groups* (columns) based on the configuration of their electron orbitals.

The chart contains 118 elements in all, but only about 90 occur naturally. The other 20 or so (with atomic numbers 104-118 and 99-103) elements are artificial – they are synthesized in nuclear reactors and some are radioactive with very short lives. The distinction between natural and artificial elements is, however, a bit uncertain because only a few atoms have (speculatively) been identified for some of the rarest natural elements. Although the Periodic Table of the Elements has appeared in many forms, the basic relationships are the same today as they were when Dmitri Mendeleyev (1834-1907) devised the first version in 1870. Some elements were unknown and omitted from the original table but were later discovered and added. Additionally, there has been a slight rearrangement so that the arrangement of the elements mirrors the order in which electrons occupy orbitals.

Chemists classify elements into different types that have related properties (shown by different colors in the table above). Hydrogen is a special element, but the other elements in Group 1 are *alkali metals*. The elements in group 2 are *alkaline earth metals*. Those elements in Groups 4 through 12 are *transition metals*. Group 17 elements are the *halogens*, and Group 18 elements are the *noble gases*. Elements between the transition metals and the halogens are called *nonmetals* or *other metals* (but different versions of the chart have them divided in slightly different ways). The asterisks in the chart show where the *lanthinides* (also called *rare earth elements*) and *actinides* (both considered transition metals) were extracted from the main chart and put as separate rows at the bottom. If we did not extract them, the chart would be too wide to fit easily on this page. Scandium (Sc) and yttrium (Y) are closely related to the lanthinides and so are commonly classified with them.

2.2.1 Groups

2.4 Perthite (exsolved alkali feldspar)

Elements in the same groups (columns) have their outermost electrons in the same kind of orbitals. This is very significant because it means the elements have similar chemical properties, form similarly charged ions and, importantly, commonly substitute for each other in mineral crystals. For example, the mineral specimen shown in Figure 2.4 is an alkali feldspar. When it first crystallized from a magma, it was a homogeneous mixture of Na-feldspar and K-feldspar. Na and K, both alkali elements (Group 1), commonly substitute for each other in minerals. When this sample cooled, however, the two different feldspar components unmixed from each other, much the same way that chicken soup and fat separate on cooling. The result is called *exsolution* (which means unmixing) and the specimen now contains thin pinkish veins of K-feldspar surrounded by Na-feldspar. We call feldspar that has exsolved like this, *perthite*.

2.2.2 Atomic Number and Mass

An element’s atomic number, the number of protons in its nucleus, is designated by the variable *Z*. *Z* is also equal to the number of electrons orbiting the nucleus in neutral (non-ionized) atoms, and is close to the number of electrons in most ions. A neutral iron atom (Fe^0), for example, has 26 protons (Z = 26) in its nucleus and 26 electrons in an electron cloud around the nucleus. Because the size of its electron cloud controls the diameter of an atom, elements with greater atomic number, with many protons and thus many electrons, are larger than those or lower atomic number.

Atomic nuclei (except one isotope of hydrogen) contain neutrons in addition to protons, and the number of neutrons, designated by *N*, may vary. This leads to isotopes of different mass numbers. Mass number is designated by the variable *A*, and we calculate the value of *A* from the number of protons and the number of neutrons: $A = Z + N$. Most chemical elements have several different naturally occurring isotopes. Some isotope varieties are generally more common than others, and some only exist in minute amounts.

2.5 Isotopes of Oxygen

Oxygen atoms, for example, may be any of three isotopes (shown in Figure 2.5). Oxygen may be ^{16}O, ^{17}O, or ^{18}O, where the superscript number denotes *A*. Examination of the equation in the previous paragraph indicates that the three isotopes of oxygen must have 8, 9, and 10 neutrons, respectively, because all must have 8 protons if they are oxygen. ^{16}O is 99.8% of all natural oxygen.

2.2.3 Moles

A *mole* of an element (or of a compound) is defined as containing 6.022×10^{23} atoms (or molecules). The number, 6.022×10^{23}, is known as *Avogadro's number*. So, one mole of carbon is equivalent to 6.022×10^{23} carbon atoms. The scale used to measure atomic mass has changed slightly over time. Today, it is standardized relative to carbon so that the mass of one mole of ^{12}C is exactly 12.0000. Consequently, all atomic masses are given in *atomic mass units* (*amus*), defined as one-twelfth the mass of ^{12}C. Both protons and neutrons have equivalent mass, about one amu, and electrons have almost no mass (less than 1/1000th the mass of protons and neutrons). So, we might expect the mass of an atom to be equal to the mass number (the total number of protons plus neutrons). But for several reasons, not worth going into here, the mass of an atom is generally close to, but not the same as, the mass number.

Elements are different from atoms. The *atomic mass*, also called the *atomic weight*, of an element is the sum of the masses of its naturally occurring isotopes weighted in accordance with their abundances. Atomic masses/weights of elements are molal quantities (and often given in units of grams/mole) but they are really dimensionless numbers because they are all calculated relative to the atomic mass/weight of a mole of carbon. Although isotope mass numbers are always integers, atomic weights of elements are not. For example, many tables and charts give the atomic weight of oxygen as 15.999 and that of iron as 55.847. When elements combine to produce a compound, the atomic weight of the compound is the sum of the weights of the elements in the compound. FeO, for example, has atomic weight 71.846 (15.999 + 55.847) grams/mole.

Most elements have very small isotopic variation in nature, no matter where they are found. Thus, most quartz (SiO_2) contains about the same relative amounts of the three natural oxygen isotopes (mostly ^{16}O) depicted in Figure 2.5 above. Furthermore, isotopic variations have extremely small effects on the properties of minerals. So, mineralogists generally do not worry much about isotopes. Small isotopic variations, however, may be significant to a geochemist trying to determine the genesis of a particular mineral or rock.

● Box 2-1 What Is a Mole of Quartz?

Quartz (SiO_2) is one of the most common and well-known minerals. A mole of quartz is 6.022×10^{23} SiO_2 molecules, and that sounds like a lot. How much quartz is that?

To answer this question, we use the atomic weights of silicon and oxygen as well as some crystallographic data. Silicon and oxygen have atomic weights of 28.0855 and 15.9994, respectively. The atomic weight of quartz, SiO_2, is therefore 60.0843 (= 28.0855 + 15.9994 + 15.9994). This means that a mole of quartz, 6.022×10^{23} SiO_2 molecules, weighs 60.0843 gm.

Crystallographers have determined that quartz crystals are made of fundamental unit cells shaped like trigonal prisms (discussed in detail in later chapters) containing three ($Z = 3$) SiO_2 molecules. Each unit cell has a volume of 112.985 Å^3. So we may calculate the volume of a mole of quartz as:

$$V = N_A \times v/Z$$

(where V, N_A, v, and Z are the molar volume, Avogadro's number, the unit cell volume, and the number of molecules per unit cell, respectively.)

$$\text{So, } V = 6.022 \times 10^{23}\ SiO_2/\text{mole} \times 112.986\ \text{Å}^3/\text{unit cell} \div 3\ SiO_2/\text{unit cell}$$

$$= 2.268 \times 10^{25}\ \text{Å}^3 = 22.68\ \text{cm}^3$$

which is slightly smaller than a golf-ball.

We can, if we wish, then calculate the density (ρ) of quartz from the molar data:

$$\rho = \text{molar weight} \div \text{molar volume} = 60.0843\ \text{gm/mole} \div 22.68\ \text{cm}^3/\text{mole} = 2.649\ \text{gm/cm}^3$$

2.2.4 Radioactive Minerals

Most common isotopes are *stable isotopes*. In 1896 Henri Becquerel discovered *unstable isotopes* and radioactivity when he unintentionally conducted an experiment. He put some radioactive samples in a drawer, along with a photographic plate, and subsequently found that the plate had recorded the image of a key that had been sitting on top of it. Although Becquerel didn’t know it, X-rays given off by uranium-rich minerals had caused the image. During the following decade, researchers including Marie and Pierre Curie and Ernest Rutherford determined that some elements, termed *radioisotopes*, emit alpha (*α)* and beta (*β)* particles, and gamma (*γ)* radiation as they decay to form *daughter isotopes*. So, minerals are radioactive if they contain radioisotopes, and the amount of radioactivity depends on isotope concentration. Most minerals that contain potassium, uranium, and thorium are radioactive, but many other elements besides these three can also contribute to radioactivity.

Radioactive minerals are quite rare but many of them, like those seen n Figures 2.6, 2.7 and 2.8 below, make spectacular mineral specimens. *Torbernite* (copper-uranium phosphate), *autunite* (calcium-uranium phosphate), and *uraninite* (uranium oxide) are three of the most common examples. Uraninite is the main ore for uranium; the specimen seen here comes from a mine in Topsham, Maine.

2.6 Tobernite

2.7 Autenite

2.8 Uraninite on calcite

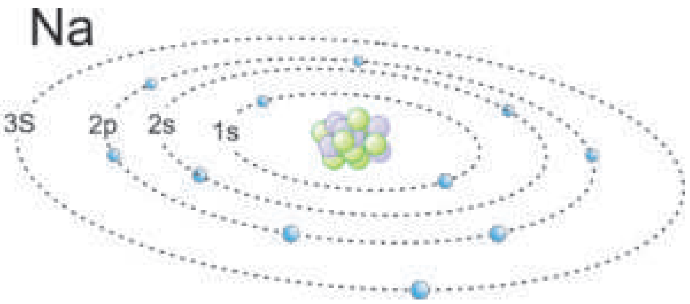
2.2.5 Periods

In atoms, electrons are in orbitals of different energies around atomic nuclei. Electrons are always moving, and orbitals are regions around a nucleus where electrons are likely to be found. We designate an orbital using a number and a letter, for example 1s or 1p – the number refers to a specific electron shell and the letter to a subshell. S subshells can hold up to 2 electrons, p subshells up to 6 electrons, d subshells up to 10 electrons, and f subshells up to 14 electrons. From lowest to highest energy, the orbitals and the maximum number of electrons they can hold are listed in the table below. s orbitals are spherical, p orbitals are dumb-bell shaped, d and f orbitals have more complicated shapes. The shape of an atom's outermost occupied orbital is often important because it can affect mineral properties such as color. But, for simplicity, in the drawings below we show all orbitals as circular.

Electron Orbitals

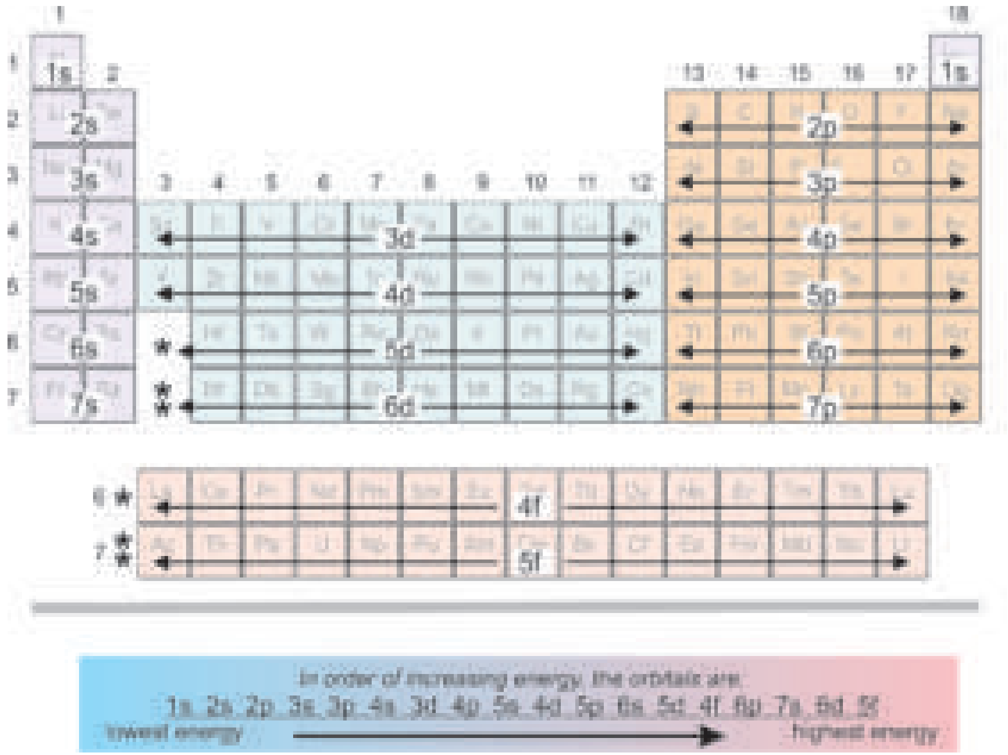
orbital	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	5d	6p	7s	5f	6d	7p
max # electrons	2	2	6	2	6	2	10	6	2	10	6	2	14	10	6	2	14	10	6
increasing energy →																			

In a neutral (non-ionized) atom, the number of electrons is equal to the atom's atomic number. So, a hydrogen atom (atomic number 1) contains one electron, a helium atom (atomic number 2) contains two electrons, a lithium atom (atomic number 3) contains three electrons, and so forth to high atomic number. Electrons populate orbitals sequentially, filling the lowest energy orbitals first and proceeding to higher energy orbitals. Thus, hydrogen has one electron in a 1s orbital. Helium has two electrons in a 1s orbital, lithium has two electrons in a 1s orbital and one electron in a 2s orbital, etc.



2.9 Electron orbits in a sodium atom

For an example of electron configuration in a heavier element, consider sodium. This schematic drawing in Figure 2.9 shows orbitals and electrons in a sodium atom. The electrons are orbiting a nucleus that contains protons and neutrons (but they are not all visible). Sodium has atomic number 11, so a neutral atom has 11 protons and 11 electrons. Natural sodium also has 12 neutrons. The electrons fill the 1s, 2s, and 2p orbitals. One additional electron is in the 3s orbital.



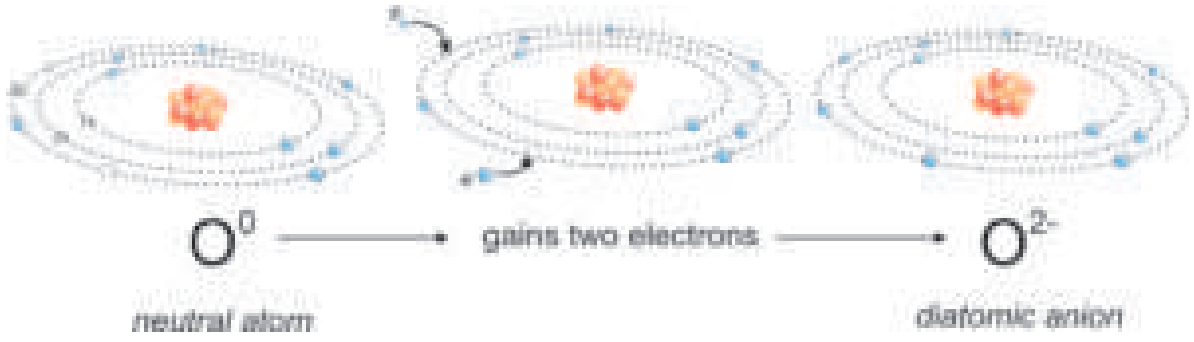
2.10 Electron orbitals of valence electrons

We call electrons that contribute to chemical bonding *valence electrons*. These electrons are generally in the outermost electron shells (but may be in an inner shell for transition metals). This chart (Figure 2.10) shows the orbitals of valence electrons for different elements. Elements in the same period (row) of the periodic table have their valence electrons in the same s or p shell, or (for transition elements) in a d orbitals of the next lower shell.

The first period contains only two elements (H and He), while the second and third have eight each. Electrons for second and third period elements are in 2s, 2p, 3s, or 3p orbitals. The fourth through seventh periods contain some elements with valence electrons in s or p orbitals, but also contain 20 elements having valence electrons in d-orbitals. The sixth and seventh periods contain elements with valence electrons in s, p, d, or f orbitals. The lanthanides and actinides have valence electrons in f orbitals. Thus, as seen in the chart above, elements with high atomic number (compared with elements of low atomic number) have electrons in higher-energy orbitals.

2.3 Ions

Atoms are somewhat unstable if valence electrons do not completely fill outer shells. They are very stable when the outer shells are fully occupied. So, atoms commonly give up, or borrow electrons, producing *ions*, to obtain this stability. As a result, they may become *cations*, which have a net positive charge because there are more protons than electrons, or *anions*, with a net negative charge because there are more electrons than protons.



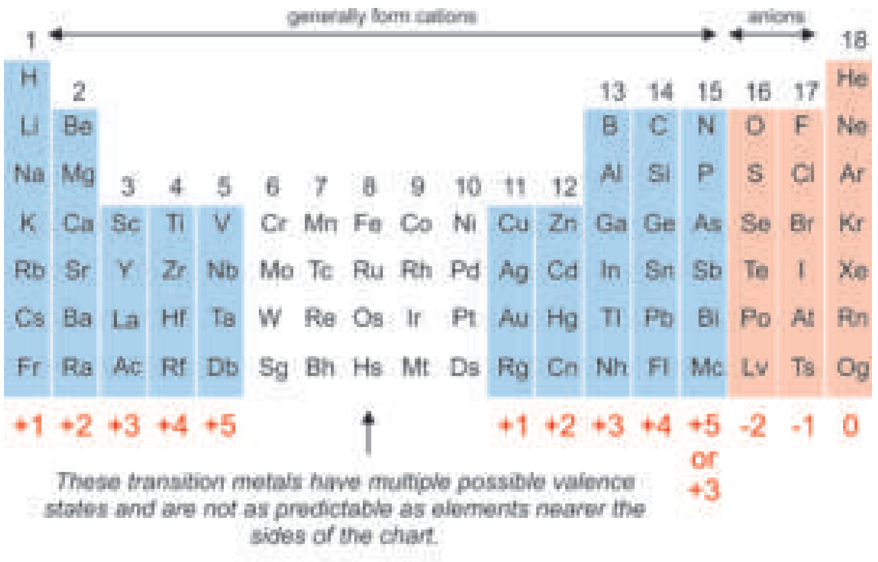
2.11 Forming an oxygen anion

The schematic drawings in Figure 2.11 show how a neutral oxygen atom can gain two electrons to become an anion. The neutral atom has 8 protons in its nucleus and 8 electrons. It contains two 1s electrons and six electrons in its outer shell (2s and 2p orbitals). Thus, 2 additional electrons are needed to fill the outer shell. Commonly, two electrons move in to stabilize the atom – and the result is an oxygen anion. The ionic charge (-2) is calculated as the number of protons (still 8) less the number of electrons (now 10).

Different cations and anions may have different ionic charge. We call all ions with a charge of +1 or -1 *monovalent*. Those with a charge of +2 or -2 are *divalent*. *Trivalent* and *tetravalent* refer to charges of +3 or -3 and +4 or -4. The oxygen ion shown above is a diatomic anion.

Some elements ionize more easily than others. Those that ionize most easily to become cations are called *metallic elements*. The degree to which elements are metallic generally decreases from left to right in the Periodic Table. The elements on the right side of the table, which ionize to become anions, are *nonmetallic*.

2.3.1 Typical Valences



These transition metals have multiple possible valence states and are not as predictable as elements nearer the sides of the chart.

2.12 Valences of typical ions

The chart seen here shows the most common ions for different columns in the Periodic Table. Common cations are shaded blue and common anions are shaded red. The red numbers below the columns are typical valences. This table is not to suggest that all the elements always form ions. But, when they do, for most elements, their likely ionic form is predictable as shown. The three most abundant elements in the Earth’s crust (oxygen, silicon, and aluminum) are on the right side of the Periodic Table, in groups 13, 14, and 16. Oxygen typically has a charge of -2, silicon of +4, and aluminum of +3. Transition elements in the periodic chart commonly exist in more than one valence state.

Helium and other elements in Group 18 of the Periodic Table have completely filled outer shells and, consequently, do not ionize. Elements in groups on the left side of the table have “extra” electrons in outer shells, and readily give up those electrons to become cations. Elements in group 1 (*alkali elements*) generally have a valence (ionic charge) of +1. Those in group 2 (*alkaline earth elements*) usually have a valence of +2. Elements in Group 13, Group 14, and Group 15 typically ionized to form cations with charge of +3, +4, and +5, respectively, although other ions are possible.

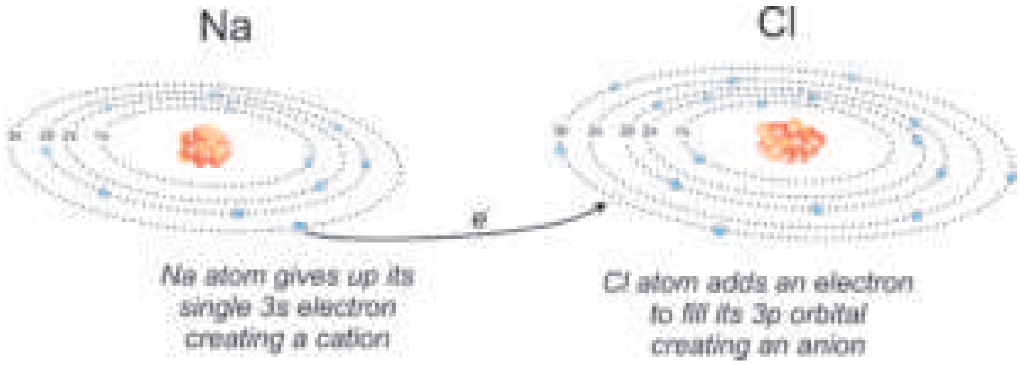
Elements in Groups 16 and 17 on the right side of the Periodic Table, have room for a small number of additional electrons in their outer shells and consequently accept extra electrons to become anions. Elements in group 17 (*halogens*) are lacking a single electron to fill their outer shells completely. So, they typically become monovalent anions (charge of -1) because they acquire an extra electron to fill the shell. Oxygen and other elements in Group 16 typically form divalent anions.

The properties of the *transition metals* in the central portion of the table (groups 3 through 12) are less predictable. When ionized, elements in groups 3, 4, and 5 usually have valences of +3, +4, and +5, respectively. The rest of the transition metals exist in a number of ionic states, typically +2 or +3.

2.4 Bonding in Minerals

2.4.1 Ionic Bonds

Negatively and positively charged particles attract each other. Protons (positively charged) attract electrons (negatively charged) in atoms. Similarly, positively charged cations attract negatively charged anions, producing *ionic bonds* in minerals.



2.13 Ionic bonding to form halite (NaCl)

We call the process of losing electrons to become a cation *oxidation*. Gaining electrons, and becoming an anion, is *reduction*. The formation of cations and anions go hand in hand. Metals becoming cations donate electrons to non-metals becoming anions. Oxidation produces metal cations with a positive charge that may combine with oxygen anions (O^{2-}) to form ionic oxides.

The drawing shown in Figure 2.13 is a schematic showing how sodium and chlorine can combine to make the mineral *halite* (NaCl). First sodium (Na) and chlorine (Cl) react to produce the ions Na^+ and Cl^- (when a 3s electron from sodium is added to the 3p orbital in chlorine). Na is oxidized as Cl is reduced. These two ions then bond, producing NaCl.

Oxidation and reduction also occur when iron and oxygen combine to form hematite (Fe_2O_3). Two Fe atoms each donate 3 electrons that are picked up by three O^0 atoms. So, the iron atoms become Fe^{3+} while the oxygen atoms become O^{2-}. The ions combine to produce (Fe_2O_3). But, iron sometimes oxidizes to Fe^{2+} and combines with oxygen to form the mineral *wüstite* (FeO). A third iron oxide mineral, *magnetite* (Fe_3O_4), contains both Fe^{2+} and Fe^{3+}. Wüstite, hematite and magnetite are all minerals, but wüstite is not a common mineral on Earth (although it is found in meteorites) because under normal Earth surface conditions, iron easily oxidizes to become trivalent. The bonds in all three iron oxides, however, are not entirely ionic; they are partially covalent (discussed later in this chapter).

2.4.1.1 Common Cations and Anions

Common Cations, Anions, and Anionic Groups		
cations	anions	anionic groups
monovalent		

Na^+	Cl^-	$(NO_3)^-$
K^+	F^-	$(OH)^-$
H^+		
divalent		
Fe^{2+}	O^{2-}	$(SiO_4)^{4-}$
Ca^{2+}		$(SO_4)^{2-}$
Mg^{2+}		$(CO_3)^{2-}$
		$(WO_4)^{2-}$
other ions		
Al^{3+}		$(BO_4)^{5-}$
Fe^{3+}		$(PO_4)^{3-}$
Si^{4+}		
C^{4+}		

The table seen here lists the most common cations and anions in Earth's crust. For the most part, these are the same elements that we discussed at the beginning of this chapter when we considered the composition of the crust and mantle.

While thinking of individual ions bonding together to form minerals seems straightforward, in reality atoms are seldom unbonded to others. Single atoms are very reactive. They tend, when possible, to bond to other atoms to form molecules and often compounds. Sometimes, they bond to other atoms of the same element. For example, N_2, composed of molecules containing two nitrogen atoms, dominates the Earth's atmosphere. Small atoms with several valence electrons, such as silicon or carbon, are especially reactive. They seldom exist by themselves, readily combining with oxygen, and sometimes other elements, to form strongly bonded anionic units called *molecular ions*, also known as *polyatomic ions*. Molecular ions are so strongly bonded that they behave like individual anionic units in many minerals. So when minerals dissolve, molecular ions such as $(CO_3)^{2-}$ will not dissociate in water.

The right-hand column of the table lists the most common and important molecular ions. They include, from top to bottom, the *nitrate*, *hydroxyl*, *silicate*, *sulfate*, *carbonate*, *tungstate*, *borate* and *phosphate* groups. Most mineralogy and geology texts, this one included, classify minerals based on their anion species because the properties of minerals with the same anions are generally very similar. (This classification system was described in the previous chapter.) So, we often write mineral formulas with parentheses to emphasize any anions or anionic groups that are present.

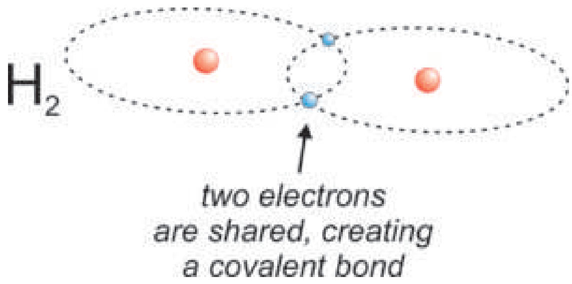
Any of the cation species listed in the table can combine with the anions or molecular anions to produce a long list of different ionic compounds. For example, all these minerals contain Ca^{2+}:

lime CaO	fluorite CaF_2	larnite Ca_2SiO_4	anhydrite $CaSO_4$	calcite $CaCO_3$	scheelite $CaWO_4$

Lime, *fluorite*, *larnite*, *anhydrite*, *calcite*, and *scheelite* belong, respectively to the oxide, halide, silicate, sulfate, carbonate, and tungstate mineral groups. Additional Ca^{2+} minerals with more complicated formulas include *sinjarite* ($CaCl_2 \bullet 2H_2O$), *colemanite* ($Ca_2B_6O_{11} \bullet 5H_2O$), *nitrocalcite* ($Ca(NO_3)_2 \bullet 4H_2O$), and *apatite* ($Ca_5(PO_4)_3(OH)$). Thus, Ca^{2+} can combine to make minerals with all except one of the anion and anionic species listed in the table above. The lone exception is nitrate, $(NO_3)^-$. But, synthetic calcium nitrate ($CaNO_3$), called *Norwegian saltpeter* is sometimes manufactured for industrial use.

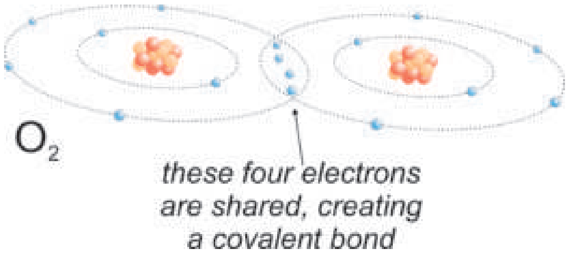
2.4.2 Covalent Bonds

Rather than giving up or gaining electrons to become ions, atoms with incompletely filled energy levels may become stabilized by sharing electrons. The sharing of pairs of electrons between atoms produces a covalent bond. If the sharing is complete, the bond is 100% covalent. This is the case for diatomic gases such as N_2, but does not occur in common minerals except for diamond.



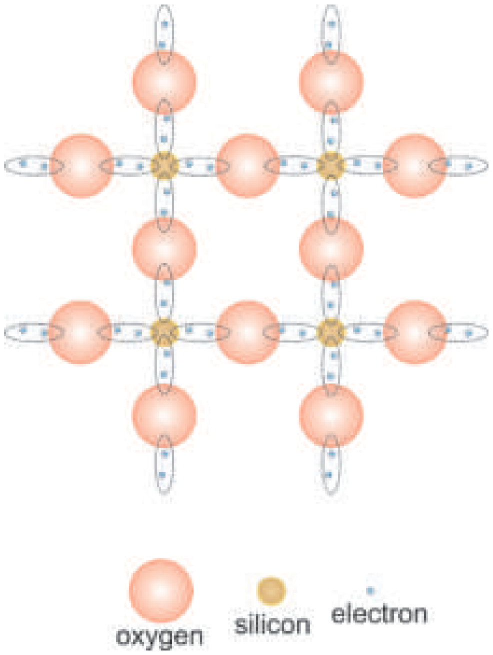
2.14 Covalent bonding to make hydrogen gas

The simplest example of a covalent bond involves two hydrogen atoms combining to produce H_2 gas, shown in Figure 2.14. Hydrogen atoms have one proton in their nucleus and one electron in orbit. If two hydrogen atoms share electrons, this effectively puts two electrons in the outer orbits (1s) of each atom, completely filling the orbits and making a very stable diatomic molecule, H_2. Fluorine, chlorine, and other halogen elements form covalently bonded diatomic gasses (F_2, Cl_2, etc.) like hydrogen.



2.15 Covalent bonding to make oxygen gas

Sometimes covalent bonds involve more than a single pair of shared electrons. Figure 2.15 shows how two oxygen atoms can share four electrons to form covalent bonds, and produce O_2 gas. By sharing four electrons, each atom has a total of 8 electrons in its 2s and 2p orbitals, making the outer shells fully occupied and stable. Because there are two pairs of electrons shared, we call this kind of covalent bond a *double bond*.



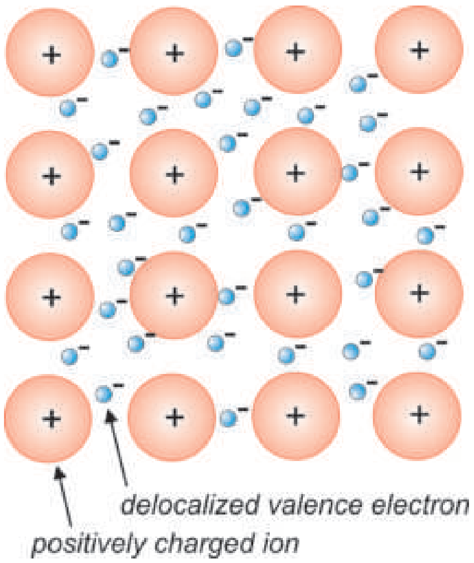
2.16 Simplified view of bonding in quartz

For a mineralogical example of covalent bonding, let's consider quartz (SiO_2). The drawing shown in Figure 2.16 is the atomic arrangement in quartz reduced to two dimensions. Four oxygen atoms surround each silicon atom, and each oxygen atom bonds to two silicon atoms. A lone silicon atom has 4 electrons in its outer shell (3s and 3p orbitals). But, each of the surrounding oxygen atoms can share an electron with the silicon atom, bringing the total number of electrons to 8, filling the outer shell, and making it stable. And, each silicon atom can share one electron with each of its four surrounding oxygen atoms. So, oxygen, which begins with 6 electrons in its outer level (2s and 2p orbitals), gains 2 electrons, bringing the total to 8, which stabilizes the atom.

Many elements form both covalent and ionic bonds. As mentioned previously, Cl^- forms ionic bonds with Na^+ to make the mineral halite. But, two Cl atoms can also bond covalently to form a stable gas, Cl_2. The two types of bonds are not exclusive – ionic bonds and covalent bonds form a spectrum, and in nature, 100% ionic and covalent bonds do not exist. In nearly 100% ionic bonds, valence electrons are almost exclusively associated with one atom. (But, even the highly ionic NaCl bond has a slight covalent character.) In nearly 100% covalent bonds, electrons are shared more or less evenly between two atoms. Diatomic gases such as H_2 and N_2 are extremely close to being 100% covalent.

So, many minerals (and other substances) contain bonds that are partly ionic and partly covalent. For example, the preceding discussion of covalent bonding in quartz was an oversimplification. In actuality, silicon-oxygen bonds are not completely covalent – there is still some ionization and electrons are more localized around oxygen than silicon. The overall bonding is about half covalent and half ionic. And, although they behave as anions, $(SiO_4)^{2-}$, $(SO_4)^{2-}$, $(CO_3)^{2-}$, $(OH)^-$ and all other molecular ions (listed previously in a table) are held together by partially covalent bonds. This explains why they act as individual ionic units in ionic crystals.

2.4.3 Metallic Bonds



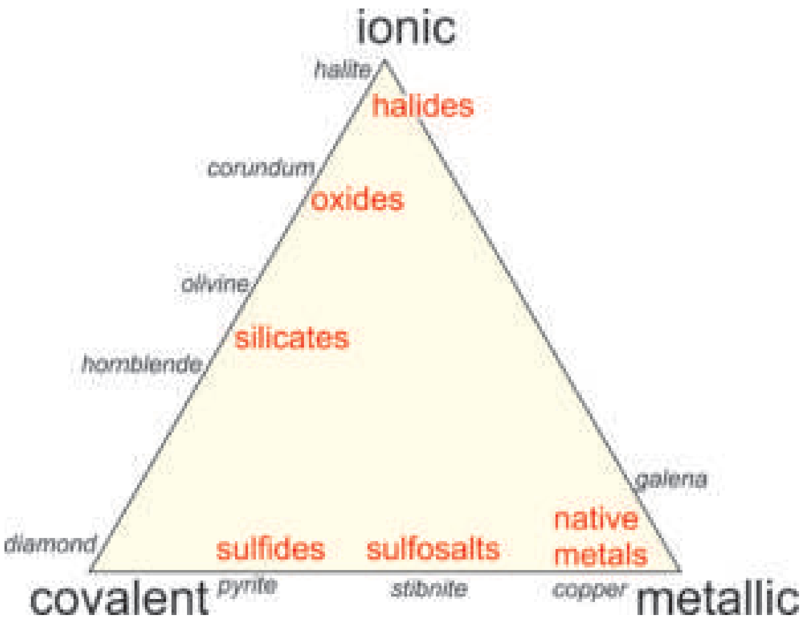
2.17 Metallic bonding

In covalent bonding, pairs of atoms share electrons. In a third kind of bonding, *metallic bonding*, many atoms share the same electrons. Individual atoms give up their valence electrons and the delocalized electrons are free to move and interact with all the positively charged ions in the structure (Figure 2.17). Metallic bonding, is especially common in minerals involving transition metals. Gold, silver, and copper are examples of minerals with metallic bonds. Because valence electrons move easily throughout the structure, metallically bonded compounds are good conductors of heat and electricity. Electrons are easily transferred along wires, for example. Minerals with metallic bonds may be malleable and have only low-to-moderate hardness, reflecting the loose nature of their bonds.

2.4.4 Other Kinds of Bonds

Besides the three kinds of bonds just discussed, some minerals include other types of bonds such as *van der Waals bonds* and *hydrogen bonds*. These bonds do not involve valence electrons but instead result from weak electrostatic forces due to uneven charge distribution in a crystal structure. Very weak van der Waals bonds are important in graphite and some clay minerals, for example. This explains why graphite is much softer than diamond, which has the same composition but covalent bonds. In the mineral *brucite*, combinations of hydrogen and van der Waals bonds hold sheets of Mg^{2+} together. Clay minerals have excellent cleavage because covalent and ionic bonds create strongly bonded layers, but weak van der Waals and hydrogen bonds hold the layers together. So, the minerals split easily into sheets. Because most mineral properties are explained by ionic, covalent, or metallic bonds and we can ignore van der Waals and hydrogen bonds for most purposes.

2.4.5 Ionic, Covalent, and Metallic Crystals



2.18 Different kinds of bonds in different minerals

As shown in the triangular diagram (Figure 2.18), bonding in most minerals is neither 100% ionic, 100% covalent, nor 100% metallic, but some come close. Most minerals contain combinations of ionic and covalent bonding. Metallic ore minerals such as pyrite (FeS_2), stibnite (Sb_2S_3), and copper (Cu) generally have little ionic character. Most of them, especially those in the sulfide and sulfosalt groups, contain combinations of covalent and metallic bonding. Metallic and ionic bonds do not often combine, although galena (PbS) may be one example in which they do.

The degree to which a bond is ionic depends on both elements involved. For example, because alkali elements (group 1) have a very strong tendency to become cations, and halogens (group 17) have an equal tendency to become anions, halite (NaCl) and other alkali halides form crystals in which bonds are nearly 100% ionic. Fluorite (CaF_2), too, is nearly completely ionic. Alkaline earth oxides such as periclase (MgO) or lime (CaO), involving cations from group 2 and oxygen from group 16, are about 75% ionic. Many other oxides too, are mostly ionic. Silicates, the most common kind of mineral in Earth’s crust, are generally about 50% ionic and 50% covalent. And, bonds in diamond (C) are entirely covalent.

2.4.5.1 Bonding and Mineral Properties

The nature of chemical bonding in minerals controls many properties. The table below makes some comparisons. Covalent bonds are stronger than ionic bonds, which in turn are stronger than metallic bonds. Consequently, covalent minerals are hard and tenacious, while metallic ones are usually not, and ionic minerals fall between. Melting temperatures follow a similar pattern (covalent compounds generally melt at the highest temperatures due to their stronger bonds), while solubility in water is greatest for ionic crystals (because of their weak bonds and easy ionization).

Bond type also affects crystal symmetry. Both ionic and metallic bonds are nondirectional so bonding can occur equally in all directions. In contrast, covalent bonds involve pairs of atoms and are linear. Consequently, metallic and ionic minerals generally have high symmetry compared with covalent ones.

Characteristics of Minerals Dominated by Different Kinds of Bonds

property	ionic bonds	covalent bonds	metallic bonds
common elements involved	from opposite sides of the Periodic Chart	close together in the Periodic Chart	transition metals
electrical conductivity	low	low	high
thermal conductivity	low	low	high
solubility in water	high	low	very low
melting temperature	moderate to high	high	variable
hardness	medium to hard	very hard	often malleable
ability to break	brittle, good cleavage	brittle, common fractures	variable
crystal symmetry	high symmetry	low symmetry	very high symmetry
transparency	fully to partially transparent	partially transparent or opaque	opaque
how common?	most nonmetallic minerals	some minerals	most metallic minerals
examples	halite (NaCl); calcite ($CaCO_3$)	diamond (C); sphalerite (ZnS)	copper (Cu); silver (Ag)

2.5 Compositional Variation in Minerals

2.19 Cleavelandite (albite-rich plagioclase)

Most natural minerals are formed from combinations of many elements. Unlike mechanical mixtures (such as two things being ground up together) the elements are ordered and intimately bonded together. The resulting crystalline solutions are *solid solutions*. Common plagioclase (a feldspar), for example, is mostly a solution of $CaAl_2Si_2O_8$ (anorthite) and $NaAlSi_3O_8$ (albite). The sample seen herein Figure 2.19 is near the albite end of the spectrum. It contains blades of a variety of plagioclase called cleavelandite with a few flakes of muscovite on top.

Some minerals, such as hornblende, contain many elements, are complex solid solutions, and have long and complicated formulas. Other minerals, including plagioclase and other feldspars have limited compositional variations. Still others, such as fluorite (CaF_2) or quartz (SiO_2), have relatively simple formulas and vary little from their ideal compositions.

We may broadly classify the elements that comprise a mineral in one of three categories: major elements, minor elements, and trace elements. *Major elements* are those fundamental to a mineral; they control a mineral’s basic atomic structure and gross properties. They must be in the mineral or the mineral has been misidentified. *Minor elements* are those present in small amounts, usually as replacements for a major element. Such elements, perhaps in amounts up to a several weight %, may affect color and a few other properties, but the basic atomic arrangement of a mineral is controlled by its major element chemistry. Minerals also contain extremely small amounts of elements called *trace elements*. Trace elements are in all minerals and provide valuable information for geologists attempting to determine how, when, and where specific minerals formed. They have little effect on most mineral properties. A notable exception to this is sometimes color; even trace amounts of some elements can have major effects on a mineral’s color.

Mineralogists can acquire mineral analyses in many ways. In the past, most chemical analyses were determined by titration and other “wet chemical” techniques. Today we use sophisticated analytical instruments, including *atomic absorption spectrophotometers* and *electron microprobes*. We normally report analytical results by listing oxide weight percentages. We must normalize these values if we wish to have mineral formulas. As an example of chemical variability in minerals, let’s consider olivine. An example of olivine is shown in Figure 2.20, below.

2.20 Crystals of olivine

The table below lists analyses of six olivines from different geologic environments. The top part of the table presents the analyses in terms of element weight %; the middle part presents the same information in terms of oxide weight %; the bottom part presents the composition in terms of the number of atoms in an olivine formula. The three parts of the table are redundant; values from one can be converted to the others by an arithmetical process called *normalization* (described later in this chapter). Most mineralogists and petrologists prefer to consider oxide weight % (for reasons explained in a later chapter) or numbers of atoms (because numbers of atoms directly translate into mineral formulas).

Olivine Analyses						
Burma	Finland	New Zealand	Minnesota	Greenland	Germany	
Element wt%						
Si	19.50	19.21	19.15	14.22	14.09	13.94
Ti	0.00	0.03	0.01	0.72	0.12	0.00
Al	0.00	0.29	0.11	0.26	0.04	0.00
Fe	0.86	3.39	6.11	44.79	50.84	54.01
Mn	0.00	0.18	0.10	0.00	0.78	0.22
Mg	34.88	32.60	31.27	4.93	0.63	0.00
Ca	0.00	0.00	0.11	0.94	1.56	0.00
Na	0.00	0.00	0.01	0.00	0.00	0.00
O	45.43	45.20	44.56	33.86	32.06	31.41
Total	100.67	100.90	101.43	99.72	100.12	99.58
Oxide Weight %						
SiO_2	41.72	41.10	40.97	30.42	30.14	29.82
TiO_2	0.00	0.05	0.02	1.20	0.20	0.00
Al_2O_3	0.00	1.10	0.42	0.98	0.15	0.00
FeO	1.11	4.36	7.86	57.62	65.40	69.48
MnO	0.00	0.23	0.13	0.00	1.01	0.28
MgO	57.84	54.06	51.85	8.18	1.04	0.00

CaO	0.00	0.00	0.15	1.32	2.18	0.00
Na_2O	0.00	0.00	0.03	0.00	0.00	0.00
Total	100.67	100.90	101.43	99.72	100.12	99.58
Atoms per 4 Oxygen						
Si	0.978	0.968	0.979	0.957	1.001	1.011
Ti	0.000	0.001	0.000	0.028	0.005	0.000
Al	0.000	0.015	0.006	0.018	0.003	0.000
Fe	0.022	0.086	0.157	1.516	1.817	1.970
Mn	0.000	0.005	0.003	0.000	0.028	0.008
Mg	2.022	1.899	1.848	0.383	0.052	0.000
Ca	0.000	0.000	0.004	0.044	0.078	0.000
Na	0.000	0.000	0.001	0.000	0.000	0.000
Total	3.022	2.974	2.998	2.946	2.984	2.989

As the analysesabove show, Mg, Fe, and Si are major elements in olivines. Olivine may also contain Ca, Mn, Ti, and sometimes Ni or Cr, but except in extremely rare circumstances, these elements are minor or trace elements.

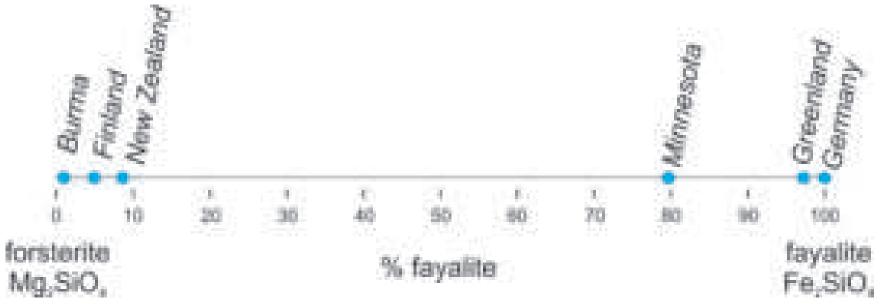
The compositions of these six olivines are all different. Silicon, magnesium, and iron are especially variable. How can we make better sense of it all? The answer is to use the atom numbers in the bottom third of the table to write formulas for each olivine. The ideal *stoichiometry* (ratios of elements) of olivine is $(R)_2SiO_4$, where R is usually Fe, Mg, Mn, or Ca. Thus, a general formula is $(Fe,Mg,Mn,Ca)_2SiO_4$ and a good olivine analysis should produce a formula close to this. Formulas for each of the six olivines – seen in the table below – come out to be very close to ideal. Apparent deviations from ideal stoichiometry (for example, the numbers of Si in the formulas are not exactly equal to 1) can mostly be attributed to inclusions of other minerals within the olivine, or to analytical error.

Normalized Olivine Formulas

specimen source	formula	% forsterite Mg_2SiO_4	% fayalite Fe_2SiO_4
Burma	$(Mg_{2.022}Fe_{0.022})Si_{0.978}O_4$	98.94	1.06
Finland	$(Mg_{1.899}Fe_{0.086}Mn_{0.005}Al_{0.015}Ti_{0.001})Si_{0.968}O_4$	95.67	4.33
New Zealand	$(Mg_{1.848}Fe_{0.157}Mn_{0.003}Ca_{0.004}Al_{0.006})Si_{0.979}O_4$	92.16	7.84
Minnesota	$(Mg_{0.383}Fe_{1.516}Ca_{0.044}Al_{0.018}Ti_{0.028})Si_{0.957}O_4$	20.19	79.81
Greenland	$(Mg_{0.052}Fe_{1.817}Mn_{0.028}Ca_{0.078}Al_{0.003}Ti_{0.005})Si_{1.001}O_4$	2.77	97.23
Germany	$(Fe_{1.970}Mn_{0.008})Si_{1.011}O_4$	0.00	100.00

Chemical substitutions in some minerals involve many elements and are complex. In olivine the substitutions are relatively simple. We can describe the compositions of most natural olivines as combinations of the *end members* (represented by ideal formulas) called *forsterite* (Mg_2SiO_4), *fayalite* (Fe_2SiO_4), *tephroite* (Mn_2SiO_4), and *calcio-olivine* (Ca_2SiO_4). In contrast with olivine, many minerals (for example amphiboles and micas) have lengthy formulas and have many elements substituting in their structures. For such minerals, choosing useful end members is difficult and arbitrary.

The six olivines considered above contain very little besides forsterite and fayalite. This is typical for most olivines and, if we ignore the other components, we get the percent values in the two columns on the right in the table. The % forsterite and % fayalite were calculated, respectively, from the ratio of Mg/(Mg+Fe) and the ratio of Fe/(Mg+Fe) in each olivine. The binary (2-component) diagram below (Figure 2.21) shows the compositions plotted on a line anchored by pure forsterite on the left, and pure fayalite on the right. The sample from Burma is nearly 100% forsterite (Mg_2SiO_4), while that from Germany is 100% fayalite (Fe_2SiO_4). The other olivines fall between.



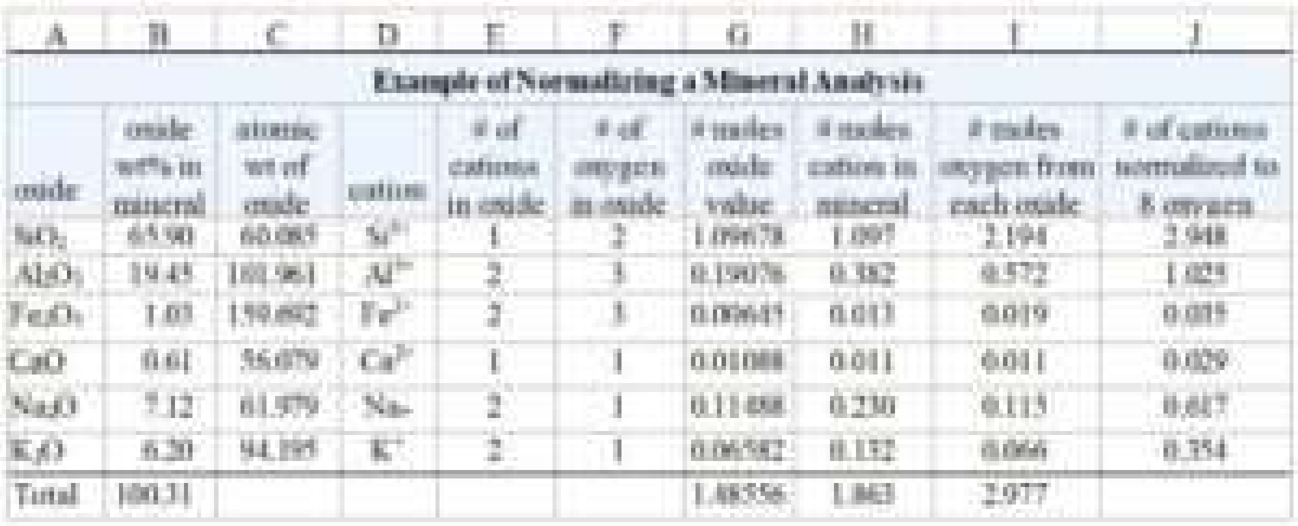
2.21 Comparing olivine compositions

The degree to which elements may substitute for each other depends on the elements and on the mineral. In olivine, Fe and Mg mix freely, so any composition between fayalite and forsterite is possible. Olivines can incorporate only minor amounts of Ca, however, so no compositions midway between calcio-olivine and forsterite are found in nature. In contrast, Ca, Mg, and Fe mix freely in garnets; natural garnets can have any composition between end members grossular ($Ca_3Al_2Si_3O_{12}$), almandine ($Fe_3Al_2Si_3O_{12}$), and pyrope ($Mg_3Al_2Si_3O_{12}$).

2.5.1 How to Normalize a Mineral Analysis

We normally report mineral analyses in values of oxide weight %, but mineral formulas are written in terms of numbers of atoms. Normalization is the process of converting an analysis into a formula. Normalization is a tedious but straightforward arithmetical operation when done by hand and, today there are Excel spreadsheets and programs to do it for you.

The table below gives the chemical analysis of a feldspar from Grorud, Norway. Column A lists the oxides and column B gives the results of the analysis. Columns C, D, E, and F give chemical data for the oxides.



Example of Normalizing a Mineral Analysis

A	B	C	D	E	F	G	H	I	J
oxide	oxide wt% in mineral	atomic wt of oxide	cation	# of cations in oxide	# of oxygen in oxide	# moles oxide value	# moles cation in mineral	# moles oxygen from each oxide	# of cations normalized to 8 oxygen
SiO_2	65.90	60.085	Si^{4+}	1	2	1.09678	1.097	2.194	2.948
Al_2O_3	19.45	101.961	Al^{3+}	2	3	0.19076	0.382	0.572	1.025
Fe_2O_3	1.03	159.692	Fe^{3+}	2	3	0.00645	0.013	0.019	0.035
CaO	0.61	56.079	Ca^{2+}	1	1	0.01088	0.011	0.011	0.029
Na_2O	7.12	61.979	Na^{+}	2	1	0.11488	0.230	0.115	0.617
K_2O	6.20	94.195	K^{+}	2	1	0.06582	0.132	0.066	0.354
Total	100.31					1.48556	1.863	2.977	

The Grorud feldspar contains 65.90 wt % SiO_2, 19.45 wt % Al_2O_3, 1.03 wt % Fe_2O_3, 0.61 wt % CaO, 7.12 wt % Na_2O, and 6.20 wt % K_2O. To convert from % grams of oxides to moles of oxides, we divide the oxide weight % values (column B) by oxide atomic weight (column C); column G shows the results. The values in column G are relative values only; they total to 1.486, which has no scientific meaning.

To calculate relative numbers of cations, we multiply the values in column G (moles of oxides) by the number of cations in each oxide (column E). To calculate moles of oxygen, we multiply the values in column G by the number of O in each oxide (column F). Columns H and I give the results of these calculations.

Using the numbers in column H and the oxygen total of 2.977, we could write the formula of the feldspar as $Ca_{0.011}Na_{0.230}K_{0.132}Fe_{0.013}Al_{0.382}Si_{1.097}O_{2.977}$, but normal feldspar analyses are written with 8 atoms of oxygen. So, in the last column (J) we have multiplied all the atom numbers in columns H and I by a constant factor so that the number of atoms of oxygen is exactly 8. The values in column J give us the normalized formula for the feldspar $(Ca_{0.029}Na_{0.617}K_{0.354})(Fe_{0.035}Al_{1.025}Si_{2.948})O_8$. The parentheses remind us which elements substitute for each other.

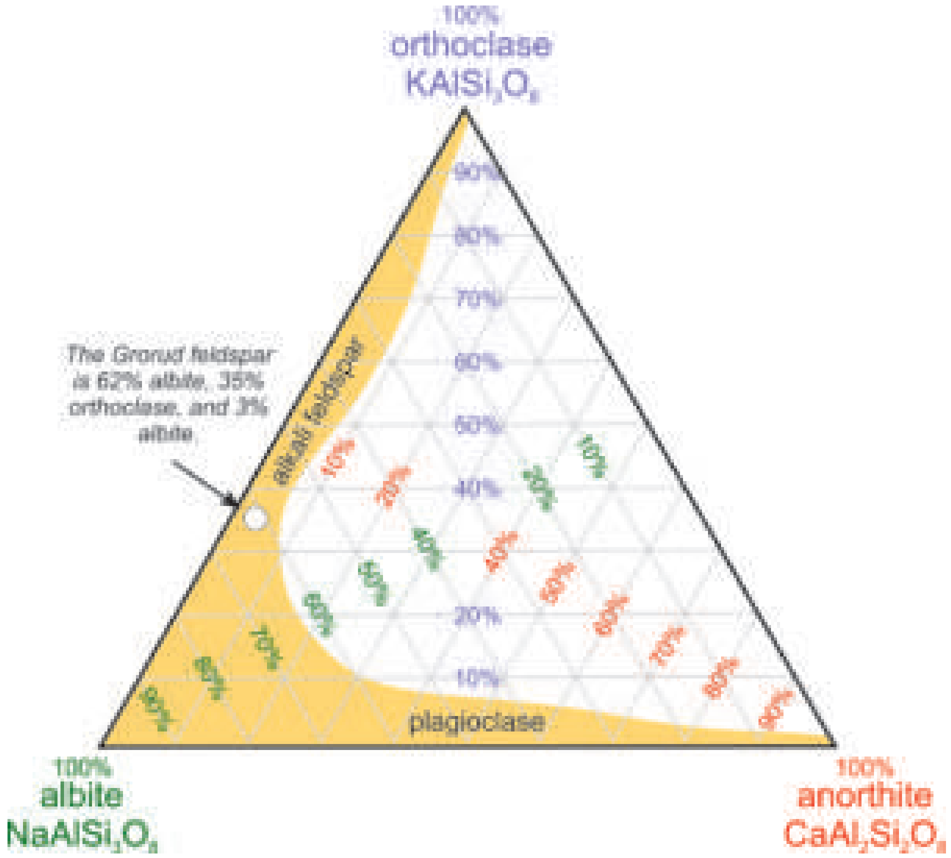
Most feldspars are primarily solutions of three end members: *anorthite* ($CaAl_2Si_2O_8$), *albite* ($NaAlSi_3O_8$) , and *orthoclase* ($KAlSi_3O_8$). So, ideal feldspar formulas have stoichiometry described by $(Ca,Na,K)(Al,Si)_4O_8$; the Grorud feldspar comes very close to this. Any discrepancy is due to analytical imprecision.

If we ignore the small amount of Fe that is present, the Grurud feldspar composition can be described as:

X_{An} = 0.029 $CaAl_2Si_2O_8$ (= 2.9% anorthite)
X_{Ab} = 0.617 $NaAlSi_3O_8$ (= 61.7% albite)
X_{Or} = 0.354 $KAlSi_3O_8$ (= 35.4% orthoclase)

The numbers 0.029, 0.617, and 0.354 are called *mole fractions*; they are equivalent to percent divided by 100.

Above we plotted olivine compositions on a line – on a binary diagram. Lines work for depicting solid solutions with two end members but not for solutions, like feldspars, that have three. We use triangular (ternary) diagrams for that purpose. And, for solutions with more than three end members, we are out of luck because we cannot easily draft diagrams in more than two dimensions.



2.22 Ternary feldspar diagram

The diagram seen in Figure 2.22 is a *ternary feldspar diagram* with end members anorthite, albite, and orthoclase at the corners. The red numbers label lines of constant anorthite content, the purple numbers label lines of constant orthoclase content, and the green numbers label lines of constant albite content. Thus, any feldspar made of combinations of albite, anorthite, and orthoclase can be plotted on diagrams like this.

The yellow region shows a range of compositions that includes most common feldspars. Except in very high temperature igneous rocks, feldspars are either *alkali feldspars* (solutions dominated by orthoclase and albite) or *plagioclase* (solutions dominated by albite and anorthite). Solutions between anorthite and orthoclase do not exist in nature. The white dot shows where the composition of the Grorud feldspar plots; it is an alkali feldspar that is 62% albite.

2.6 Common Minerals

We classify rock-forming minerals in many ways. Often, geologists contrast *primary minerals* and *secondary minerals*. Primary minerals are those that are present from the time a rock first forms. Secondary minerals form later by chemical or physical reaction within the rock. Often, such secondary reactions involve H_2O or CO_2 and occur during weathering, diagenesis, or other low-temperature alteration of a preexisting rock. The distinction between primary and secondary minerals is not exact. A primary mineral in one rock may be a secondary mineral in another.

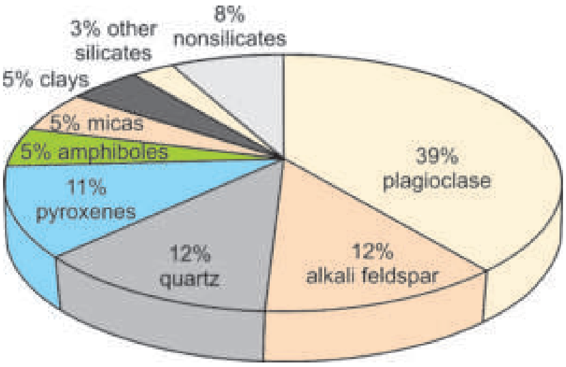
We further divide primary minerals into *essential minerals* and *accessory minerals*. Essential minerals are those whose presence is implied by the name of the rock. All limestones, for example, contain calcite or dolomite, and all granites contain quartz and K-feldspar. Essential minerals, for the most part, control rock properties.

Accessory minerals are generally present in minor amounts and do not affect most rock properties. These minerals may be made of common elements such as iron in magnetite (which is a common accessory mineral). Accessory minerals also commonly contain incompatible elements, elements that are not easily incorporated into essential minerals. Zirconium (Zr), for example, often concentrates in zircon, $ZrSiO_4$, a minor accessory mineral in many rocks. Phosphorus (P) may lead to formation of phosphate minerals such as apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, also a common accessory mineral. In most igneous and metamorphic rocks, silicates make up the essential minerals, while oxides, sulfides, and other kinds of minerals make up the accessory minerals.

2.6.1 Common Elements Make Up the Common

Minerals

Although more than 90 natural elements exist on Earth, many exist in very small amounts. Occasionally they may be concentrated in accessory minerals, but more often they are just minor diluents for major elements. It is estimated that 14 elements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, P, Mn, Ba, C) make up more than 99.7 wt % of Earth's crust. We can expect the common minerals to be made from these elements. And, we can expect minerals made of other elements to be rare.



2.23 Common minerals in the crust

Mineralogists have identified more than 5,000 minerals. Of these, fewer than 200 are common, and fewer than 50 are common enough to be considered essential minerals. Abundant oxygen and silicon, together making up nearly three quarters of Earth's crust, naturally lead to an abundance of *silicate minerals*. It is no wonder that other types of minerals, or minerals that include rarer elements as key components, are less common. Of the known minerals, about 92% are silicates. All the nonsilicates together only make up about 8% of the total. The pie chart shows the most common minerals and mineral groups n Earth's crust.

2.24 Plagioclase, a feldspar

The pie diagram above shows estimated abundances of different minerals in the crust. Plagioclase, like the plagioclase shown in this photo (Figure 2.24), is the most abundant mineral (40% of the total) in Earth’s crust because it comprises more than half of the basalt that makes up the oceanic crust. Alkali feldspar and quartz, the major components in granite, make up about another 25%. The other minerals account for 37% of the total.

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3 Mineral Properties

3.1 Calcite crystals on purple-blue fluorite. From the Annabel Lee Mine, Cave-in-Rock Mining District, southern Illinois, USA

3 Mineral Properties

KEY CONCEPTS

- Mineral names derive from mineral appearance, composition, provenance, and many other things. Many are named after well-known mineralogists.

- A mineral's common appearance (its habit) includes both crystal shape and the way that multiple mineral crystals may grow together.
- Mineral crystals have shapes related to the arrangements of atoms within them.
- We typically use physical properties such as luster, color, diaphaneity, crystal shape, streak, hardness, and cleavage to identify and distinguish different minerals.
- Other properties, including magnetism and reaction to hydrochloric acid are sometimes diagnostic.

3.1 Naming Minerals

Mineral names are based on mineral appearance, mineral chemistry, where the mineral is found, a famous scientist, or anything else deemed important by a mineral's discoverer. The Commission on New Minerals and New Mineral Names of the International Mineralogical Association reviews proposed new names and descriptions and judges their appropriateness. The Commission also occasionally discredits old names. Absolute identification and classification of minerals require knowledge of their composition and atomic structure. Mineralogists must include such information when they submit names to the Commission for approval.

3.2 Halite crystals from the Great Salt Lake, Utah

Determining mineral composition and structure may require time and equipment unavailable to most mineralogists or to mineralogy students, but fortunately we can use other methods to tell minerals apart. Differences in composition and structure lead to differences in appearance and in many other properties of minerals we use for identification. For example, the mineral halite, shown here, is most easily identified by its cubic, often clear crystals, by its softness, and by its salty taste.

Most of the properties discussed in this book fall into two general groups: *hand specimen properties*, which are easily determined using large samples, and *optical properties*, which we can only see with specially prepared slides and a *polarizing light microscope*, also called a *petrographic microscope*. This chapter reviews hand specimen properties and discusses their use in identification. We cover optical properties in the next chapter.

3.2 Mineral Identification

3.3 Pyrite cubes in sandstone

Give a mineral specimen to a nongeologist and ask them to describe it. Generally, they mention the appearance, especially color, first. With a little prodding, they may go on to describe the shape and nature of visible crystals.

For example, they might describe pyrite as metallic, being gold in color, and forming cubic crystals. (This is true of many pyrite crystals, but other crystal shapes are common.) They might describe a piece of the variety of quartz called *rose quartz* as hard, pinkish, glassy, and partially transparent.

Metallic and *glassy* are terms describing *luster*. *Gold, clear,* and *pinkish* describe *color*. Transparent describes *diaphaneity*. *Cubic* describes *crystal shape*, a property related to *symmetry*. These four properties (luster, color, diaphaneity, and shape) are basic for mineral identification. Other properties including *streak* (the color of a mineral when powdered), the way a mineral breaks (*cleavage, parting, fracture*), and *hardness* are also common keys to identification. Still, other properties can be important for specific minerals.

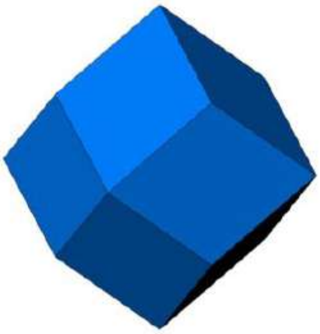
3.4 Rose quartz on top of clear quartz

Given a single property, for example *luster*, we can sort minerals into groups. In the case of luster, we usually start by dividing minerals into those that are *metallic* and those that are *nonmetallic*. The pyrite seen above is metallic. The quartz is nonmetallic. There are, however, many metallic and many nonmetallic minerals; other properties must be considered if minerals are to be identified. Nonmetallic minerals can, for instance, be divided further based on more subtle luster differences.

Ultimately, we can identify minerals by name or at least place them into small groups based on their properties. It is tempting, then, to come up with a standard list of properties that we should evaluate when identifying minerals. However, most mineralogists know that, depending on the sample and circumstances, some properties are more important than others. Rather than going through a long list or filling out a standard table, experienced mineralogists focus on the properties that are most exceptional or unique. Sometimes, a single property, such as strong *effervescence* by hydrochloric acid (diagnostic of calcite), may serve for mineral identification. And, being *magnetic* usually identifies magnetite. (Metallic iron in meteorites is also magnetic.) At first, mineral identification may seem tedious, but with a little experience, it is possible to find shortcuts to make the process more efficient.

3.3 Crystal Shape

3.6 Natural euhedral garnet crystal



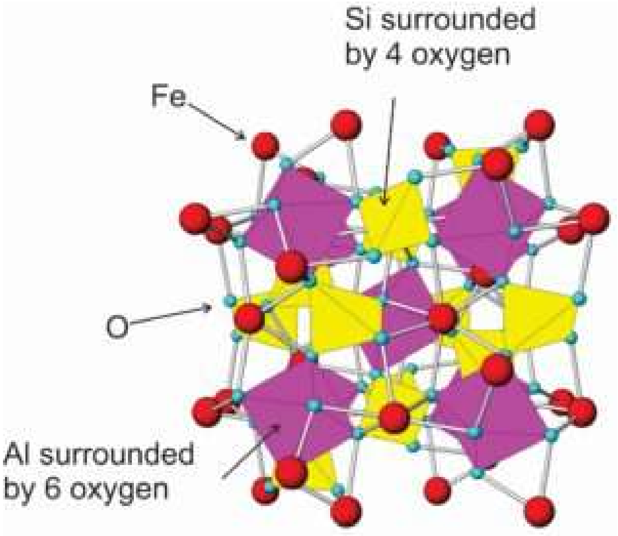
3.5 Dodecahedron

To most people, a *crystal* is a sparkling gem-like solid with well-formed faces and a geometric shape. For many scientists, including all mineralogists, *crystal* and *crystalline* also refer to any solid compound having an ordered, repetitive, atomic structure, which may or may not result in crystal faces and a gemmy appearance.

We use the term “crystal” in both ways. When a mineralogist refers to a garnet crystal, the reference may be to a *dodecahedron*, a twelve-sided crystal with diamond-shaped faces like the drawing seen here and the real garnet next to it. We call crystals, such as the well-formed garnet crystal with well-developed faces, *euhedral*.

3.7 Anhedral garnet crystal

On the other hand, petrologists and mineralogists may refer to *crystals of garnet* in a rock. The crystals may not have any smooth faces at all. The garnet seen in the photo here, which was picked out of garnet gneiss (a metamorphic rock), lacks crystal faces entirely. If no faces are visible, as in this photograph, the crystal is *anhedral*. Those crystals that fall between euhedral and anhedral are called *subhedral*.

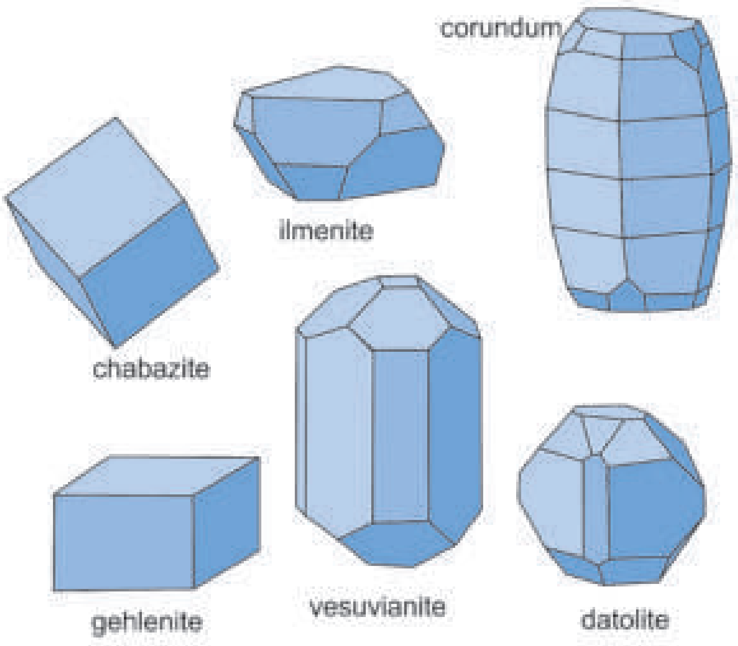


3.8 The atomic arrangement in the garnet *almandine*

Mineral crystals always have an ordered arrangement of atoms within them, but the crystals may not be geometrically shaped or smooth on the outside. All garnet crystals, for example, have the same highly ordered arrangement of atoms shown in this ball and stick drawing, but only some garnet crystals have visible crystal faces. In fact, most natural garnet is anhedral or, perhaps, subhedral. So, the garnet in the photo above is typical.

With just a few exceptions, all minerals are crystalline, but perfectly formed crystals with flat faces are rare. Nonetheless, because crystal shape reflects the crystal's atomic arrangement, when faces on a mineral are fully or partially developed, crystal shape can be a powerful identification tool. When no faces are visible, we must rely on other properties to identify a mineral.

3.3.1 Crystal Forms



3.9 Forms and combinations of forms

Mineralogists use the term *form* to refer to a group of identically shaped faces on a crystal. The faces of a form are related by crystal symmetry and have identical chemical and physical properties. If a crystal contains only one form, all crystal faces are the same size and shape. Euhedral garnet crystals, for example, generally have one form consisting of 12 identical diamond-shaped faces like the dodecahedron in Figure 3.5, earlier in this chapter.

The drawings in Figure 3.9 show common forms for six different minerals. Different samples of the same mineral may crystallize with different forms, but those shown here are typical. Like garnet crystals, chabazite crystals generally have only one form, typically containing six identical nearly (but not quite) square faces. The other five drawings show crystals with more than one form. In the ilmenite, corundum, vesuvianite and datolite drawings, the different forms have distinctive different shapes. In the gehlenite drawing, all faces are rectangular but not all are the same size. The gehlenite crystal contains three forms (three pairs of identical rectangular faces) with different sizes.

3.3.2 Mineral Habit

3.10 Blocky halite

3.11 fibrous actinolite

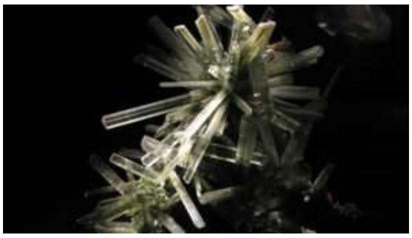
3.12 reticulated cerussite

3.13 platy wulfenite

3.14 botryoidal hematite

3.15 stellate pyrophyllite

3.16 Radiating pyrite



3.17 Prismatic gypsum

3.18 Acicular natrolite

The photos above show examples of different mineral habits. *Habit*, a property closely related to crystal shape, includes shape and size of crystal faces, how forms combine, how well developed different forms are, and the way multiple crystals grow together. Habit, thus, is the characteristic appearance a mineral can have. Some examples of different habits are shown in the photographs above.

The most useful terms describing habit are self-explanatory. Common ones used to describe the habit of single crystals include *equant* (equidimensional), *acicular* (needlelike), *tabular*, and *bladed*. These and other terms are defined below.

Terms Used to Describe Shapes of Individual Crystals (With Example Minerals)	
equant	the same dimensions in all directions (garnet, spinel)
blocky	equant with a nearly square cross sections (halite, galena)
acicular	needlelike (actinolite, sillimanite)
tabular or platy	appearing to be a plates or a thick sheet (gypsum, graphite)
capillary or filiform	hairlike or threadlike (serpentine, millerite)
bladed	elongated and flattened in one direction (kyanite, wollastonite)
prismatic or columnar	elongated with faces parallel to a common direction (apatite, beryl)
foliated or micaceous	easily split into sheets (muscovite, biotite)

For describing an assembly of multiple crystals, we use terms such as *massive, granular, radiating*, and *fibrous*. We list and define these terms and others in the table below.

Terms Used to Describe Properties of Crystal Aggregates	
massive	appearing as a solid mass with no distinguishing features
granular	composed of many individual grains
radiating or divergent	containing crystals emanating from a common point
fibrous	composed of fibers
stalactitic	appearing stalactite shaped

lamellar or tabular	appearing like flat plates or slabs growing together
stellated	containing an aggregate of crystals giving a starlike appearance
plumose	having feathery appearance
arborescent or dendritic	appearing like a branching tree or plant
reticulated or latticelike	net-like, composed of slender crystals forming a lattice pattern
colloform or globular	composed of spherical or hemispherical shapes made of radiating crystals
botryoidal	having an appearance similar to a bunch of grapes
reniform	having a kidney-shaped appearance
mammillary	having breastlike shape
drusy	having surfaces covered with fine crystals
elliptic or pisolitic	composed of very small or small spheres

Unfortunately, although museum specimens and pictures of minerals in textbooks often show distinctive shapes and habits, most mineral samples do not. Small anhedral crystals without flat faces, or massive aggregates of many small crystals, are typical, often rendering shape and habit of little use for identification. Additional complications arise because some minerals, for example calcite, have different crystal shapes or habits, depending on how they grow. Nonetheless, shape and habit reflect the internal arrangement of atoms in a crystal and, when visible, can be important diagnostic properties. For example, the movie makers blew it in the movie *Congo*. See the Box 3-1 below.

● Box 3-1 What's Wrong With This Picture?

3.19 A bogus diamond in the movie Congo

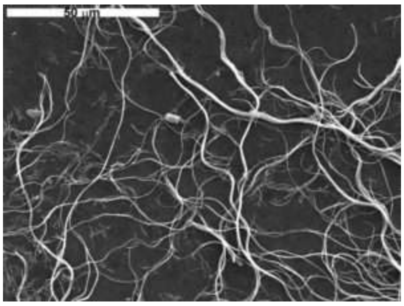
In the 1995 movie Congo, an exploration team goes to Africa to seek large, flawless diamonds. When the diamonds are shown, the movie immediately loses credibility with mineralogists because the crystals are hexagonal prisms (long crystals with a hexagonal cross section). Mineralogists know that diamond crystals can never be hexagonal prisms. The photo shows actor Timothy Curry holding a quartz crystal, not a diamond crystal.

● Box 3-2 Asbestiform Minerals and Health Risks

3.20 Chrysotile mineral specimen

We use the term *asbestiform* to describe a mineral habit characterized by small, strong, and flexible fibers, equivalent to hairs or whiskers. *Asbestos* is a commercial name for any marketable asbestiform mineral. For legal and regulatory purposes, however, the US Environmental Protection Agency has developed a more restrictive definition and defines asbestos as being one of six specific minerals. Other countries have similar legal definitions.

Mineralogists have described many asbestiform mineral varieties, but most are rare and only a few are produced for sale. The photo seen here shows “white asbestos,” composed of the mineral *chrysotile*. Chrysotile, which accounts for about 95% of the commercial market, is a member of the serpentine mineral group. It is a widespread but minor mineral in many altered ultramafic rocks.



3.21 Scanning electron microscope image of chrysotile fibers

Some commercial asbestos is composed of *crocidolite* (“blue asbestos”) or *amosite* (“brown asbestos”), varieties of the amphiboles *riebeckite* and *grunerite*, respectively. Other minerals that may be asbestiform include other amphiboles (*anthophyllite, tremolite, actinolite*), clays (*sepiolite, palygorskite*), and some members of the zeolite mineral group.

Historically, asbestos has had many uses. Since around 1880, it has been mined in large quantities because it is tough, flexible, and fire and chemical resistant. Between 1900 and 1986, builders sprayed asbestos on walls, ceilings, and pipes in many buildings in the United States. Industries have used asbestos in brake linings, roof shingles, and other applications. Unfortunately, asbestos easily crumbles to make a fine dust that people can inhale. Fibers can become embedded in lung tissue and cause asbestosis (a chronic breathing disorder that may be fatal), lung cancer, or mesothelioma (another form of cancer). For the most part, epidemiologists have documented these diseases in workers exposed to high levels of asbestos over long times.

In 1907 health workers reported the first asbestos-related diseases, but it was not until around 1960 that the threat posed by asbestos was accepted as serious. In 1974 the Environmental Protection Agency (EPA) banned asbestos for most commercial use in the United States, and soon afterward launched a vigorous program to remove asbestos from commercial structures. However, American companies still ship many products containing asbestos to developing countries. Despite the ban and efforts to eliminate asbestos from our environment, it is still common in many buildings and as a component in urban dust.

Click on the arrow below to be taken to a video that shows some spectacular images of crystals that have different crystal habits. This video is one of many produced by the Envisioning Chemistry Project.

For additional views of many different mineral habits with a discussion, go the video linked below:

▶ Video 3-2: Examples of mineral habits (10 minutes)

3.4 Mineral Appearance

3.4.1 Luster

Luster refers to the general appearance or sheen of a mineral. It refers to the way in which a mineral reflects light.

For a good discussion, with examples, of many different mineral lusters, watch the video linked below:

▶ Video 3-3: Examples of mineral lusters (7 minutes)

3.4.1.1 Metallic and Submetallic Lusters

3.22 A 200 lb cluster of stibnite crystals from China

Minerals that have the shiny appearance of polished metal are said to have a *metallic luster*. Some could be used as mirrors. Well-crystallized pyrite, is a good example. Other commonly metallic minerals include chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), native copper (Cu), native gold (Au), hematite (Fe_2O_3), and magnetite (Fe_3O_4). The photo seen here is stibnite

(Sb_2S_3). Most of minerals with a metallic luster are sulfides, oxides, or native elements.


3.23 Golden chalcopyrite, grey sphalerite, and white fluorite from Peru

Minerals that do not appear metallic have a *nonmetallic* luster. Those that appear only partially metallic are called *submetallic*. The chalcopyrite ($CuFeS_2$; gold-bronze color) seen in this photo is metallic, the minor dark grey sphalerite (ZnS) in the photo might be considered submetallic, and the hard-to-pick-out fluorite (CaF_2) (semi-clear and white) is nonmetallic. Other commonly submetallic minerals include, cinnabar (HgS), and cuprite (Cu_2O).

3.4.1.2 Nonmetallic Lusters

Mineralogists use many terms to describe nonmetallic lusters. The most commonly used terms are listed in the table below.

Terms Used to Describe Luster of Nonmetallic Minerals		
luster	**meaning**	**example minerals**
vitreous	Having a glassy appearance	quartz, tourmaline
resinous	Having the appearance of resin	sphalerite, sulfur

greasy	Reflecting light to give a play of colors; similar to oil on water	chlorite, nepheline
silky	Having surfaces appearing to be composed of fine fibers	chrysotile (asbestos), gypsum
adamantine	A bright, shiny, brilliant appearance similar to that of diamonds	diamond, cerussite
pearly	Appearing iridescent, similar to pearls or some seashells	muscovite, talc
dull	Not reflecting significant amounts of light or showing play of colors	kaolinite (clay), niter

Vitreous Minerals

Vitreous minerals are nonmetallic minerals that have a glassy appearance. The adjective is derived from the Latin *vitrium*, meaning glass. Quartz (SiO_2) is an excellent example. Calcite ($CaCO_3$), topaz ($Al_2SiO_4F_2$), and fluorite (CaF_2) are other minerals that may be vitreous. The two photos below show vitreous calcite and topaz.

3.24 Vitreous calcite from the Pyrenees Mountains, France

3.25 Vitreous topaz, Minas Gerais, Brazil

Resinous Minerals

Resinous minerals have a luster similar to violin resin or pine pitch. The most common mineral example is a resinous variety of sphalerite (ZnS) such as that shown in the photo below (Figure 3.26). Sphalerite, however, has other appearances. In fact, the name *sphalerite* is from the Greek *sphaleros* which means deceiving or treacherous. This name refers to the many different appearances that sphalerite may have. Its luster can be metallic, submetallic, resinous or adamantine. Some samples are transparent with a vitreous luster. The photo on the right below shows *amber*, which is fossilized tree resin, with an insect inclusion. Amber is a *biomineral*, not a true mineral.


3.26 Dark metallic sphalerite with orange resinous sphalerite on top


3.27 Amber with an included insect

Greasy Minerals

Greasy minerals show a *play of color* – color change with angle of view – that resembles grease or maybe fat. Examples are the opal and cordierite seen in the two photos below. Besides opal and cordierite, jadeite and a few other minerals sometimes have a greasy luster. However, this luster occurs most commonly in opal (a mineraloid) and in minerals that contain many small inclusions.


3.28 Opal (moss opal variety)


3.29 Cordierite from Madagascar

A good short discussion of play of color can be found at:

▶️ Video 3-4: Play of colors (5 minutes)

Silky Minerals

Silky minerals appear to have a parallel arrangement of fine fibers, sometime making them have the luster of silk. If the fibers are coarse, we may describe minerals as *fibrous* instead of *silky*. *Ulexite* (a hydrated borate mineral shown in the photo on the left below) is a classic but rare example of a silky mineral. Satin spar, in the photo on the right below, is a variety of gypsum ($CaSO_4 \cdot 2H_2O$). It gets its name from its fibrous appearance.


3.30 Silky ulexite


3.31 Satin spar (gypsum)

Adamantine Minerals

We use the term *adamantine* to describe crystals that sparkle or appear brilliant; *diamond* (C) is perhaps the best-known example. But, *Herkimer diamonds*, a variety of quartz (SiO_2) from Herkimer, New York can also be adamantine. The two photos below show a Herkimer diamond and a real diamond. Other minerals that are sometimes adamantine include *anglesite* ($PbSO_4$), *cerussite* ($PbCO_3$), and corundum (Al_2O_3). Some synthetic minerals, including *cubic zirconia* (ZrO_2) are also adamantine. All these natural and synthetic stones can have their sparkle enhanced with proper faceting.

3.32 Herkimer diamond (quartz)

3.33 (Real) diamond

Pearly Minerals

Pearly minerals show a *play of color* that resembles that of pearls. Light reflecting from pearly minerals may appear to have washed out rainbow colors. The play of colors is due to a layered atomic arrangement, so pearly minerals generally have excellent planar cleavage. The two photos below show pearly muscovite and talc. These minerals are somewhat *dichroic*, which means their colors change with angle of view. But, that property cannot be seen in standard photos.

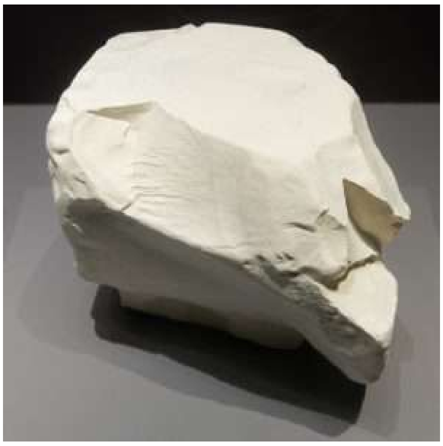

3.34 Pearly muscovite


3.35 Pearly talc

Dull and Earthy Minerals

Dull minerals show no remarkable luster – because they have non-reflective surfaces. *Kaolinite* (Figrure 3.36, below) is a good example – it is usually a fine-grained aggregate of small grains, white, and drab. Besides kaolinite, the other clay minerals, such as *montmorillonite* or *illite*, also have dull lusters.

We say that dull minerals are *earthy* if they have a brownish or reddish color resembling dirt. Common *hematite* is an excellent example (although some hematite may be metallic). The hematite seen in the photo below (Figure 3.37) can be described as being earthy, and Figure 3.14 showed another example of earthy hematite. Besides hematite, *limonite* and other metal oxides and hydroxides are commonly earthy.


3.36 Kaolinite from the Pyrenees


3.37 Hematite from New York

3.4.2 Diaphaneity

3.38 Iceland spar, a variety of calcite

Diaphaneity refers to a mineral’s ability to transmit light. Some minerals are *transparent*. When they are thick, some distortion may occur, but light passes relatively freely through them. For example, we can see the clouds in the distance through the clear *Iceland spar* (calcite) crystal in the photo seen here. Because it is so clear, Iceland spar has been used in some industrial applications. Unfortunately, it is not very durable because calcite is very soft. Very few minerals are as transparent as the calcite seen here. Thin sheets of muscovite and some quartz come close.

3.39 Dogtooth spar on top of orpiment

Minerals that do not transmit light as well as clear calcite may be *translucent*. Although it is not possible to see through them as with transparent minerals, if thin enough, translucent minerals transmit light. Both the whitish calcite and the darker colored orpiment in this photo (Figure 3.39) are translucent. Many other minerals exhibit this same property. For example, quartz comes in many different colors but, unless very finely crystallized, it is generally translucent to some degree. Calcite, gypsum, topaz, and many micas, are often commonly translucent.

3.40 Molybdenite on quartz

Some minerals are neither transparent nor translucent, and are *opaque* instead. Opaque minerals, do not transmit light unless the mineral is exceptionally thin. Most opaque minerals have metallic lusters and belong to the sulfide, oxide, or native element groups. This photo (Figure 3.40) shows a hexagonal flake of opaque *molybdenite* (MoS_2) on top of translucent *quartz*. Pyrite and magnetite are two more common examples of opaque minerals.

3.4.3 Color

3.41 Three different samples of corundum

Color is often used for quick identification of minerals. Sometimes, it can be diagnostic, but for many minerals it is ambiguous or even misleading. The deep red color of rubies may seem distinctive. Ruby is, however, just one variety of the mineral *corundum*. *Sapphires* are different colored varieties of the same mineral. The photos show just a few of the many colors that corundum may have. To add to the confusion, other minerals, such as *spinel* or *garnet*, may have the same deep red color as ruby. Color is ambiguous because many things can give a mineral its color.

Color is one of the most misunderstood mineral properties. It is easy to look at a ruby illuminated by white light and say it has a red color. If the ruby is illuminated by light of a different color, it may not appear red. Color, then, is not a property of a mineral. It is instead the result we observe when light and a mineral interact. When we see that a mineral has color, what we are really observing is the color of the light that is being reflected or transmitted to our eye. Normal light, called white light, includes many different colors. When white light strikes a mineral surface, if all of the colors are reflected back to our eyes, the mineral will appear white. If none of the colors are reflected back to our eye, the mineral will appear black. Most minerals, like ruby, appear to have color because only one or a few wavelengths make it back to our eye. The other wavelengths of light are scattered in other directions or are absorbed or transmitted by the mineral in some way.

3.42 Pyrite with minor hematite on dolomite

3.43 Chalcopyrite that is tarnishing

Metallic minerals, especially sulfides, tend to be constant in their coloration. So mineralogists commonly use color as a key tool for sulfide identification. However, metallic minerals easily tarnish, so we need a fresh surface to see the true color. The photos above show pyrite on top of dolomite (left photo) and chalcopyrite (right photo). These minerals are both sulfides, but pyrite is FeS_2 and chalcopyrite has formula $CuFeS_2$. Both sulfides are quite common and color usually distinguishes one from the other – pyrite is more golden or brass colored, and chalcopyrite generally has a yellowish tint and sometimes appears a bit greenish. Notice that the chalcopyrite is tarnishing. The pyrite specimen also contains a few crystals of dark colored hematite.

3.44 Light purple amethyst and orangish citrine from Namibia

Color is often a poor property to use for identifying nonmetallic minerals because many things can cause minerals to have different colors. For example, quartz may be colorless, rosy (rose quartz), yellow (citrine), purple (amethyst), milky, smoky, or black. The photo seen here contains both light purplish amethyst and orangish citrine.

The most significant control on color is a mineral’s chemical composition. Elements that give a mineral its color are called *chromophores*. It does not take large amounts of chromophores to color a mineral. Minor amounts, less than 0.1 wt% of transition metals such as iron and copper, may control a mineral’s color because electrons in the d-orbitals of transition metals are extremely efficient at absorbing certain visible wavelengths of light. The remaining wavelengths are reflected and give minerals their color.

3.45 Green sphalerite from the Adirondack Mountains, New York

3.46 Yellow sphalerite from the Adirondack Mountains, New York

If the elements controlling the selective reflection of certain wavelengths are major components in a mineral, the mineral is *idiochromatic*, or “self-coloring.” Sphalerite (ZnS), for example, is an idiochromatic mineral. It changes from white to yellow to green to brown to black as its composition changes from pure ZnS to a mixture of ZnS and FeS. The two photos seen here are from the same mining district in New York but are different colors. Compare these with other photos of sphalerite earlier in this chapter (Figures 3.23 and 3.26). Sphalerite has a lot of looks!

3.47 Azurite and malachite from southeast Utah

Many copper minerals are idiochromatic and have green or blue coloration, while many manganese minerals are pinkish. These colors derive from selective absorption of certain colors by copper and manganese. Idiochromatic elements may have different effects in different minerals. Malachite and azurite, seen in the photo here, are both hydrated copper carbonates, but malachite is green and azurite is blue. In both minerals the color is due to copper.

Ruby and sapphire are examples of *allochromatic* varieties of corundum. In allochromatic minerals, minor or trace elements determine the color. Very small amounts of iron and titanium give sapphire a deep blue color. Small amounts of chromium give ruby and other gemstones deep red colors. Like the effects of idiochromatic elements, the effects of allochromatic elements may be different in different minerals. Allochromatic chromium is also responsible for the striking green color of emerald (a variety of the mineral *beryl*), chrome diopside, and some tourmalines.

Structural defects in minerals may also influence their color. Radiation damage gives quartz, for example, a purple, smoky, or black color. The purple color of many fluorites is caused by *Frenkel defects* (out of place ions in the atomic structure). Other causes of coloration include the oxidation or reduction of certain elements (especially iron), and the presence of minute inclusions of other minerals.

3.4.4 Streak

3.48 Red hematite streak

Although it would never occur to many people to check a *mineral’s* streak, streak is sometimes a key diagnostic property. It is not a useful property for identifying most silicates but is especially useful for distinguishing oxide and sulfide minerals. The streak of a mineral is the color it has when finely powdered. For mineral identification, it is much more reliable than mineral color, and it is easy to determine. The usual method of determining streak is to rub the mineral against a ceramic *streak plate* or other piece of unglazed ceramic. Figure 3.48 shows a red streak from the mineral hematite, and the photo below (Figure 3.49) shows a yellow streak from sulfur.

3.49 Yellow sulfur streak

Steak color is a good diagnostic property because the mineral is finely powdered, so structural and other nonchemical effects are minimized. Calcite, for example, comes in many different colors, but calcite’s streak is always white. Pyrite (fool’s gold) is yellow but has a dark colored streak, as does chalcopyrite. Gold, which has a color similar to pyrite’s (in hand specimen), has a yellow-gold streak.

Mineralogists routinely use streak when identifying minerals, both in the laboratory and in the field, but it cannot be determined for minerals harder than the hardness of a streak plate. The table below lists some minerals that often have diagnostic streak colors.

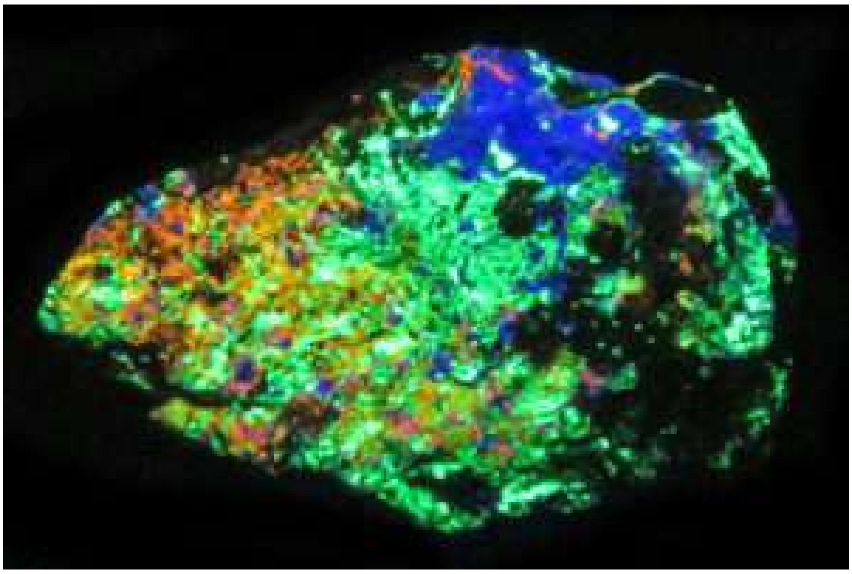
Examples of Minerals that Do Not Have a White Streak

mineral	streak color
magnetite, ilmenite	black
galena	lead gray
rutile	pale or light brown
goethite	yellow brown to ocher yellow
sphalerite	white to light brown or yellow
sodalite	very pale blue to white
azurite	light blue
chrysocolla	very pale blue to gray or tan
malachite	pale green
orpiment	pale yellow to yellow
sulfur	light yellow to yellow
realgar	orange or reddish yellow
cinnabar	dark red to scarlet
hematite	rust red to blood red

Streak can be extremely useful for telling dark-colored minerals apart, especially metallic ones. For example, *hematite* may be red, gray, or black in hand specimen and may or may not have a metallic luster. It always, however, has a diagnostic red streak that helps distinguish specular hematite from galena, or other kinds of hematite from similarly colored minerals. White and colorless streaks are considered the same because we cannot make the distinction using a standard streak plate, and (unfortunately) most minerals have a white or colorless streak.

3.4.5 Luminescence

Some minerals will emit light when they are activated by an energy form other than visible light. We call such an effect *luminescence*. Examples of luminescence include *fluorescence, phosphorescence, and thermoluminescence.*



3.50 Willemite, hardystonite, clinohedrite, and calcite

This photo is a fluorescent specimen from the Franklin Mine in New Jersey. It is illuminated with short wavelength ultraviolet light and contains green willemite (Zn_2SiO_4), blue hardystonite ($Ca_2ZnSi_2O_7$), orange clinohedrite ($CaZnSiO_4 \bullet H_2O$), and minor red calcite ($CaCO_3$). *Fluorescent* minerals like the ones seen here give off visible light when they are struck by energy of a shorter wavelength. If the visible emission continues after the energy source is turned off, the mineral is *phosphorescent*. *Pectolite* is an example of a phosphorescent mineral.

Thermoluminescent minerals such as some tourmalines give off visible light in response to heating. Some varieties of fluorite, calcite, and apatite also have this property.

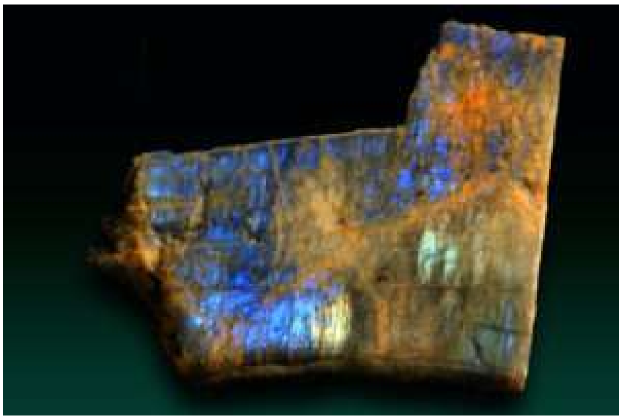
3.4.6 Play of Colors

We discussed play of colors earlier in this chapter (for example the pearly luster that is sometimes exhibited by micas or talc) but it is worth returning to the topic to consider some special examples. When it enters some crystals, white light can be separated into individual wavelengths of varying intensities emitted in different directions, somewhat like light coming out of a prism. The play of colors is a form of light scattering due to very fine particles in the minerals or to textures of mineral surfaces. The two photos on the right below (Figures 3.52 and 3.54) show examples of *opalescence* (most notably exhibited by *opals*, but also by a variety of K-feldspar called *moonstone*).

3.51 Limonite

3.52 Opal

3.53 Labradorite



3.54 Moonstone

The limonite photo above (Figure 3.51) displays *iridescence*, sometimes described as being similar to the colors on top of an oil slick. This play of colors commonly appears when metallic minerals such as bornite tarnish or, in this case, when limonite tarnishes. The fourth photo (bottom left, Figure 3.53) shows labradorite, a feldspar, displaying *labradorescence*. Labradorescence is a variety iridescence.

Chatoyancy and *asterism* are two special scattering effects most easily seen in gemmy polished minerals, such as the two *cabochons* (gems that have been shaped and polished instead of faceted) and the polished tiger’s eye stone seen in the photos below.

3.55 Moonstone showing chatoyancy

3.56 Star of India showing asterism

3.57 Tiger’s eye quartz

Chatoyant minerals show a bright band of scattered light, often perpendicular to the long direction of a crystal. Such minerals are sometimes said to have a *cat’s-eye* (like the *moonstone* above) or *tiger’s-eye* (like the *quartz* above) appearance. The *satin spar* variety of gypsum is also chatoyant.

Asterism, a property sometimes visible in rubies, sapphires, garnets, and some other gems, refers to scattered light appearing as a “star.” The example shown above in(Figure 3.56 is a famous sapphire called the *Star of India* that is in the American Museum of Natural History in New York. It has spectacular asterism. Chatoyancy and asterism are caused by closely packed parallel fibers or inclusions of other minerals within a mineral crystal.

For some additional pretty examples of chatoyancy and asterism, see the video at:
▶ Video 3-5: Chatoyancy and asterism (3 minutes)

3.5 Strength and Breaking

The color and shape of minerals are obvious to anyone, but mineralogists note other, more subtle, properties too. Several relate to the strength of bonds that hold atoms in crystals together. These properties are especially reliable for mineral identification because they are not substantially affected by chemical impurities or defects in crystal structure.

3.5.1 Tenacity

3.58 Jade figurine and cabochon

The term *tenacity* refers to a mineral’s toughness and its resistance to breaking or deformation. Those that break, bend, or deform easily have little tenacity. In contrast, strong unbreakable minerals have great tenacity. The photo here shows samples of the gemstone *jade* shaped and polished to produce a figurine and a cabochon. Gemmy jade may be either of two minerals: *jadeite* (a pyroxene) or *nephrite* (a rock containing amphibole). In either case, jade is one of the most tenacious natural materials known. It does not easily break or deform, even when under extreme stress. That is one reason, besides beauty, that it is prized as a gemstone.

The nature of its chemical bonds controls the tenacity of a mineral. Ionic bonding often leads to rigid, *brittle* minerals. Halite is an excellent example of a brittle mineral. It shatters into many small pieces when struck. Quartz, too, is brittle, although the bonding in quartz is only about half ionic. Many metallic minerals, such as native copper, are *malleable*, which means we can shape them with a hammer. Native copper is also *ductile*, which means we can stretch it out into wire-like shapes. Other minerals, such as gypsum, are *sectile*, which means they can be cut into thin pieces with a knife.

Some minerals, including talc and chlorite, are *flexible* due to weak van der Waals and hydrogen bonds holding well-bonded layers of atoms together. When force is applied, slippage between layers allows bending. When pressure is released, they do not return to their original shape. Still other minerals, notably the micas, are *elastic*. They may be bent but resume their original shape after pressure is released if they were not too badly deformed. In micas and other elastic minerals, the bonds holding layers together are stronger than those in chlorite or clays.

Terms Used to Describe Tenacity

brittle	easily broken or powdered
malleable	capable of being hammered into different shapes
sectile	capable of being cut into shavings with a knife
ductile	capable of being drawn into a wire-like shape
flexible	capable of being bent into a different shape
elastic	a bendable mineral that returns to its original shape after release

3.5.2 Fracture, Cleavage, and Parting

Fracture is a general term used to describe the way a mineral breaks or cracks. Terms used to describe fracture include *even*, *conchoidal, splintery*, and others defined in the table below. Because atomic arrangement is not the same in all directions within a crystal, and chemical bonds are not all the same strength, most crystals break along preferred directions. The orientation and manner of breaking are important clues to crystal structure. If the fractures are planar and smooth, we say that the mineral has *good cleavage*. Cleavage involves minerals breaking parallel to planes of atoms. We use geometric terms such as *cubic, octahedral*, *rhombohedral*, or *prismatic* to describe cleavage when appropriate.

Terms Used to Describe Fracture	
even	breaking to produce smooth planar surfaces (halite)
uneven / irregular	breaking to produce rough and irregular surfaces (rhodonite)
hackly	fracturing to produce jagged surfaces and sharp edges (copper)
splintery	forming sharp splinters (kyanite, pectolite)
fibrous	forming fibrous material (chrysotile, crocidolite)

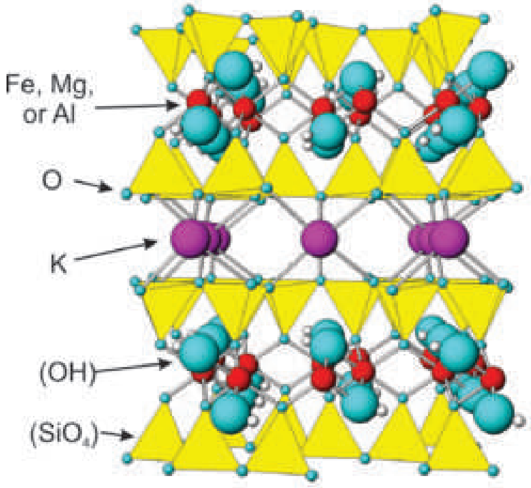
conchoidal	breaking with curved surfaces as in the manner of glass (quartz)

Terms Used to Describe Cleavage	
basal	well developed planar cleavage in one direction only; also sometimes called “platy” (micas)
cubic	three cleavages at 90˚to each other (galena)
rhombohedral	three cleavages not at 90˚to each other (calcite)
octahedral	four cleavages that produce 8-sided cleavage fragments (fluorite)
prismatic	multiple directions of good cleavage all parallel to one direction in the crystal (tremolite)

If a mineral cleaves along one particular plane, a nearly infinite number of parallel planes are equally prone to cleavage. This is due to the repetitive arrangement of atoms in atomic structures. The spacing between planes is the repeat distance of the atomic structure, on the order of angstroms (1Å = 10^{-10} m) for mineral crystals. The whole set of planes, collectively referred to as a *cleavage*, represents planes of weak bonding in the crystal structure. The vast majority of minerals exhibit cleavage but the nature of the cleavage is highly variable.

Micas, including muscovite and biotite, are the best examples of minerals with one excellent cleavage. The photo below (Figure 3.59) shows cleavage in biotite; the mineral can be easily broken into very thin sheets. Molybdinite, too, has only one direction of cleavage and breaks into sheets (see the molybdenite in Figure 3.40). The micas, molybdenite, and many other minerals cleave into thick slabs or sheets. We say these minerals have *basal cleavage.*

3.59 Biotite



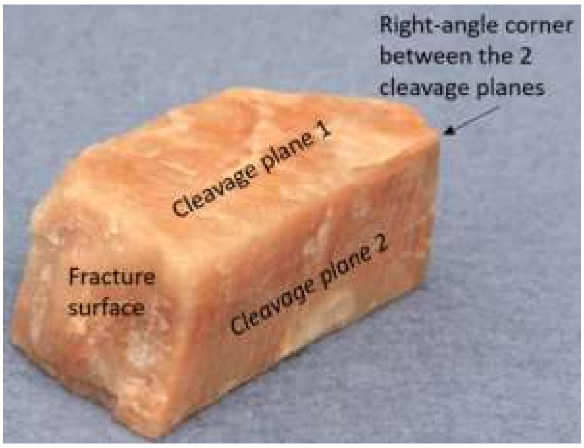
3.60 The atomic arrangement in micas

The ball and stick model in Figure 3.60 shows the atomic arrangement in micas. It is similar to the arrangement in all sheet silicates. The layered structure explains why micas cleave as they do. Micas cleave into sheets because the bonds to the potassium ions are very weak compared to all bonding in other directions.

3.61 Quartz showing conchoidal fracturing

Minerals that have more than one direction of weakness will have more than one cleavage direction. The direction and angular relationships between cleavages, therefore, give valuable hints about atomic structure. Minerals that are equally strong in all directions, such as quartz and olivine, have no cleavage and fracture to form irregular surfaces. These minerals break along curved surfaces to form *conchoidal fractures* similar to what happens when a glass breaks. Figure

3.61 shows a sample of quartz fractured in many curving directions.



3.62 K-feldspar

Feldspars, like the K-feldspar shown, have two cleavages, two planar directions that they break. One is *very good* (meaning it is easily observed) and the other better described as distinct (meaning it often shows). The angle between the two feldspar cleavages is about 90°, which explains why the specimen in the photo appears to have a square cross section. Cleavages in feldspar are, however, generally not as well developed as cleavages in minerals like mica and, so, may be hard to discern. Feldspars are typical – in ideal specimens the cleavages and angles between them can be easily seen. But, in many specimens, they cannot.

3.63 Albite is one of the most common feldspars. Click on this image for a

3-dimensional view.

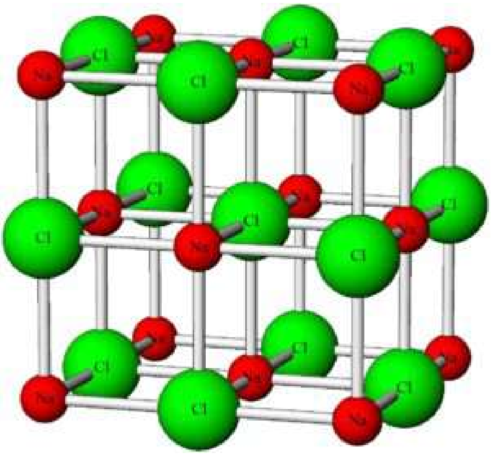
The photo seen here shows albite, another kind of feldspar. Hints of cleavage can be seen, but it is not obvious how many cleavages are present or what their angular relationships are. But, *if you click* on the photo of albite, you will get to a 3-dimensional photograph that you can rotate so you see the cleavage. Look closely and you will see that the angle between cleavages is just about 90°.

Some minerals with two cleavages, such as kyanite, easily break into long splintery pieces. Anthophyllite, too, sometimes forms bladed crystals. The photos below show typical blue blades of kyanite and a cluster of bladed anthophyllite crystals.

3.64 Kyanite

3.65 Anthophyllite

Other minerals, including halite and calcite, may have three directions of cleavage. The ball and stick model below shows the atomic arrangement in halite. Atoms are evenly spaced and all bonds are perpendicular. Consequently, halite has *cubic cleavage* – three directions of cleavage at 90° to each other. In the blue/gray halite crystal below, the cleavages created a cube, and additional cleavage traces can be seen as fine cracks. Figures 3.2 and 3.10 also show halite. The cleavage cannot be seen in Figure 3.2 but is very clear in Figure 3.10



3.66 Halite

3.67 Halite

3.68 Calcite showing rhombohedral cleavage

Like halite, calcite has three good cleavages. But, unlike halite, the cleavages are not perpendicular. So calcite cleaves into shapes called *rhombs*. This photo shows a bunch of calcite cleavage fragments. Compare the shape with the clear calcite shown in Figure 3.38. Besides calcite, other carbonate minerals, collectively belonging to the *rhombohedral carbonate group*, cleave the same way. Other minerals, such as fluorite, may have four, or more, cleavages.

The four fluorite crystals shown below in Figure 3.69 have the same atomic arrangements and so cleave the same way. All fluorite is essentially CaF_2 but color varies due to minor chemical impurities.

3.69 Fluorite

The ease with which a mineral cleaves is not the same for all minerals or for all the cleavages in a particular mineral. Mineralogists describe the quality of a particular cleavage with qualitative terms: *perfect, good, distinct, indistinct*, and *poor*. Some minerals contain only poorly developed cleavage, other, like calcite have perfect cleavage. Whether perfect or not, when present, cleavage can be a good property to help identify minerals. For examples, some specimens of pyroxene and amphibole may appear as similar dense dark minerals. But, pyroxenes have two cleavages at about 90^o to each other, and amphiboles have two cleavages at 60^o to each other.

Click on the image below to explore a 3-dimensional model of cleavage in biotite, K-feldspar, and quartz.

3.70 Link to a 3-dimensional sample with varying kinds of cleavage

Crystal faces and cleavage surfaces may be difficult to tell apart. In some minerals, principal cleavage directions are parallel to crystal faces, but in most they are not. A set of parallel fractures suggests a cleavage, but if only one flat surface is visible, there can be ambiguity. However, this problem is sometimes mitigated because crystal faces often display subtle effects of crystal growth. *Twinning* (oriented intergrowths of multiple crystals) and other *striations* (parallel lines on a face), *growth rings* or layers, *pitting*, and other imperfections make a face less smooth than a cleavage plane and give it lower reflectivity and a more drab luster.

3.71 Calcite from Chihuahua, Mexico

The photo seen in Figure 3.71 is of a calcite crystal that shows visible striations on its crystal faces. The lines are artifacts of crystal growth and are not related to cleavage.

Some minerals exhibit *parting*, a type of breaking that is often quite similar to cleavage. Parting occurs when a mineral breaks along structural planes but, unlike cleavage, parting is not found in all samples of a particular mineral and does not repeat to form many parallel planes that are only a few angstroms apart. Several things can induce parting, perhaps most commonly it occurs because of twinning (when multiple crystals grow together and share atoms). Distinguishing parting from cleavage can, sometimes, be problematic.

Cleavage is an excellent property for mineral identification. Often the quality and number of cleavages may be seen in hand specimen. Sometimes we use a hand lens to identify the set of fine parallel cracks more irregular than twinning and striations, which suggest a cleavage that is too poorly developed to see with the naked eye. We may estimate angles between cleavages and, if we need accurate angular measurements, we can use techniques involving a *petrographic microscope* or a device called a *goniometer*.

For many good examples of mineral fracture and cleavage, watch the video linked below:

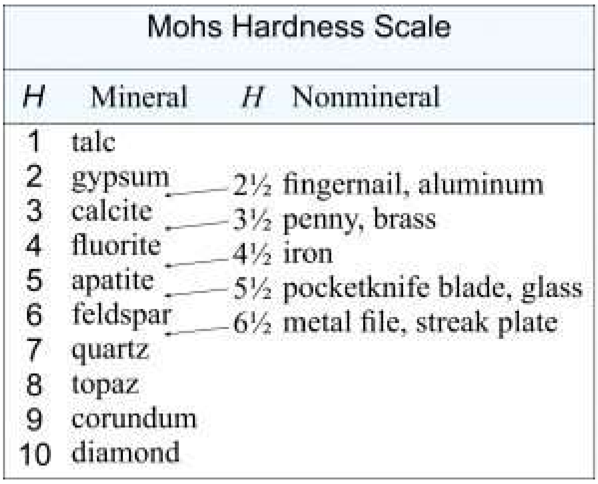
▶ Video 3-6: Examples of mineral fracture and cleavage (8 minutes)

A good additional perspective on cleavage can be found at:

▶ Video 3-7: Mineral cleavage (5 minutes)

3.5.3 Hardness

Hardness is a mineral’s resistance to abrasion or scratching. *Relative hardness* (symbolized by *H*) is determined by trying to scratch a surface of one mineral with an edge or corner of a second mineral. If a scratch or abrasion results, the first mineral is the softer. *Absolute hardness* is not quite the same as relative hardness. It is the measure of a material’s ability to resist permanent deformation. Although rarely done by mineralogists, values of absolute hardness may be determined in several ways; the easiest is to use an indenting tool similar to ones used to measure the hardness of steel. The indenting tool measures the force necessary to produce a permanent indentation in a flat surface.



Mohs Hardness Scale

H	Mineral	*H*	Nonmineral
1	talc		
2	gypsum	2½	fingernail, aluminum
3	calcite	3½	penny, brass
4	fluorite	4½	iron
5	apatite	5½	pocketknife blade, glass
6	feldspar	6½	metal file, streak plate
7	quartz		
8	topaz		
9	corundum		
10	diamond		

This table gives the relative hardness scale that is used by mineralogists. Based on ten well-known minerals, it is called the *Mohs Hardness Scale*, named after Austrian mineralogist Friedrich Mohs who developed it in 1812. The Mohs scale ranks minerals by their ability to scratch each other. The Mohs scale is related to absolute hardness but does not measure the same thing because resistance to scratching depends on additional factors.

If we compare the Mohs hardness scale with absolute hardness, we find that the Mohs scale is not linear and is close to being exponential. The hardnesses of the softest minerals are more similar than the hardnesses of the four hardest ones (quartz, topaz, corundum, diamond). Gypsum (H = 2) is only slightly harder than talc (H = 1), but diamond (H = 10) has a hardness five times greater than corundum (H = 9).

3.72 Fingernail scratching gypsum

We can estimate relative hardness by conducting scratch tests to compare the hardness of an unknown mineral to the minerals in the Mohs hardness scale. Many labs are equipped with boxes of known minerals for this purpose.

Alternatively, we can approximate hardness by comparing mineral hardness with the hardness of a fingernail, penny, pocketknife, glass, or several other common objects – the most commonly used are listed in the table above. Figure 3.72 shows gypsum being scratched with a fingernail. Gypsum, one of the softest minerals known, has a hardness of 2 on the Mohs hardness scale; fingernails have a hardness of about 2½. A penny has hardness of 3½, iron has hardness of about 4½, a pocketknife has hardness of 5½, and a metal file has hardness of 6½.

Scratch tests are often straightforward, but there can be complications. Mineral specimens may be too small or too valuable to scratch. Large samples may consist of many grains loosely cemented together so that scratch tests are not possible. Others may cleave or fracture when we perform tests. In still other cases, the results of scratch tests may be ambiguous, especially if two minerals have the same, or nearly the same, hardness.

Most minerals have hardness greater than 2 and less than 7. The tables below, list some examples of relatively common minerals that fall outside this range.

Hardest Minerals		
name	**formula**	**hardness**
cordierite	$(Mg,Fe)_2Al_4Si_5O_{18}$	7
quartz	SiO_2	7
andalusite	Al_2SiO_5	7½
zircon	$ZrSiO_4$	7½
beryl	$Be_3Al_2Si_6O_{18}$	7½ to 8
spinel	$MgAl_2O_4$	7½ to 8
topaz	$Al_2SiO_4(F,OH)_2$	8
chrysoberyl	$BeAl_2O_4$	8½
corundum	Al_2O_3	9
diamond	C	10

Softest Minerals		
name	**formula**	**hardness**
talc	$Mg_3Si_4O_{10}(OH)_2$	1
molybdenite	MoS_2	1 to 1½
graphite	C	1 to 2
pyrophyllite	$Al_2Si_4O_{10}(OH)$	1½

covellite	CuS	1½ to 2
orpiment	As_2S_3	1½ to 2
realgar	AsS	1½ to 2
gypsum	$CaSO_4{\bullet}2H_2O$	2
stibnite	Sb_2S_3	2
sylvite	KCl	2

The hardness of a mineral relates to its weakest bond strength. So, because bonds are usually not the same in all directions in minerals, hardness may vary depending on the direction a mineral is scratched. In kyanite, for example, hardness varies from 4½ to 6½ depending on the direction of the scratch test. In most minerals, however, hardness is about the same in all directions. While the general relationship between hardness and bond strength is known, mineralogists have difficulty predicting hardness for complex atomic structures. For some simple ionic compounds, however, theoretical calculations match measurements well. Minerals with high density, highly charged ions, small ions, or covalent bonding tend to be hardest.

3.6 Density and Specific Gravity

3.73 Borax crystals from Boron, California

The Greek letter *ρ* (rho) symbolizes *density*. We usually give the density of a mineral in units of grams/cubic centimeter (gm/cm^3). Density varies slightly depending on pressure or temperature, but most minerals have values between 2 and 8 gm/cm^3. Borax, shown in this photo, has density of about 1.8 gm/cm^3, lower than all other common minerals.

The polymorphs *diamond* and *graphite* are both made of carbon (C), but due to differences in atomic arrangements, diamond has density of 3.5 gm/cm^3, while graphite's is 2.2 gm/cm^3. Graphite forms under Earth surface conditions, but diamond, with its high density, only forms deep in Earth where pressures are great. The Laws of Thermodynamics tell us that high pressures favor dense minerals, which makes sense because at high pressure things are squeezed together.

Accurate determination of density can be difficult or impossible because it requires knowing the volume of a crystal – which can be difficult to measure with accuracy. A related property, *specific gravity* (*G*), is often used instead.

Specific gravity (unitless) is the ratio of the mass of a mineral to the mass of an equal volume of water at 1 atm, and because mass and weight are proportional, we normally determine specific gravity by comparing weights. If a mineral is at normal Earth surface conditions, density and specific gravity have about the same values.

3.74 Barite from Baia Sprie, Romania

Because specific gravity varies greatly between minerals, we can easily distinguish minerals with high, moderate, or low specific gravity simply by picking them up. We use the term *heft* for estimations of *G* made by holding hand specimens; heft can be useful in mineral identification. For example, the mineral *barite* ($BaSO_4$), such as the example in Figure 3.74, sometimes exists as massive white material that is easily confused with feldspars. However, its great heft, easily discerned by picking it up, helps identify it. Similarly, we can distinguish *cerussite* (lead carbonate) from other carbonate minerals by its heft.

Specific gravity differences can also help in the separation of minerals. In the laboratory, researchers separate crushed rock into mineral components by “floating” samples in liquids of different specific gravities. In these *heavy liquids*, which are much denser than water, minerals separate as some float and others sink according to their specific gravities. In mining operations, ore minerals are often separated from valueless minerals by using gravity separation techniques that depend on specific gravity differences. This occurs in natural systems, too. Placer gold deposits form when gold from weathered rock, because of its high specific gravity, concentrates in stream beds.

3.75 Gold nugget on quartz

The lightest minerals have specific gravities on the order of 1.8 to 2. They are mostly borates (such as borax), halides (*e.g.*, halite), and sulfates (*e.g.*, gypsum). Silicates (including quartz and all the other common rock-forming silicates) and carbonates (*e.g.*, calcite or dolomite) range from about 2.5 to 3.5. Oxides and sulfides may have specific gravities as great as 7 or 8 but are highly variable. And, native metals (*e.g.*, copper, silver, or gold) range up to 19 or 20. The photo in Figure 3.75 shows a gold nugget with quartz beneath it. It came from a placer. Gold has specific gravity of about 19.3 and quartz has specific gravity of 2.7.

The specific gravity of a mineral depends, in part, on how its atoms are packed together within a crystal. For example, the left part of the table below lists the specific gravities for quartz and four other SiO_2 polymorphs. Stishovite, coesite, quartz, cristobalite, and tridymite all have different densities because they do not have the same atomic arrangements. The densest two – stishovite and coesite – are only found in very high pressure rocks or in meteorite impact craters.

Specific gravity also depends on composition. This can be demonstrated by looking at *isostructural minerals* – minerals with the same atomic arrangement but with different compositions. Consider the garnet group minerals for example. The table below lists names, compositions and specific gravities for seven garnets. The specific gravity values vary from 3.54 for pyrope to 4.33 for almandine, reflecting the atomic weights of the garnets' elemental constituents. Several examples of garnet can be seen in Figures 3.5 to 3.7.

Specific Gravities of Some Silica Polymorphs

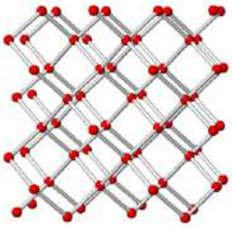
mineral	formula	*G*
stishovite	SiO_2	4.35
coesite	SiO_2	3.01
quartz	SiO_2	2.65
cristobalite	SiO_2	2.32
tridymite	SiO_2	2.26

Specific Gravities of Some Garnet Minerals

mineral	formula	*G*
pyrope	$Mg_3Al_2Si_3O_{12}$	3.54
grossular	$Ca_3Al_2Si_3O_{12}$	3.56
uvarovite	$Ca_3Cr_2Si_3O_{12}$	3.80
andradite	$Ca_3Fe_2Si_3O_{12}$	3.86
spessartine	$Mn_3Al_2Si_3O_{12}$	4.19
almandine	$Fe_3Al_2Si_3O_{12}$	4.33

● Box 3-3 Graphite and Diamond

3.76 Diamond



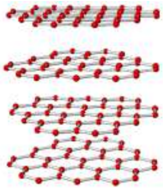
3.77 Carbon atoms in diamond

The photos in Figures 3.79 and 3.81 show a diamond crystal and a graphite crystal. Graphite and diamond are *polymorphs* (same compositions but different atomic arrangements).

Both minerals are made of carbon but they have different properties and appearances because the carbon atoms are arranged differently in the two minerals. The drawings in Figures 3.77 and 3.79 show how carbon atoms are arranged in each.

As shown in the atomic drawings, in diamond, each carbon atom is covalently bonded to four others, creating an overall cubic 3-dimensional network that has the same properties in all directions. In graphite, carbon atoms are covalently bonded to form sheets that contain interconnected 6-carbon rings; very weak van der Waals bonds hold the sheets together.

3.78 Graphite



3.79 Carbon atoms in graphite

Diamond is a tenacious mineral that does not cleave easily. Graphite, because of its layered atomic arrangement, has excellent basal (planar) cleavage. Graphite has a hardness of 1½ and diamond has a hardness of 10. Diamond has a denser structure than graphite – the specific gravity of diamond is about 3.5, and graphite’s is 2.1 to 2.3. Because of its high density, diamond only forms deep within Earth. This is true for all high density minerals – they only form where pressure is great.

3.7 Magnetism

3.80 Magnetite

Magnetism derives from a property called the *magnetic moment* that results from the spinning and orbiting of electrons. The sum of all the magnetic moments of all the atoms in a mineral gives it magnetism. Minerals may be ferromagnetic, diamagnetic, or paramagnetic.

In *ferromagnetic minerals*, the moments of a mineral's electrons are aligned in a constructive way and the minerals have properties similar to those of metallic iron. Ferromagnetic minerals may be magnetized. Magnetite (Figure 3.80) and pyrrhotite are examples of ferromagnetic minerals, but magnetite is much more ferromagnetic than pyrrhotite.

Diamagnetic minerals exhibit little magnetic character overall but may be weakly repelled by a strong magnetic field. Pure feldspars, halite, and quartz all exhibit weak diamagnetism. An impure feldspar, however, may contain iron, which results in *paramagnetism*, which means it is attracted to a strong magnet. Other commonly paramagnetic minerals include garnet, hornblende, and many pyroxenes.

3.81 Magnetic separator for laboratory use

For routine mineral identification, only a few minerals – for practical purposes only magnetite – can be identified because of their magnetism. In the field, rocks that contain magnetite will attract a magnet. This sometimes help distinguish different rock formations. And, in the laboratory, subtle differences in the magnetic properties of minerals are routinely used to separate different minerals in crushed rock samples. Figure 3.81 shows a device used for this purpose. Magnetism, thus, can be an important property of minerals.

3.8 Electrical Properties

3.82 Native copper from Pima County, Arizona

Electricity can be conducted when a mineral’s electrons can move throughout its structure. So, minerals with metallic, or partially metallic bonds – like many sulfides – are good conductors. The native metals, such as copper, are the best examples. This photo (Figure 3.82) shows a “branch” of native copper with several small quartz crystals on it. The branch was extracted from a rock matrix. Sulfide minerals, because they commonly have partially metallic bonds, are also good conductors.

Small amounts of electrical conduction may also occur in minerals with defects or other imperfections in their structures. And, some minerals, while being unable to conduct electricity, may hold static charges for brief times. They may be charged by exposure to a strong electric field, a change in temperature, or an application of pressure. A mineral charged by temperature change is *pyroelectric*; a mineral charged by pressure change is *piezoelectric*. Because they are difficult to measure, however, electrical properties are not often used for mineral identification.

3.9 Reaction to Dilute Hydrochloric Acid

3.83 Hydrochloric acid effervescing on calcite

One chemical property, the reaction of minerals to dilute (5%)

hydrochloric acid (HCl), is included here because it is diagnostic for calcite, one of the most common minerals of the Earth’s crust. Drops of acid placed on coarse samples of calcite cause obvious bubbling or fizzing, called *effervescence*, seen in the photo here (Figure 3.83).

Dolomite, a closely related carbonate mineral, effervesces when finely powdered but not when coarse. Other carbonate minerals, such as smithsonite ($ZnCO_3$), aragonite ($CaCO_3$), and strontianite ($SrCO_3$), effervesce to different degrees. They are distinguished by crystal form, color, and other properties. Although acid tests have limited use, most mineralogy labs are equipped with small bottles of HCl and eyedroppers to aid in carbonate identification. Many geologists carry a small bottle of dilute hydrochloric acid when they go in the field so they may distinguish between rocks that contain calcite and rocks that do not.

3.10 Additional Properties

Minerals possess many other properties (for example, *solubility, radioactivity*, or *thermal conduction*). Because they are of little use for mineral identification in most cases, we will not discuss them individually here.

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4 Crystals and Crystallization

4.1 Light blue aquamarine (beryl), black tourmaline with light colored orthoclase. The specimen is from Namibia.

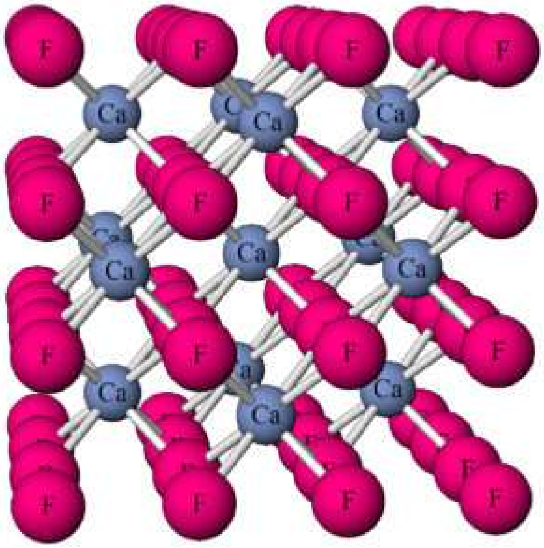
4 Crystals and Crystallization

KEY CONCEPTS

- With just a few exceptions, all minerals are crystalline.
- Crystalline substances have an orderly and repetitive atomic arrangement.

- Crystals grow from small seeds and sometimes become very large.
- Igneous minerals precipitate from a magma; most of them are silicates.
- Aqueous minerals precipitate from water; they include compounds of high solubility.
- Hydrothermal minerals precipitate from warm flowing waters.
- Metamorphic minerals form by solid-state reactions during metamorphism.
- Some minerals form during weathering or diagenesis.
- Minerals may not form or be stable under all conditions.
- Minerals may have defects involving misplaced or missing atoms.
- Minerals may be heterogeneous.
- Mineral crystals may be twinned, containing domains with slightly different atomic orientations.

4.1 Crystalline and Noncrystalline Solids



4.2 The arrangement of atoms in fluorite (CaF_2)

By definition (with just a few special exceptions) minerals must be *crystalline*. This means that they are solids with an orderly repetitive atomic arrangement. For example, this ball and stick model (Figure 4.2) shows the atomic arrangement in fluorite (CaF_2). Fluorite is one of a small number of common minerals that are *isotropic.* Isotropic minerals have very symmetrical atomic arrangements and atoms are arranged in a cubic pattern. The same atoms are encountered in any direction through the mineral and, consequently, mineral properties are the same all directions. The photo in Figure 4.3 shows light purple cubic fluorite crystals. They are interpenetrating deformed cubes. Many spectacular specimens of cubic fluorite crystals are found in museums.

4.3 Fluorite crystals on top of scheelite and calcite

Other isotropic minerals, besides fluorite, include diamond (C), almandine ($Fe_3Al_2Si_3O_{12}$), gold (Au), pyrite (FeS), silver (Ag), spinel ($MgAl_2O_4$), and sodalite ($Na_3Al_3Si_3O_{12}•NaCl$). All these minerals, have a cubic arrangement of atoms, although their crystals may not be cubes. Still, their crystals, when euhedral, are equant and generally have many identical faces.

Most minerals, however, are *anisotropic*. This means that they have different properties in different directions.

Consequently, their crystals are not as symmetrical as fluorite’s. Yet, crystals may possess other symmetry, even if they do not resemble a cube.

4.4 Barite from near Cartagena, Columbia

So, well-formed mineral crystals often exhibit symmetry. But, it may not be cubic symmetry like fluorite – other shapes are possible. For example, the blue-gray barite ($BaSO_4$) crystals seen in this photo are tabular and have a long, an intermediate, and a short dimension. Barite is an anisotropic mineral. The crystals have lots of symmetry, but it is different from that of fluorite. Still, when compared with many minerals, barite crystals are quite symmetrical. Olivine, topaz, some pyroxenes, and topaz all sometimes have crystal shapes similar to barite’s.

4.5 “Snowflake” obsidian (volcanic glass)

Some mineral-like substances are *noncrystalline*, which means they have a random atomic structure. Natural volcanic glass, obsidian, is an example. This photo (Figure 4.5) shows a specimen of *snowflake obsidian.* It contains black volcanic glass (obsidian) with white patches. Obsidian is noncrystalline but over time it will sometimes begin to crystallize, creating the white patches seen here. The patches consist of cristobalite, a variety of SiO_2, and a polymorph of quartz.

Amorphous solids are generally isotropic, so they have the same properties in all directions. This gives the materials properties that are sometimes very useful. For example, window glass is made by melting mixtures containing mostly quartz sand, and allowing the melt to solidify quickly so atoms cannot arrange themselves in a crystalline structure. The process produces a noncrystalline isotropic glass, so light can pass through it equally well in all directions. This is one reason why manufactured glass makes a better window than transparent minerals.

● Box 4-1 Making Glass from Minerals

4.6 Pouring molten glass

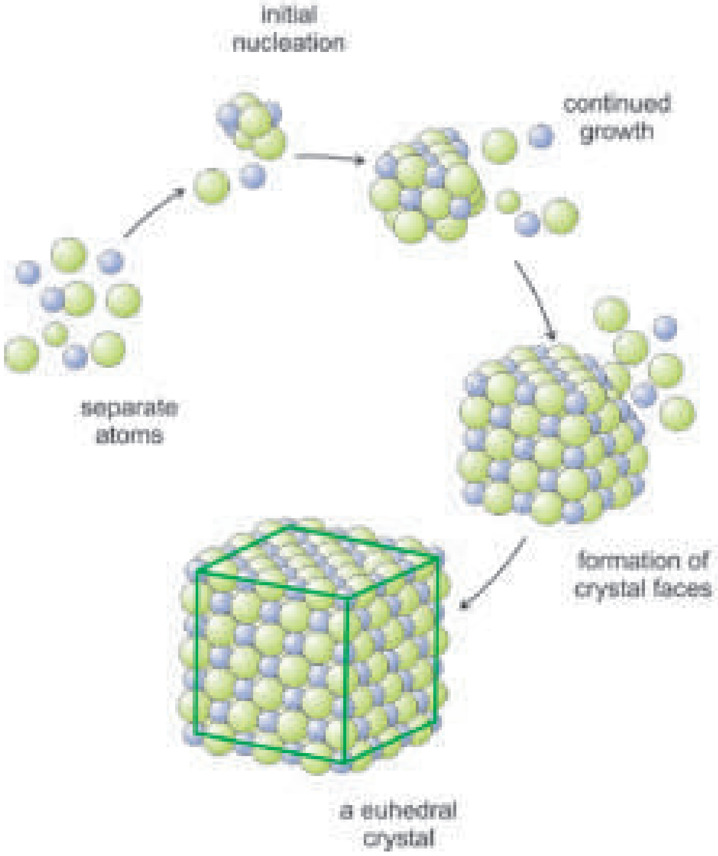
Glass manufacturers make glass by melting ingredients and cooling the melt so quickly that crystals cannot form. The most common kind of glass, which is used to make bottles or window panes, is soda-lime-silica glass. People have manufactured similar glasses since Roman times.

Soda-lime-silica glasses typically contain about 75 wt% SiO_2, 15 wt% Na_2O, and 10 wt% CaO. Raw ingredients are usually the minerals quartz (SiO_2), trona [$Na_3H(CO_3)_2•2H_2O$], and calcite ($CaCO_3$). In the United States, we obtain high-quality quartz and calcite from many places. Most of the trona comes from the Green River Formation in Wyoming, where trona beds are up to 9 m (30 ft) thick.

Glass manufacturers heat the mineral ingredients to between 1,550 and 1,600 °C (2,820 and 2,910 °F), producing a homogeneous melt as CO_2 and H_2O escape into the atmosphere. Quenching, to produce a final glass, is done in various ways depending on the product wanted.

Manufacturers change glass properties by adding small amounts of other ingredients. The addition of boron produces heat-resistant glass such as Pyrex® or Vycor®. Lead gives glass the optical properties needed for making imitation crystals. Aluminum can make glass resistant to weathering. Fluorine makes glass opaque. Lithium reduces the melting point of glass. Trace amounts of metals change glass color: Iron makes glass green, nickel makes it brown or orange, and cobalt makes it blue.

4.2 Forming Crystals



4.7 From a few atoms to a euhedral crystal

The formation of crystals involves the bringing together and ordering of constituent atoms. Crystals grow from a small single molecule to their final visible form. This can happen in many different ways and settings, but the principle mechanisms are three:

- crystals growing as magma cools
- crystals precipitating from water
- crystals forming by chemical reactions

The drawing shows separate atoms coming together to produce a cubic crystal. In this example, the crystal is euhedral with six identical faces. But, even if it did not develop crystal faces, the atoms could still be in a cubic pattern, and the product material would still be crystalline.

4.2.1 Igneous Minerals

In *magma* (molten rock), kinetic energy means that atoms are always in motion. The photo in Figure 4.8 shows *lava* (magma that has reached Earth's surface) in Hawaii. When magma is at high temperature, it is completely liquid because high kinetic energy ensures that no solid is stable. Some atoms collide and may form bonds temporarily before breaking apart again. A balance exists between the formation of bonds and the rate at which they break apart. If bonds break as fast as they form there will be no net crystallization.

4.8 Basalt lava flow in Hawaii

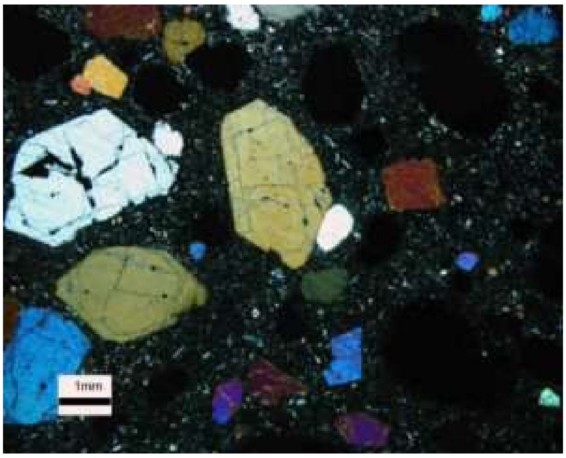
4.9 Gabbro, an intrusive igneous rock, in Italy

As magma cools, kinetic energy decreases when atoms slow down. Eventually, if magma cools sufficiently, atoms will slow down enough so that some bonds will begin to persist. This is the beginning of the formation of crystals from a melt, and the beginning of the formation of igneous minerals. Initial crystallization creates small nuclei, many of which continue as the centers of crystals during continued growth. Because of high temperatures and the molten state of magma, atoms are quite mobile and easily move toward the nucleii and to surfaces of growing crystals. So crystals may become large, like the dark colored pyroxene and light grey plagioclase in the gabbro in Figure 4.9.

The table below lists some common minerals in igneous rocks. Almost all are silicates because the magmas that produce igneous rocks are dominated by oxygen and silicon. Other abundant elements include aluminum, iron, magnesium, calcium, sodium, and potassium. These are the elements that make up most igneous minerals.

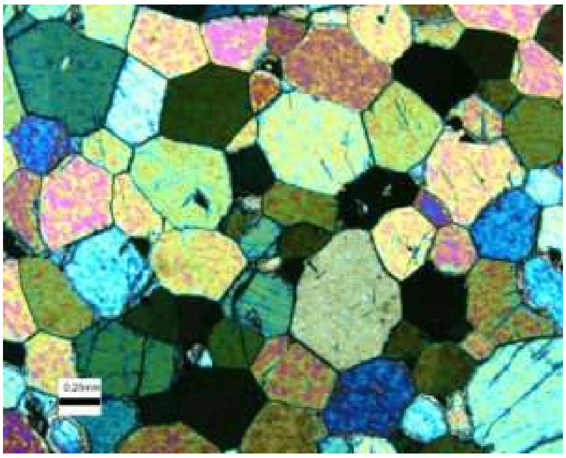
Common Minerals in Igneous Rocks

class or group	minerals or series	chemical formula
olivine	olivine	$(Mg,Fe)_2SiO_4$
pyroxene	diopside augite orthopyroxene	$CaMgSi_2O_6$ $(Ca,Mg,Fe,Na)(Mg,Fe,Al)(Si,Al)_2O_6$ $(Mg,Fe)_2SiO_6$
amphibole	hornblende	$(K,Na)_{0-1}(Ca,Na,Fe,Mg)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$
mica	biotite muscovite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$ $KAl_2(AlSi_3O_{10})(OH)_2$
feldspar	orthoclase microcline sanidine plagioclase	$KAlSi_3O_8$ $KAlSi_3O_8$ $KAlSi_3O_8$ $(Ca,Na)(Si,Al)_4O_8$
feldspathoid	leucite nepheline	$KAlSi_2O_6$ $(Na,K)AlSiO_4$
silica	quartz	SiO_2
oxide	magnetite ilmenite	Fe_3O_4 $FeTiO_3$
sulfide	pyrite pyrrhotite	FeS_2 $Fe_{1-x}S$
other	titanite zircon apatite	$CaTiSiO_5$ $ZrSiO_4$ $Ca_5(PO_4)_3(OH,F,Cl)$



4.10 Olivine and pyroxene crystals surrounded by glass

If the conditions are right, igneous mineral crystals may develop prominent crystal faces. The photo here is a microscope view of Hawaiian basalt. It was obtained using a petrographic microscope. The colors, called interference colors, are not the true colors of the minerals, but the large colorful crystals are olivine and pyroxene. Because they had room to crystallize and grow from the magma, some of them have (imperfectly formed) crystal faces. The black material with fine white flecks in the background is basaltic glass and fine crystals of plagioclase.



4.11 Olivine crystals in dunite

If crystals do not have room to grow individually and crystallize simultaneously, the result may be a rock with crystals forming a *mosaic pattern* as seen here. Olivine, pyroxenes, feldspars, and many other minerals commonly develop in this way. This view shows grains of olivine in a dunite (a rock composed nearly entirely of olivine). The colors, like the colors in the previous figure, are not true mineral colors but are artifacts of the way this rock was viewed.

Igneous processes are quite variable. Some magmas cool slowly underground, so mineral crystals grow to be large. Other magmas extrude as lavas and cool quickly to form basalt or another extrusive rock. Mineral crystals in extrusive rocks may be so small that they cannot be seen with the naked eye or even with a microscope. Silicate minerals dominate igneous rocks but magma compositions vary somewhat. So igneous rocks have variable compositions and consequently variable mineralogies.

4.2.1.1 Pegmatites

4.12 A typical pegmatite containing quartz and alkali feldspar

Pegmatites are exceptionally coarse grained igneous rocks. In some pegmatites, crystals may be huge. The photo seen here shows white quartz, salmon-colored feldspar and black riebeckite in a pegmatite. The hand lens is about 2 cm across. Pegmatites form during the final stages of magma crystallization. Most have overall composition similar to that of granite.

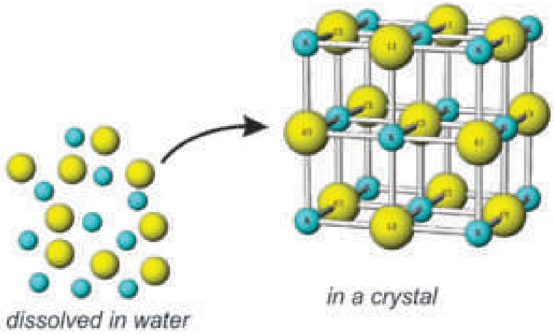
The largest crystals in the world have been found in pegmatites. A single crystal of the mica phlogopite from Ontario, Canada, is 4.2 m (14 ft) wide and 10 m (33 ft) long. A quartz crystal from a Russian pegmatite weighs more than 907 kg (2,000 lbs.). The largest quartz crystal on record, however, was from a pegmatite in Brazil and weighed more than five tons.

4.13
"Watermelon"
tourmaline
from Brazil

Some pegmatites are enriched in elements that are normally minor components of magmas. The photo seen here is a crystal of "watermelon" tourmaline from a pegmatite. Tourmaline is really the only common mineral that contains boron.

Other elements that concentrate in pegmatites include cesium, beryllium, zirconium, niobium, uranium, thorium, tantalum, tin, rare earth elements, chlorine, fluorine, lithium, and phosphorus. Consequently, pegmatites are sometimes mined for these elements. Pegmatites also yield gemstones, including varieties of tourmaline like the one shown, bright green feldspar called *amazonite*, several varieties of beryl (*emerald*, *aquamarine*, and *heliodor*), and others.

4.2.2 Aqueous Minerals



4.14 Forming sylvite from dissolved K and Cl

A similar process – similar to crystallization from magma – occurs when minerals precipitate from water to form aqueous minerals. *Aqueous* means involving water. Water may contain ions of different sorts and, as long as kinetic energy is high, or the water is not saturated, no crystals will form. Ions will bond temporarily, only to break apart and return to solution. This can change if conditions change.

Most substances are more soluble in water at high temperature than at low temperature. So, a decrease in temperature may lead to oversaturation, nucleation, and precipitation of aqueous minerals. During this process, unbonded dissolved ions become organized in a crystal structure. For example, K^+ and Cl^- may combine to form the mineral sylvite (KCl). And, similarly, calcium carbonate precipitates to form calcite ($CaCO_3$) if concentrations of Ca^{2+} and CO_3^{2-} in water are high enough.

Crystal precipitation from water may also occur because of chemical change. Suppose, for example, that seawater evaporates. The concentration of dissolved material in the remaining water will increase, leading to oversaturation and, eventually, precipitation of crystals. Besides changes in temperature and composition, changes in pressure, pH, or other things may also lead to the formation of aqueous or igneous crystals. The photos below show two examples.


4.15 Salt deposits at the Great Salt Lake, Utah

4.16 Veins of gypsum in red sandstone

Inland lakes or seas commonly precipitate calcite, halite, gypsum, and other minerals. In some places evaporating waters have deposited salt beds thicker than 300 m. Figure 4.15 shows salt that was deposited by Utah’s Great Salt Lake. Similar deposits are found along the shores of The Dead Sea (between Jordan and Israel) and other seas and lakes in arid regions. On a much smaller scale, minerals precipitating from slowly moving groundwater can fill holes, fractures, and cracks in rocks. Figure 4.16 shows veins of gypsum in Utah’s Moenkopi Formation. Gypsum is commonly associated with red sandstones and mudstones like the rock seen in this photo.

The table below lists some typical aqueous minerals. The most common ones are minerals with high solubilities in water, such as calcite, halite, and other salts.

Common Aqueous Minerals		
mineral class or group	**important minerals or mineral series**	**chemical formula**

silica	quartz	SiO_2
carbonate	calcite dolomite magnesite	$CaCO_3$ $CaMg(CO_3)_2$ $MgCO_3$
halide	halite sylvite	NaCl KCl
sulfide	gypsum anhydrite	$CaSO_4 \cdot 2H_2O$ $CaSO_4$
native element	sulfur	S

4.17 A geode with amethyst and white quartz

Other minerals, having lower solubility but composed of elements in great abundance, slowly form from aqueous solutions. Quartz is an example. At low temperature, quartz may precipitate in *geodes* such as the one seen here. This geode contains amethyst, a purple variety of quartz, and also more common clear white quartz. Note the concentric layers in this specimen. The layers have slightly different compositions because the composition of the water changed a bit as crystallization occurred.

4.2.3 Hydrothermal Minerals

4.18 Travertine deposits in Hot Springs State Park, Wyoming

If chemical precipitation occurs at elevated temperatures, we call the process *hydrothermal*. *Travertine* and *tufa* deposited by hot springs are examples of hydrothermal deposits. Both are composed of calcite that precipitated from hydrothermal solutions, but tufa is more porous than travertine. The photo shows travertine terrace deposits in Wyoming.

Hydrothermal minerals are also created underground. Occasionally, hot circulating groundwater deposits minerals in sufficient quantity to make a valuable ore deposit. Minerals deposited this way include oxides, sulfides, and some others. The table below lists some common hydrothermal ore minerals.

Minerals Common in Hydrothermal Ore Deposits		
mineral class	**mineral or mineral series**	**chemical formulas**
sulfide	pyrite pyrrhotite chalcopyrite galena sphalerite molybdenite	FeS_2 $Fe_{1-x}S$ $CuFeS_2$ Pbs ZnS MoS_2

tungstate	wolframite	$(Fe,Mn)WO_4$
oxide	magnetite cassiterite pyrolusite	Fe_3O_4 SnO_2 MnO_2
native elements	gold silver	Au Ag

Hydrothermal ore deposits vary. In some, ore minerals are concentrated in veins or vugs, in others they are disseminated throughout a body of rock. Many spectacular mineral specimens come from hydrothermal deposits. Hydrothermal minerals are often brightly colored because they contain transition metals. Many are metallic and many form highly symmetrical crystals. The photos below show three examples.

4.19 Sphalerite from the French Alps

4.20 Pyrite from Elba Island, Italy

4.21 Blue azurite and green malachite from Bisbee, Arizona

4.2.4 Metamorphic Minerals

4.22 A large red garnet in a mylonite

Metamorphism sometimes involves recrystallization and coarsening of a rock with no change in mineralogy. Often, however, it involves chemical reactions and replacement of preexisting minerals by new ones. Bonds are broken and atoms migrate by solid state diffusion or are transported short distances by intergranular fluids to sites where new minerals crystallize and grow. The photo shows a large red garnet crystal in a highly deformed metamorphic rock called a *mylonite*. Large minerals of this sort in metamorphic rocks are called *phenocrysts*.

The mineralogy of metamorphic rocks is more diverse than in sedimentary or igneous rocks. Nearly all the minerals found in igneous rocks can be present in metamorphic rocks. Many minerals that are found in sedimentary rocks may be present as well. In addition, other minerals, uncommon or nonexistent in igneous and sedimentary rocks, form through metamorphism. The table below lists only a few of the more common metamorphic minerals.

Common Metamorphic Minerals

(besides those common in igneous and sedimentary rocks)

mineral	chemical formula
cordierite	$(Mg,Fe)_2Al_4Si_5O_{18}$
tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
wollastonite	$CaSiO_3$
andalusite	Al_2SiO_5
kyanite	Al_2SiO_5
sillimanite	Al_2SiO_5
staurolite	$Fe_2Al_9Si_4O_{23}(OH)$
chloritoid	$(Fe,Mg)A_{l2}SiO_5(OH)_2$
garnet	$(Ca,Fe,Mg)_3(Al,Fe)_2Si_3O_{12}$
zoisite	$Ca_2Al_3Si_3O_{12}(OH)$

4.23 Green diopside with white dolomite and calcite

Metamorphism may involve replacement of one mineral by another. For example, calcite may become aragonite or vice versa. Both minerals are $CaCO_3$, but their atomic structures differ. Mineralogical changes due to metamorphism, however, usually involve several different minerals reacting together. Dolomite ($CaMg(CO_3)_2$) and quartz (SiO_2) may react to form diopside ($CaMgSi_2O_6$) if a limestone containing quartz is metamorphosed at high temperature. The photo here shows green diopside surrounded by dolomite and calcite.

4.2.5 Weathering and Diagenesis

4.24 A weathering rind on a sandstone

Weathering is the breaking down or decomposition of rocks and minerals because of reactions with the atmosphere or water, and sometimes biological organisms. The process occurs in place at or near Earth’s surface, and is distinct from erosion, which involves transportation of material by water, wind, gravity and other agents. During weathering, large rocks or mineral grains typically break apart. Simultaneously, new minerals may form from old ones. Iron oxides, quartz and clay often dominate highly weathered material. These minerals formed as other minerals disappeared. The photo shows a boulder with a distinct red layer of iron oxide on its outside that formed by weathering.

Diagenesis can occur after weathering has taken place, especially after a sediment is deeply buried. It involves physical and chemical changes in sediments that occur as the sediments are lithified and turn into a sedimentary rock. Diagenesis commonly leads to minerals disappearing and being replaced by others through processes involving both weathering and low-temperature metamorphism. Thus, no sharp boundary exists between diagenesis and metamorphism, although many geologists choose an arbitrary burial temperature of 200 ^{o}C as the beginning of metamorphism. Agents of diagenesis include pressure and heat caused by burial. Often, hydrothermal solutions are involved as well.

Chapter 7 includes a more detailed discussion of weathering and diagenesis.

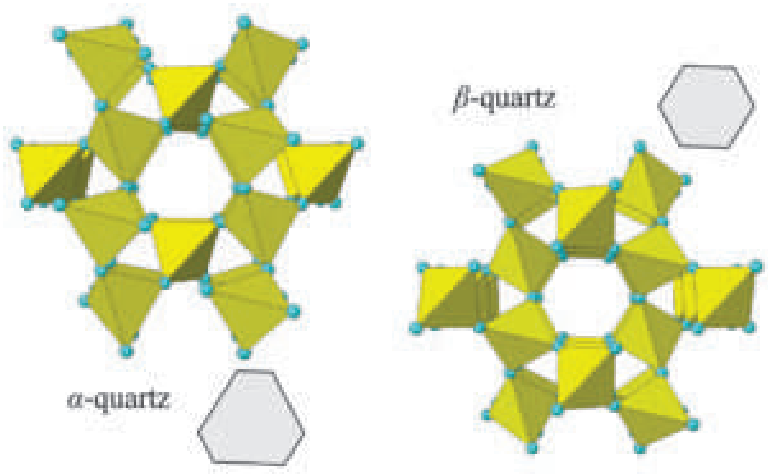
4.3 Mineral Stability and Polymorphs

Of the thousands of known minerals, a relative few are very common. A key reason is that many minerals are only stable under specific conditions. In 1878, J. Willard Gibbs defined a form of energy that determines compound stability. We now call it the *Gibbs free energy* and indicate it by the variable *G*.

Notions involving Gibbs free energy form the basis for the field of *thermodynamics*. As pointed out by Gibbs, natural chemical systems are most *stable* when energy is minimized. So, minerals and mineral assemblages with low Gibbs energy are more stable than those with high energy. Consequently, *unstable minerals* break down to form different minerals, with lower Gibbs free energy, over time. Thus, minerals with relatively low Gibbs energies are more common than others.

Elements can combine in many ways to form crystals, but as atoms bond, they naturally tend to arrange themselves in the way that minimizes Gibbs free energy. For example, mineralogists have identified more than half a dozen naturally occurring polymorphs of silica (SiO_2). *Polymorphs* are minerals that have identical compositions but different arrangements of atoms and bonds. The polymorph with the lowest chemical energy is the *stable* form of SiO_2. Different polymorphs have the lowest energy under different pressure-temperature conditions. At room temperature and pressure α-quartz has the lowest energy and is stable; the other polymorphs are thermodynamically unstable.

Under normal Earth surface conditions, because α-quartz is stable, we would expect it to form to the exclusion of the others. This is generally the case, but there are exceptions. For kinetic and other factors, natural systems may not always reach lowest (stable) energy conditions. So, especially at low temperatures, we sometimes find examples of *metastable* SiO_2 polymorphs – these are minerals that should, in principle react to become α-quartz if we waited long enough. At elevated temperatures and pressures, metastable α-quartz cannot persist. It changes into other SiO_2 minerals (such as cristobalite, coesite, tridymite or stishovite) that have lower chemical energy (Box 4-2).



4.25 The difference between α-quartz and β-quartz

A change from one polymorph to another can be a *reconstructive transformation* involving major rearrangement of atoms and bonds. Alternatively, it may be a *displasive transformation* that involves bonds stretching or shrinking (not breaking) and angles between bonds changing, as one mineral turns into another. An example of a displasive transformation is the polymorph change when high-temperature SiO_2, β-quartz, turns into α-quartz with cooling. It is very subtle, but, as seen in Figure 4.25, the difference between the two polymorphs is whether the structure contains perfectly hexagonal symmetry and openings. β-quartz does (drawing on the right) and α-quartz does not (drawing on the left). The video below shows the structure of α-quartz. Look closely and you will see that it begins with a view down the channel similar to the photo on the left above in Figure 4.25.

A third kind of transformations is an *order-disorder transformation*. These involve atoms ordering and arranging in slightly different ways and are gradual changes that occur over a range of pressures or temperatures. Transformations of any kind may occur quickly or may be very slow. Reconstructive transformations are generally sluggish, and may not occur even if they should. For example, all diamonds should turn into graphite (a reconstructive transformation) at Earth’s surface, but they do not. In contrast, displasive transformations, such as α-quartz turning into β-quartz are instantaneous and reversible. Heat a quartz crystal to just over 573 °C and it changes into β-quartz . Cool the same crystal and it will change back into α-quartz. Order-disorder transformations, the third kind of transformation, occur at different rates depending on how fast temperature, and sometimes pressure, change. If the rate of change is fast, no transformation may occur.

● Box 4-2 Silica Polymorphs

4.26 Small crystal fragments of coesite

Many known minerals have composition SiO_2. Some of the most important include quartz, tridymite, cristobalite, coesite, and stishovite. This photo shows grains of coesite; the largest is about 0.4 mm across. The coesite looks a lot like quartz, but has a different internal arrangement of silicon and oxygen atoms. For some spectacular scanning electron microscope images of silica polymorphs, see Figure 12.35 in Chapter 12.

Two different polymorphs are called quartz: *α-quartz* and *β-quartz*. *α*-quartz is by far the most common of the silica polymorph. Because it is stable at lower temperature than *β*-quartz, *α*-quartz is sometimes called *low quartz*, and *β*-quartz is sometimes called *high quartz*. At 1 atm pressure, *β*-quartz exists only at high temperatures. Upon cooling it will turn into α-quartz at 573°C, so we have no room temperature samples to examine.

Tridymite and *cristobalite* are silica polymorphs that, like *β*-quartz, are found in high-temperature rocks – mostly only in silica-rich volcanic rocks. They are unstable at room temperature and pressure and should become *α*-quartz. However, some samples of these two minerals persist as metastable minerals. For example, the *snowflakes* that form in volcanic glass (see Figure 4.5) consist of metastable cristobalite crystals.

Coesite and *stishovite* are dense silica polymorphs that form at very high pressure. They are unstable at Earth’s surface. Coesite, which forms at pressures above 25 Kbar (equivalent to 75 km depth in Earth), was first found in meteorite impact craters, later in a few eclogite xenoliths from the mantle, and more recently in what are called *ultrahigh-pressure (UHP)* crustal rocks. Stishovite forms at even greater pressures (and depths) than coesite. We see it today as microscopic grains in meteorite impact craters and in some rare ultra-high pressure rocks. Whether in impact craters, xenoliths, or UHP rocks, both coesite and stishovite often show signs of reacting to become α-quartz, although the reactions do not always go to completion.

An important corollary to the laws of thermodynamics, the *phase rule*, says that the number of stable compounds that can coexist in any chemical system must be small. Thus, not only are stable minerals predictable, they are limited to a small number. For a given rock, the stable minerals may not be the same under all conditions. If a rock is metamorphosed due to pressure or temperature changes, minerals may react to produce new minerals with lower Gibbs free energy. When they stop reacting, they have reached *equilibrium*. If the Gibbs free energy is minimized, the system is at *stable equilibrium*.

4.27 Black crystals of magnetite from Bolivia

Consider a chemical system containing Fe-metal and O_2. These elements can exist in their pure forms (as metallic iron and gaseous oxygen), but when mixed, they tend to react to produce magnetite (Fe_3O_4), or hematite (Fe_2O_3), perhaps creating minerals like the ones seen in the two photos here. Both minerals have lower Gibbs free energies than mixtures of Fe and O_2. This same principle applies to more complicated systems involving many elements, for example a rock. For any given composition rock, one (stable) mineral assemblage has the lowest energy. If the rock reaches stable equilibrium, the stable assemblage will prevail.

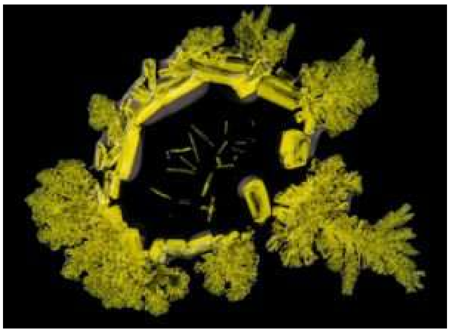
4.28 Hematite from the Czech Republic

Although the laws of thermodynamics tell us what the most stable mineral(s) should be, they do not tell us how long it will take to reach stable equilibrium. We all know from experience with cars, for example, that it may take a while for the iron in steel to rust, even though iron is unstable at Earth’s surface. The same is true for reactions involving minerals. Some low-temperature systems never reach stable equilibrium, and remain in an intermediate stage called *metastable equilibrium* when reactions cease. For example, countless numbers of diamonds exist at Earth’s surface, although graphite is a more stable form of carbon. Unless diamonds are heated, they remain metastable and do not change into graphite, no matter how long we wait. In contrast with low-temperature systems such as those at Earth’s surface, most higher-temperature natural systems approach stable equilibrium given enough time.

4.4 Factors Controlling Crystal Size and Perfection

4.4.1 Time and Temperature

● Box 4-3 Minerals Crystallizing From a Single Drop of Water



4.29 Crystals of potassium chromate

Click on this image to see a video that shows spectacular examples of crystals precipitating from water. It is a time lapse video; the crystallization occurred as the water drops evaporated. Unfortunately, only the first crystals (halite) exist in nature as minerals. Still, the other crystals are quite beautiful.

The most important factors controlling crystal size and perfection are temperature, time, abundance of necessary elements, and the presence or absence of a flux. All work together, but we can make some generalizations. *Temperature* is important because at high temperatures atoms are very mobile. Crystals can grow quickly; large and well-formed crystals may be the result. Principles of thermodynamics tell us that crystals that form at high temperatures have simpler atomic structures than those that are stable at low temperatures. This is one reason they can be large and well ordered.

Time is important because if a crystal has a long time to grow, it will naturally be larger and better ordered than one that grows quickly. More atoms will migrate to the growing crystal and order themselves in a regular way. This explains why intrusive igneous rocks, which cool slowly underground, are coarser-grained than extrusive igneous rocks of the same compositions. Some extrusive igneous rocks, such as obsidian, cool so quickly that they contain glass.

Whatever the time and temperature, crystals cannot grow large if the necessary elements are not available. In most rocks, a dozen elements or less account for 90% of the composition. Minerals composed of those elements will usually be larger than those composed of rarer elements. But, even if time, temperature, and atoms are right, crystals may not grow large. Diffusion of atoms through solids is slow, and atoms may not migrate easily to spots where crystals are growing. However, if a hydrothermal fluid is present, it can serve as a *flux* that delivers atoms to sites of crystallization. For example, the YouTube video (link above in Box 4-3) shows crystals growing from a drop of water – the water delivers atoms to sites of crystal growth.

4.30 A Brazilian pegmatite containing green emerald (beryl) and quartz

Magmas, too, can act as fluxes. So, hydrothermal and igneous minerals may grow relatively quickly, and even minerals composed of rare elements may grow to be large. This explains why large crystals of unusual composition may form in pegmatites. Pegmatites form from magmas rich in hydrothermal fluids that concentrate exotic elements like beryllium. The photo shows green beryl, one of the most common beryllium minerals, in a pegmatite from Brazil.

4.4.2 Ostwald Ripening

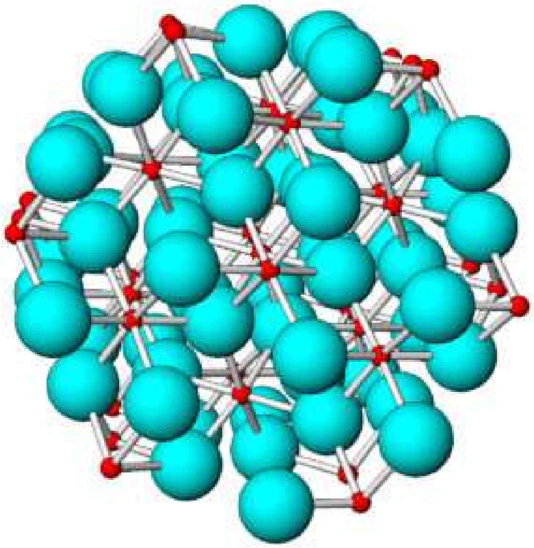
Whether in magma or aqueous solution, initial crystallization usually involves many nuclei and small crystals. As crystallization continues, however, larger crystals form at the expense of smaller ones. So, regions around large crystals become depleted in small ones. This occurs because nucleation is a kinetic process. Small nuclei composed of just a few atoms form relatively quickly compared with larger crystals. Larger crystals have greater volume-to-surface-area ratio and lower relative surface energy. This means that larger crystals are more chemically stable because molecules in the interior of crystal are less reactive and have lower energy than those on the outside. Consequently, with time, energetics trumps kinetics and molecules on the outside of small crystals diffuse and add to the outside of larger ones. This process is called *Ostwald ripening*.

 4.31 Ice that crystallized from ice cream	 4.32 Hornblende phenocrysts in andesite

Ostwald ripening explains, for example, why ice crystals form over time in initially smooth ice cream – see Figure 4.31 – which makes old ice cream crunchy. The ripening also explains why large crystals (called *phenocrysts*) surrounded by a sea of small crystals may form in some volcanic rocks. The rock seen in Figure 4.32 contains phenocrysts of black hornblende in a volcanic rock called *andesite*. The fine-grained material around the hornblende is mostly plagioclase but includes minor K-feldspar, quartz, and magnetite. Note that the hornblende is euhedral because it was surrounded by liquid (melt) as it crystallized and so atoms could easily migrate to growing crystal faces.

4.4.3 Organized Atomic Arrangements

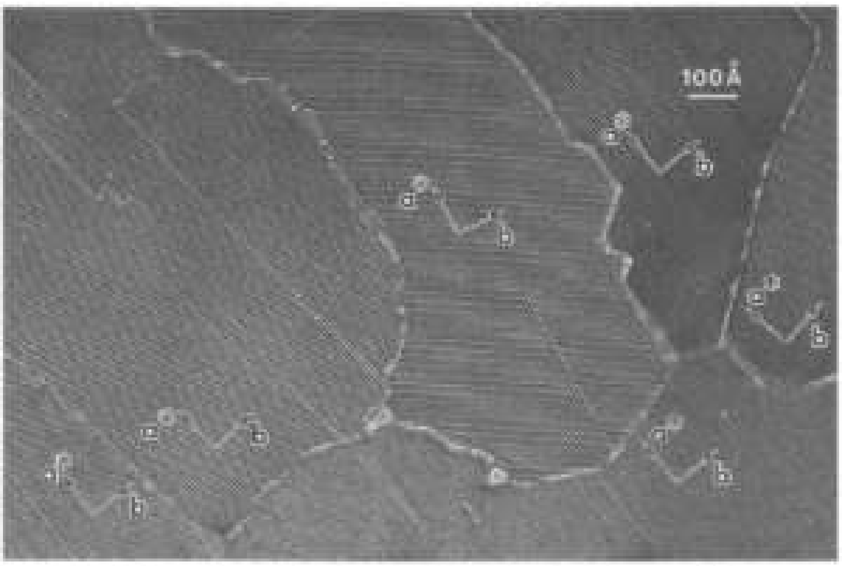
Because like charges repel and opposite charges attract, as atoms come together to form crystals, cations bond to, and are surrounded by, anions. Anions bond to, and are surrounded by, cations. This occurs even if bonding is not entirely ionic. So, crystal structures generally consist of alternating cations and anions in three dimensions. These charge balance considerations are the reasons that ideal crystals have an ordered atomic arrangement. The distribution of ions is the same in all parts of the crystal and does not depend on crystal size. If more than one arrangement is possible, crystals will naturally grow in the way that minimizes energy.



4.33 Model of corundum

Most common anions such as O^{2-}, are larger than common cations. So, we can think of oxide ionic mineral structures as involving small cations (shown in red) surrounded by larger anions (shown in blue). The number of cations around each anion depends primarily on their relative sizes. In this figure, which is based on the atomic arrangement in corundum, six anions bond to each cation, and four cations bond to each anion. In other minerals, cations and anions may have fewer or a greater number of bonds than this.

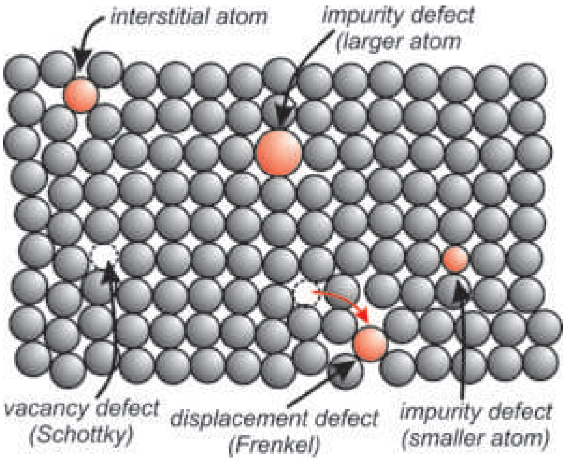
4.4.4 Crystal Defects



4.34 Transmission electron microscope (TEM) image of crocidolite

A hypothetical perfect crystal has an ordered atomic structure with all atoms in the correct places. As pointed out by C. G. Darwin in 1914, such crystals cannot exist. While a crystal may look perfect on the outside, atomic structures always contain some flaws, called *defects*.

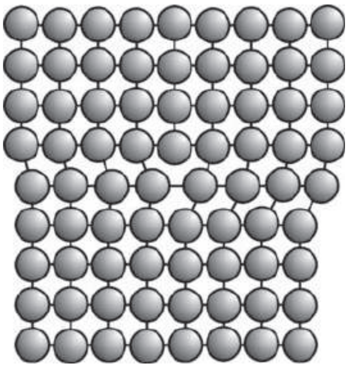
Today, techniques involving X-ray, transmission electron microscope (TEM), and, most recently, high-resolution transmission electron microscope (HRTM) allow crystallographers to look at atomic arrangements and to see relationships between individual atoms. The image in Figure 4.34 shows the atomic structure of crocidolite, an asbestiform amphibole, obtained with a transmission electron microscope. The black and white colors show atomic units composed of a small number of atoms. The entire view shows an imperfect grain composed of multiple subgrains with slightly different atomic orientations (shown by the letters and vectors labeling crystallographic axes – discussed in a later chapter). The apparent offsets in the structure, called *zipper faults*, show lines along which the atomic structure is defective. In some places, especially along subgrain boundaries, a coarsening of texture suggests small areas that have atomic structure dissimilar from that of normal crocidolite.



4.35 Some point defects

Perhaps the simplest type of defect is an *impurity defect*, occurring when a foreign atom is present in a mineral’s atomic structure (Figure 4.35). No mineral is perfectly pure. Minerals always contain minor or trace amounts of elements not described by their formula, often at levels that we cannot detect using standard analytical techniques. As seen in this schematic drawing, a larger or smaller atom may replace one normally in the structure, or an atom may occupy an interstitial site. All these examples are types of *point defects*, so named because they occur at one or a few points in the structure.

Other types of point defects include *Schottky* and *Frenkel* defects (both shown in the Figure 4.35. Schottky defects occur when an atom is displaced from a structure altogether, leaving a vacancy or hole. Such defects involve both cations and anions and, to maintain charge balance, missing anions must be matched by missing cations. Frenkel defects occur when an atom is displaced from the position it normally occupies to an interstitial site. Frenkel defects affect both cations and anions, but cation defects are more common because anions are larger and usually more tightly bonded in place.



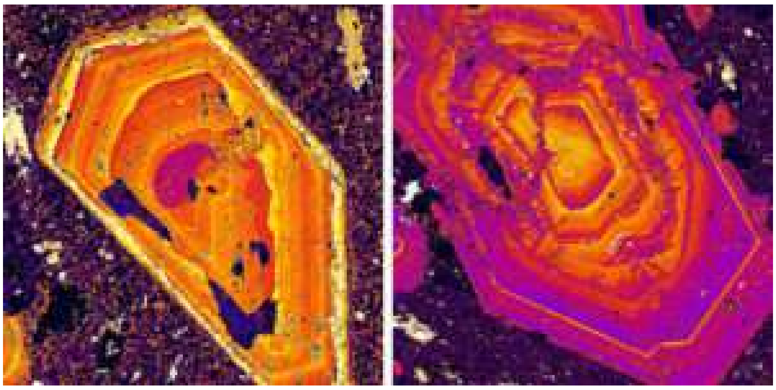
4.36 Atoms offset by an edge dislocation

Besides point defects, other types of defects include *line defects* and *plane defects*. Line defects, including *edge dislocations*, like the one shown in the schematic in Figure 4.36, are defects that end at lines in a structure. Plane defects, as their name implies, are planes along which a crystal's structure is displaced or distorted. On a large scale, grain boundaries are types of plane defects. At the atomic level, several different structures may separate slightly misoriented portions of a crystal structure so that a crystal contains *domains* having slightly different atomic orientation. Domains of this sort are clearly seen in the TEM photograph above (Figure 4.34).

4.4.5 Crystal Zoning

4.37 Zoned fluorite crystals from China

Crystallizing magmas may produce uneven mineral distribution within a rock. On a smaller scale, individual minerals develop *compositional zoning* if different parts of a mineral have different compositions. Zoning is present in many minerals but often on such a small scale that we have difficulty detecting it. Sometimes, however, zones of different compositions are large and have different colors – as can be seen in these fluorite crystals from China (Figure 4.37). Look, also, at the zoned tourmaline crystal in Figure 4.13, earlier in this chapter. Often – even if not visible with the naked eye – zoning can be seen with a petrographic microscope because zones of different composition have different optical properties. In still other cases detailed chemical analyses are needed to detect zoning's presence. Note that there is no visible zoning in Figure 4.3 (near the start of this chapter), another example of fluorite.



4.38 Scanning electron microscope (SEM) images of zoned plagioclase crystals in igneous rocks

Most zoning is an artifact of crystal growth. It may result from changes in pressure or temperature during crystallization. It may also result from changes in magma or fluid composition as crystals grow. The principles of thermodynamics dictate that zoned minerals are unstable and should homogenize over time. But they are common in nature because diffusion of elements is often not fast enough for growing minerals to remain homogeneous. Most zoning is concentric, forming as growth rings about an original crystal seed. Occasionally, it is more complex and results in compositional zones that are difficult to explain and interpret. The colorful images seen in Figure 4.38 show zoned plagioclase in an igneous rock. These images were obtained with a scanning electron microscope (SEM) and the colors show domains of different compositions that developed as the crystals grew.

4.4.6 Crystal Twinning

4.39 Swallowtail twinning of gypsum

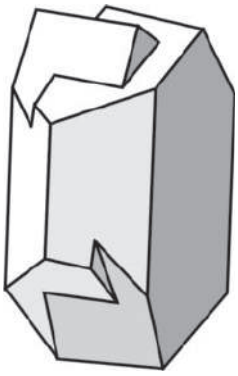
4.40 Staurolite with penetration twinning

In ideal crystals, atoms are in repetitive arrangements, oriented the same way in all parts of the crystal. *Twinning* result when different domains of a crystal have different atomic orientations. The photo of twinned gypsum on the left (Figure 4.39) is a good example. Half the crystal grew with atoms oriented differently from atoms in the other half. This kind of twinning of gypsum is called *swallowtail twinning*, for obvious reasons.

Some twinning, called *contact twinning*, appears as two or more crystal domains in contact with each other (like the gypsum above). The domains share atoms along a common surface, typically a plane called the *composition plane*. Twins differ from crystal *intergrowths* composed of crystals that grow next to each other. In a twinned crystal the structure and bonds continue across the composition plane; in intergrowths they are discontinuous.

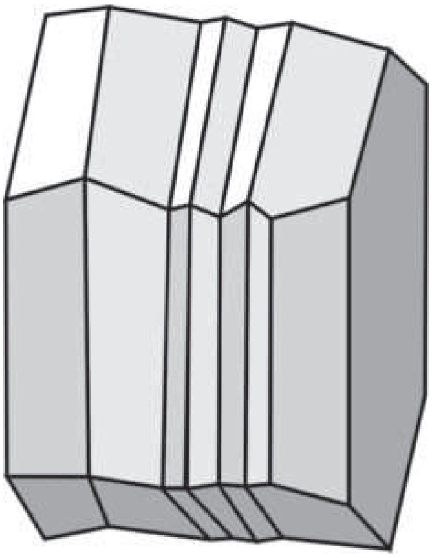
Another kind of twinning, called *penetration twinning*, appears as crystals that seem to have grown through each other. In such twins, two domains share a volume of atoms, not just a plane of atoms. The twinned staurolites in Figure 4.40 are good examples of penetration twins. The staurolite specimen includes both *cruciform* (cross-like) twins, sometimes called *fairy-crosses*, and *V-twins* that resemble slightly the twinned gypsum on the left. The fluorite crystals in Figure 4.37 also display penetration twins.

4.41 Orthoclase crystals with penetration twins



4.42 Idealized drawing of twinned orthoclase

Simple twins comprise only two domains that share common planes or volumes of atoms. The gypsum and staurolite seen above are examples. The twinned orthoclase (K-feldspar) crystals seen here are also examples of simple penetration twinning. The drawing better emphasized the nature of the crystal intergrowths.



4.43 Sketch of twinned plagioclase

4.44 Plagioclase exhibiting twin striations

Crystals with *complex twins*, in contrast with simple twins, have more than two individual twin domains. The drawing and photo (Figures 4.43 and 4.44) show complex twinning called *polysynthetic twinning* that often characterizes plagioclase, calcite, and a few other minerals. The mineral specimen shows *twin striations* (stripes) with different reflectivities, because the alternating domains contain atoms arranged in slightly different ways. The presence of striations is one way that geologists distinguish plagioclase from other feldspars, such as the orthoclase seen in Figure 4.41.

4.45 This photo shows a

relatively rare kind of twinning called cyclic twinning. The mineral is cerussite, lead carbonate.

Figure 4.45 shows another example of complex twinning called *cyclic twinning.* The mineral is cerussite ($PbCO_3$). In cyclic twins, three or more crystals seem to emanate from a central point, so the different crystal domains are not parallel but instead are radiating. This photo shows one very important feature. Identifying twins in hand specimens can be difficult, especially in poorly formed crystals. One diagnostic characteristic is the presence of *reentrant angles*, like the ones seen in this twinned cerrusite. Two crystal faces intersect to form a reentrant angle when they produce an angular concavity that points toward the interior of a crystal instead of the (normal) exterior.

Twinning comes at all scales and may be difficult to detect. Sometimes we can see it with the naked eye, sometimes we can only see it with a microscope, and sometimes we cannot detect it without more sophisticated devices.

Whether twinning is simple or complex, atoms in different twin domains are related by some kind of twin symmetry. For example, the atomic arrangements in two domains may be mirror images of each other. This is the case for all the fine striations in the plagioclase crystal in Figure 4.44 – the alternating domains are reflections of each other. If not mirror images, two twin domains may be related by rotation, such as in Figure 4.45, and there are other ways that domains can be related, too. So, there are many kinds of twins. The nature of a particular kind – whether it is simple or complex and the kind of symmetry involved – define what is called a *twin law* and allow different kinds of twins to be named. For example, the plagioclase twinning in Figure 4.44 is *albite* *twinning*, and the K-feldspar twinning in figure 4.41 is *Carlsbad twinning*. The domains in albite twinning are related by reflections across a near vertical plane. The two domains in Carlsbad twins are related by a rotation around a near vertical axis in the crystals shown.

Twins form in several ways. They may be *growth twins*, *transformation twins*, or *deformation twins*. *Growth twins* form when a crystal first grows. Atoms being added to the outside of an already existing crystal may become slightly misplaced so that all subsequent atoms are arranged in a different orientation than in the original crystal domain. Essentially, a new crystal (a new domain) develops adjacent to the original. If a common plane of atoms is oriented correctly for both domains, the result is a contact twin. If a common volume of atoms is oriented correctly for both domains, a penetration twin has been formed. These relationships are most easily visualized by looking at some of the photos and drawings above.

Transformation twins may form when an existing mineral goes through a phase transition to become a different mineral. This involves polymorphs. For example, the feldspar sanidine ($KAlSi_3O_8$) forms at high temperature in volcanic rocks. With cooling it may change into orthoclase, a different form of $KAlSi_3O_8$, and then microcline, a third form of $KAlSi_3O_8$. During the transformations, atoms in different domains of the crystal may become slightly misoriented with respect to other domains. So, twinned orthoclase and microcline crystals may be the result.

The third kind of twins, *deformation twins,* may develop if a crystal is subjected to stress. Planes or volumes of atoms may become slightly displace, producing domains with different orientations. This kind of twinning is common in calcite, although generally a microscope is needed to see it. Deformation twins are generally not of great importance to mineralogists.

4.5 Life Spans of Minerals

Some rocks and minerals have survived a long test of time. The Acasta gneiss, which formed 4.03 billion years ago, is generally considered the oldest rock on Earth. It contains two kinds of feldspars, quartz, and minor mafic minerals. The oldest known terrestrial mineral grains are detrital zircon crystals in a conglomerate from the Jack Hills of Western Australia. They are 4.40 billion years old and must have eroded from even older rocks. Some minerals in meteorites are older. Mineral grains from the Murchison meteorite, for example, are 7 billion years old – these are the oldest material found on Earth and are older than the Sun.

Deep within Earth, minerals may disappear due to melting, or they may change into new minerals by metamorphism. Occasionally, at Earth's surface, they may dissolve in water and disappear. The biggest threat to minerals, at least the minerals that we see most often, however, is that most of them are not stable when exposed to air, water, wind, and other elements at Earth surface. They just do not last very long on a geological time scale.

Many minerals commonly occurring in modern sediments and rocks are too unstable to survive in great abundance in older terrestrial rocks. They may have been in those rocks once, but they have changed into different minerals since then. Earth is 4.6 billion years old. Very few examples of the minerals discussed below have existed for more than the last 7% of Earth's history.

4.46 Millimeter sized olivine from Hawaii

4.47 A grain of green olivine, surrounded by serpentine, from the Austrian Alps

The two photos above show fresh olivine from Hawaii (Figure 4.46), and a single ancient olivine crystal (the green grain in the center of the specimen) from the Austrian Alps (Figure 4.47). Olivine was once abundant in many terrestrial Precambrian (older than 541 million years) mafic rocks, but since the Precambrian Era, most old olivine has been altered by oxygen, carbon dioxide, and water to make serpentine, iron oxides, and magnesite. Because olivine crystallizes in hot and dry magmas, it is unstable under much cooler and wetter Earth surface and near-surface conditions. Because of olivine’s and pyroxene’s tendency to weather rapidly, detrital olivine and pyroxene are largely restricted to relatively young (Cenozoic; younger than 65 million years old) sediments and sedimentary rocks. However, Precambrian olivine and pyroxene occur in Moon rocks and meteorites that have been isolated from oxygen and water.

4.48 Arborescent tridymite in a volcanic rock

Other examples of minerals generally absent from older terrestrial rocks include the quartz polymorph *tridymite*, and *aragonite*, a high-pressure polymorph of calcite. Tridymite is common in Cenozoic siliceous volcanic rocks, including rhyolites, obsidian, and andesites. However, except in stony meteorites and lunar basalts, the mineral changes to quartz over time and is rarely found in rocks that are older than Cenozoic age. The photo in Figure 4.48 show *snowflake* tridymite in a volcanic rock in Germany.

4.49 An ammonite shell composed of aragonite

Many marine organisms create shells that consist of $CaCO_3$ in the form of aragonite rather than calcite. Figure 4.49 shows an example. Unless aragonite fossils are deeply buried, they will alter to calcite. The oldest known aragonite fossil is from an organic-rich shale of Mississippian age (around 350 million years old). Geologists have only found aragonite fossils that old in three places. One of the rocks is volcanic while the others are black shale and asphaltic limestone. The presence of abundant organic matter in three of the four known rocks with Paleozoic aragonite is probably responsible for the preservation of the aragonite. The organic matter coated the fossils and probably prevented water from reaching them and promoting their conversion to calcite.

4.50 Aragonite speleothem from the Salsigne Mine in France

Inorganic aragonite sometimes forms on the ceilings or walls of caves or mines, in much the same way that stalactites and other speleothems form. It is, however, unstable, and over time turns into calcite. The change to calcite is slow, and occurs on time scales of 10 to 100 million years.

Some nonmineral materials are unstable and invert to minerals given a chance. Opal and volcanic glass are amorphous materials (although opal has been approved as a mineral name by the International Mineralogical Association). Over time, both weather or alter into more stable crystalline compounds, such as quartz. This explains why obsidian is rarely found in rocks older than the Miocene. The oldest known volcanic glass is in a 70-million-year-old welded tuff. Opal is slightly more stable than obsidian. Reaction rate calculations indicate that opal will entirely convert to quartz in about 180 million years at 20 °C , approximately 4.3 million years at 50 °C, and in only about 47 years at diagenetic temperatures of 200 °C. Not surprisingly, the oldest known opal is of Lower Cretaceous age, about 125 million years old.

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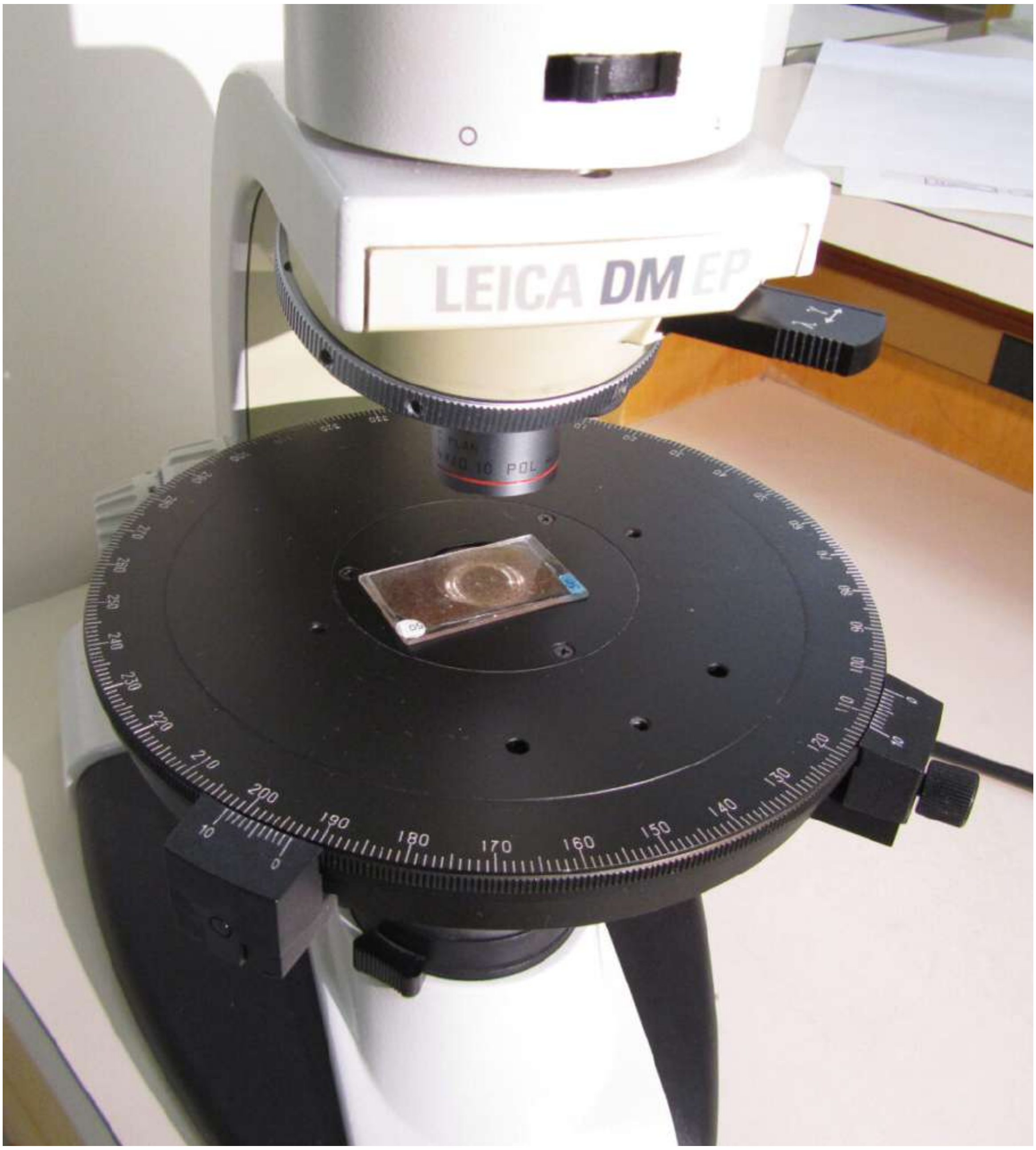
5 Optical Mineralogy



5.1 Thin section on the stage of a petrographic microscope

5 – Optical Mineralogy

KEY CONCEPTS

- Optical mineralogy involves studying rocks and minerals by studying their optical properties.

- Today, most optical mineralogy involves examining thin sections with a petrographic microscope.
- Light entering a crystal may be refracted or reflected.
- Petrographic microscopes have polarized light sources that illuminate a thin section.
- We examine thin sections in two modes: plane polarized light and cross polarized light.
- In plane polarized light we can distinguish opaque and nonopaque minerals; we can see crystal shape, habit, cleavage, color and pleochroism, and relief.
- In cross polarized light, we distinguish anisotropic from isotropic minerals, we see interference colors related to birefringence, and we can see twinning and related features.
- We use cross polarized light to learn a crystal’s optic class and optic sign, to measure extinction angles and sign of elongation, and to measure *2V*.
- A combination of optical properties allows us to identify minerals in thin section and to interpret geologic histories.

● Box 5-1 For an Alternative Approach

This chapter contains the standard and fundamental information about optical mineralogy. But there are many ways to approach this topic. For an alternative approach, and to see many excellent videos, go to “Introduction to Petrology” by Johnson, E.A., Liu, J. C., and Peale, M. at: https://viva.pressbooks.pub/petrology

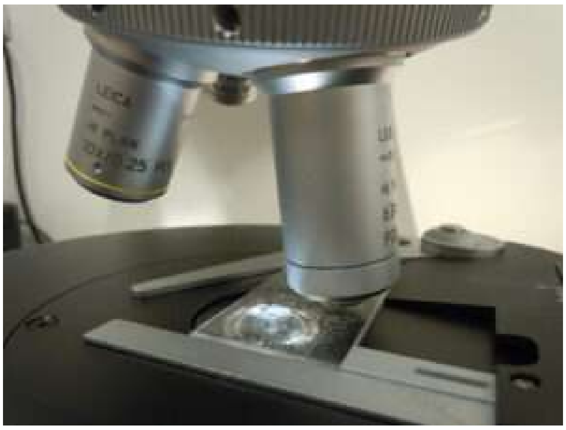
● Box 5-2 Prologue: An Introduction to Optical Mineralogy

The principles of optical mineralogy and mineral microscopy can be confusing. A standard approach into complicated science topics is to start with a discussion of underlying principles and to build to more complicated concepts. And we will do that.

But because mineral optics can seem arcane, before we jump into the underlying fundamentals, we will begin with a video that gives some background and a broad overview without all the details of optical theory and microscopy. The video finishes up by discussing the most important aspect of optical mineralogy, which is viewing rocks and minerals in thin section. And everything that follows this box in Chapter 5 is building to that end.

▶️ Video 1: An Introduction to Optical Mineralogy (9 minutes)

5.1 Introduction to Mineral Optics

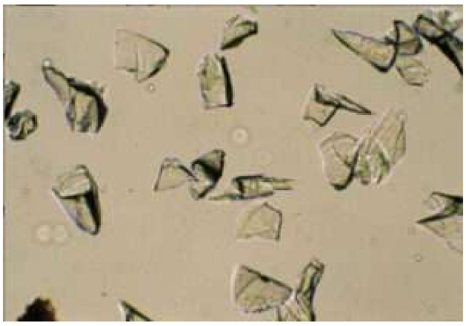


5.2 Close-up view of microscope lenses and a thin section

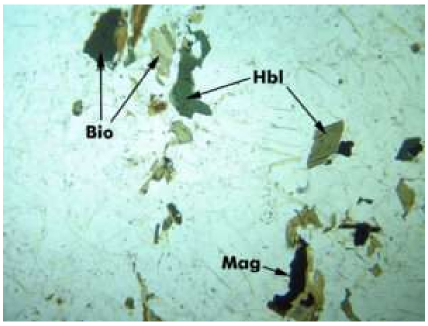
Optical mineralogy involves studying rocks and minerals by studying their optical properties. Some of these properties are macroscopic and we can see them in mineral hand specimens. But generally we use a *petrographic microscope*, also called a *polarizing microscope* (Figures 5.1 and 5.2 show examples), and the technique is called *transmitted light microscopy* or *polarized light microscopy* (PLM). A fundamental principle of PLM is that most minerals – even dark-colored minerals and others that appear opaque in hand specimens – transmit light if they are thin enough. In standard petrographic microscopes, polarized light from a source beneath the microscope stage passes through samples on the stage and then to your eye(s).

One approach to PLM involves examining *grain mounts*, which are ground-up mineral crystals on a glass slide. The grains must be thin enough so that light can pass through them without a significant loss of intensity, usually 0.10 to 0.15 mm thick. We surround a small number of grains with a liquid called *refractive index oil*, and then place a thin piece of glass, called a *cover slip*, over the grains and liquid. The photo in Figure 5.3, below, shows garnet grains in a grain mount.

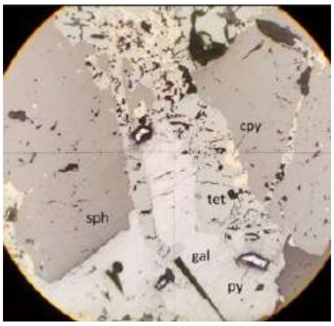
Grain mounts and refractive index oils are necessary for making some types of measurements, but are not the focus of this chapter. They were extensively used in the past, but are not much used today. For more detailed information about studying minerals in grain mounts consult an optical mineralogy textbook.



5.3 Fractured grains (<1 mm) of garnet seen in a grain mount



5.4 A metamorphic rock from Flin Flon, Manitoba, seen in thin section. The field of view is 2.5 mm across.



5.5 Ore from Butte, Montana, seen using a reflecting light microscope

Most optical mineralogy today involves specially prepared *thin sections* (0.03-mm-thick specimens of minerals or rocks mounted on glass slides). Video 1 (linked in Box 5-2) explains how we make thin sections, and Figure 5.1, the opening figure in this chapter, shows an example. Figure 5.4 above shows a microscope view of a thin section that contains several minerals (biotite, hornblende, and magnetite are labeled, and the clear grains around them are mostly quartz and plagioclase). Whether looking at grain mounts or thin sections, transmitted light microscopy allows us to determine and measure properties that are otherwise not discernible. We can identify minerals, sometimes their compositions, and we can observe mineral relationships that allow us to learn about mineral origins.

Minerals with metallic luster and a few others are termed *opaque minerals*. They will not transmit light even if they are thin-section thickness. So they always appear black when viewed with a microscope. Magnetite is an opaque mineral; the photo in Figure 5.4 contains several small black magnetite grains. For studying opaque minerals, transmitted light microscopy is of little use. *Reflected light microscopy* (RLM), a related technique, can reveal some of the same properties. As the name implies, when using RLM, the light source is above the sample and light reflects from the sample to our eye. RLM, although an important technique for economic geologists who deal with metallic ores, is not used by most mineralogists or petrologists. So we discuss it only briefly in this book. Figure 5.5 shows a view of ore from Butte, Montana, seen with a reflecting light microscope. It contains several opaque minerals: galena, sphalerite, pyrite, and chalcopyrite. They appear in various shades of black, gray, and light yellow.

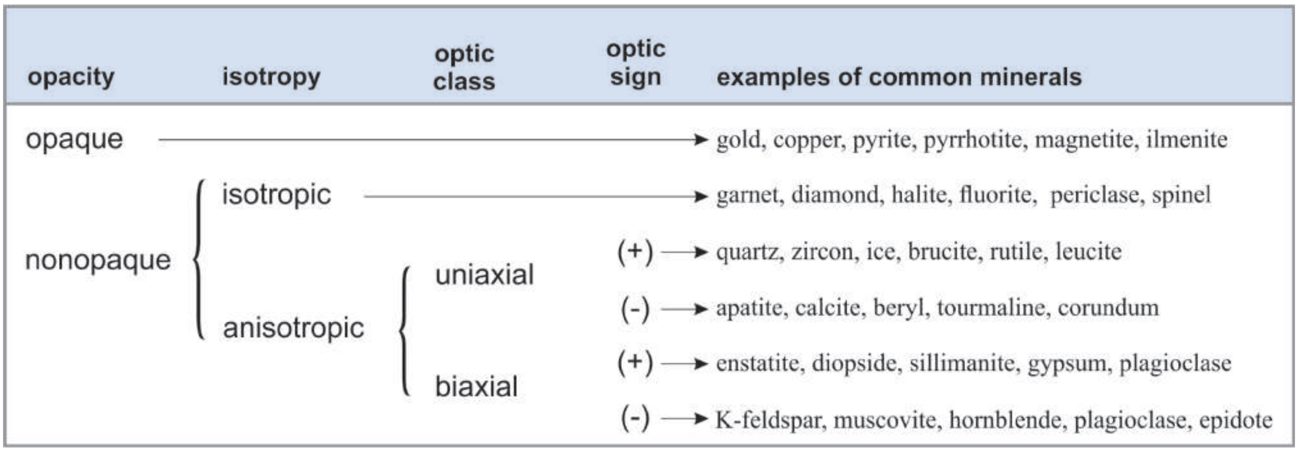
Most minerals can be identified when examined with a petrographic microscope, even if unidentifiable in hand specimen. Optical properties also allow a mineralogist to estimate the composition of some minerals. For example, we can learn the magnesium-to-iron ratio of olivine, $(Mg,Fe)_2SiO_4$, based on optical properties. And we can also determine the albite and anorthite content of plagioclase feldspar.

Box 5-3 (below) summarizes the optical properties used for mineral identification and gives the properties of some common minerals. At the largest level, we divide minerals into *opaque minerals* and *nonopaque minerals*. Opaque minerals will not transmit light unless the mineral grains are much thinner than normal thin sections. We further divide nonopaque minerals into those that are *isotropic* (having the same properties in all directions) and those that are *anisotropic* (having different optical properties in different directions). Finally, we divide the anisotropic minerals into those that are *uniaxial* and those that are *biaxial*, and according to whether they have a positive or negative *optic sign*. We discuss the details of these and other diagnostic properties below.

Besides mineral identification, the polarizing microscope reveals important information about rock-forming processes (*petrogenesis*). When we examine thin sections, distinguishing igneous, sedimentary, and metamorphic rocks is often easier than when we look at hand specimens. More significantly, we can identify minerals and distinguish among different types of igneous, sedimentary, and metamorphic rocks. The microscope allows us to see textural relationships in a specimen that give clues about when and how different minerals in an igneous rock formed. Microscopic relationships between mineral grains allow us to determine the order in which minerals crystallized from a magma, and we can identify minerals produced by alteration or weathering long after the crystals first formed. Similar observations are possible for sedimentary or metamorphic rocks. Only the microscope can give us such information, information that is essential if rocks are to be used to interpret geological processes and environments.

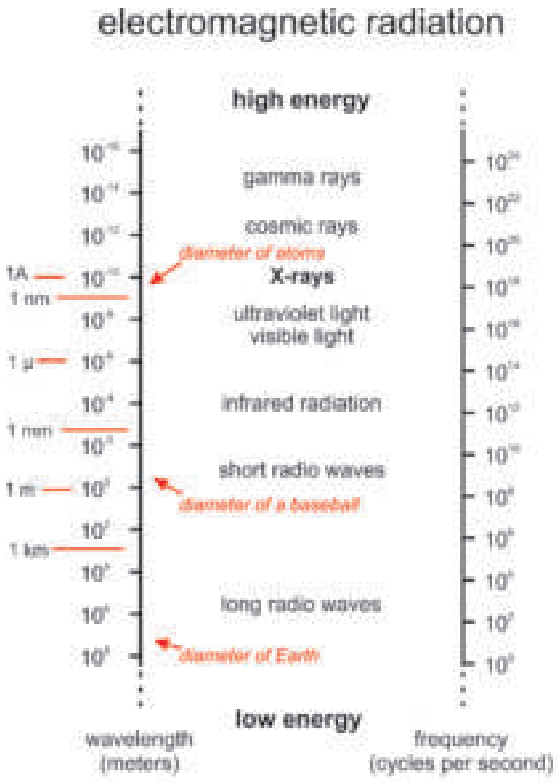
● Box 5-3 Optical Classification of Minerals

Mineralogists often classify minerals according to the mineral’s optical properties. The table below shows the basic classification scheme and gives examples of minerals belonging to each of six categories. At the highest level, we divide minerals into two groups: opaque minerals and nonopaque minerals. We further divide the nonopaque minerals into those that are isotropic and anisotropic, and then we divide the anisotropic minerals by other properties discussed later in this book. We measure these properties using a polarizing microscope such as the one in Figure 5.2 (above) and Figure 5.22 (later in this chapter).



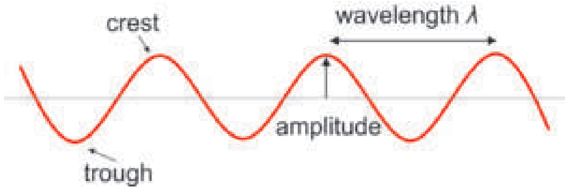
opacity	isotropy	optic class	optic sign	examples of common minerals
opaque				gold, copper, pyrite, pyrrhotite, magnetite, ilmenite
nonopaque	isotropic			garnet, diamond, halite, fluorite, periclase, spinel
	anisotropic	uniaxial	(+)	quartz, zircon, ice, brucite, rutile, leucite
			(-)	apatite, calcite, beryl, tourmaline, corundum
		biaxial	(+)	enstatite, diopside, sillimanite, gypsum, plagioclase
			(-)	K-feldspar, muscovite, hornblende, plagioclase, epidote

5.2 Light and the Properties of Light



5.6 The spectrum of electromagnetic radiation

Before starting a discussion of optical mineralogy, taking a closer look at light and its properties is helpful. Light is one form of electromagnetic radiation (Figure 5.6). Radio waves, ultraviolet light, and X-rays are other forms of electromagnetic radiation. All consist of propagating (moving through space) electric and magnetic waves (hence the term *electromagnetic*). The interactions between electric waves and crystals are normally much stronger than the interactions between magnetic waves and crystals (unless the crystals are magnetic). Consequently, this book only discusses the electrical waves of light. In principle, however, much of the discussion applies to the magnetic waves as well. Because light waves have wavelengths two orders of magnitude greater than atom sizes or bond lengths, the interactions of light with crystals does not reveal information about individual atoms in a crystal. To obtain that kind of information, we must study crystals using X-rays (Chapter 12).

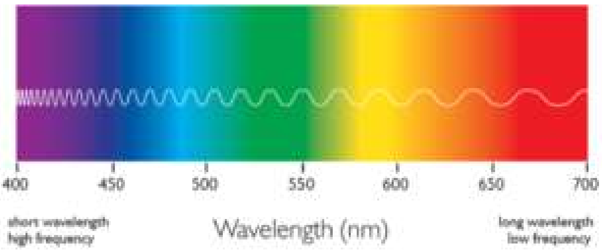


5.7 The characteristics of a wave

Light waves, like all electromagnetic radiation, are characterized by a wavelength, λ, and a frequency, ν (Figure 5.7). The velocity, v, of the wave is the product of λ and ν:

$$v = \lambda\nu$$

In a vacuum, light velocity is 3×10^8 meters per second. Velocity is slightly less when passing through air, and can be much less when passing through crystals. When the velocity of light is altered as it passes from one medium (for example, air) to another (perhaps a mineral), the wavelength changes, but the frequency remains the same.

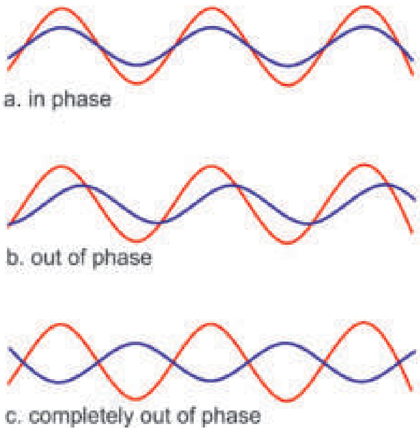


5.8 Different wavelengths and colors of visible light

Visible light has wavelengths of 390 to 770 nm, which is equivalent to 3,900 to 7,700 Å, or $10^{-6.1}$ to $10^{-6.4}$ m. Different wavelengths correspond to different colors (Figure 5.8). The shortest wavelengths (violet light) grade into invisible ultraviolet radiation. The longest wavelengths, corresponding to red light, grade into invisible infrared radiation.

Light composed of multiple wavelengths appears as one color to the human eye. If wavelengths corresponding to all the primary colors are present with equal intensities, the light appears white. White light is said to be *polychromatic* (many colored), because it contains a range, or spectrum, of wavelengths. Polychromatic light can be separated into different wavelengths in many ways. When one wavelength is isolated, the light is *monochromatic* (single colored).

5.2.1 Interference



5.9 In-phase and out-of-phase waves

Besides wavelength (λ) and frequency (ν), an amplitude and a phase characterize all waves. Amplitude (A) refers to the height of a wave. *Phase* refers to whether a wave is moving up or down at a particular time. If two waves move up and down at same times, they are *in phase*; if not, they are *out of phase*.

When two waves with the same wavelength travel in the same direction simultaneously, they interfere with each other. Their amplitudes may add, cancel, or be somewhere between. The nature of the interference depends on the wavelengths, amplitudes, and phases of the two waves. Light waves passing through crystals can have a variety of wavelengths, amplitudes, and phases affected by atomic structure in different ways. They yield *interference phenomena*, giving minerals distinctive optical properties.

In Figure 5.9*a*, two in-phase waves of the same wavelength are going in the same direction. If we could measure the intensity of the two waves together, we would find that their amplitudes have added. When waves are in phase, no energy is lost; this is *constructive interference*. In contrast, Figure 5.9*b* shows two waves that are slightly out of phase, and Figure 5.9*c* shows two waves that are completely out of phase.

When waves are out of phase, wave peaks and valleys do not correspond. If they are completely out of phase, the peaks of one wave correspond to the valleys of the other. Consequently, addition of out-of-phase waves can result in *destructive interference*, a condition in which the waves *appear* to "consume" some or all of each other's energy. (The First Law of Thermodynamics tells us that energy cannot disappear, so if two waves appear to cancel each other it means that the energy is going in another direction.) For perfect constructive or destructive interference to occur, waves must be of the same wavelength but they may have different amplitudes (as shown in Figure 5.9*c*). Interaction of waves with different wavelengths is much more complicated.

5.2.2 The Velocity of Light in Crystals and the Refractive Index

When light passes near an atom, perhaps in a crystal, the vibrating electric wave causes electrons to oscillate. The oscillations absorb energy from the light, and the wave slows. As light passes from air into most nonopaque minerals, its velocity may decrease by a third or a half. Because the frequency of the light remains unchanged, we know that the wavelength must decrease by a similar fraction (because $v = \lambda\nu$).

A wave's velocity through a crystal is described by the crystal's refractive index (n), which depends on chemical composition, crystal structure, and bond type in the crystal. The refractive index (n) is the ratio of the velocity (v) of light in a vacuum to the velocity in the crystal:

$$n = v_{vacuum} / v_{crystal}$$

Because light passes through a vacuum faster than through any other medium, *n* always has a value greater than 1. High values of *n* correspond to materials that transmit light slowly. Under normal conditions, the refractive index of air is 1.00029. Because it is much easier to work with air than with a vacuum, this is a common reference value and we often calculate refractive index as:

$$n = v_{air} / v_{crystal}$$

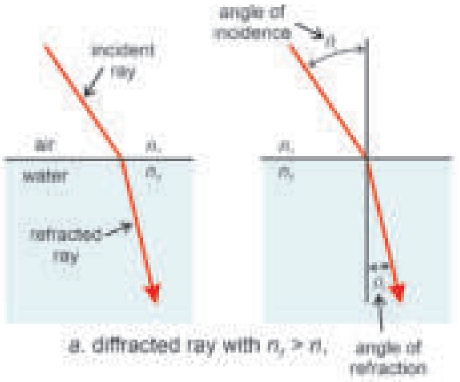
Refractive Index Values	
air fresh water fluorite borax sodalite window glass quartz garnet zircon zincite diamond	1.000293 1.333 1.434 1.466 1.480 1.52 1.533 1.78 1.923 2.021 2.419

Most minerals have refractive indices between 1.5 and 2.0 (see examples in the table to the right). Fluorite, borax, and sodalite are examples of minerals that have a very low (< 1.5) index of refraction. At the other extreme, zincite, diamond, and rutile have very high indices (> 2.0). The refractive index is one of the most useful properties for identifying minerals in grain mounts but is less valuable when we examine thin sections because it is impossible to determine precise values for *n* when viewing minerals in thin section.

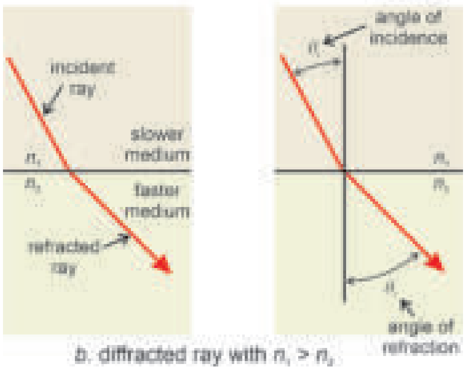
5.2.2.1 Snell’s Law and Light Refraction

5.10 Light refraction caused by a glass of water

We have all seen objects that appear to bend as they pass from air into water. A straw in a glass of soda, or an oar in lake water, seem bent or displaced when we know they are not. We call this phenomenon *refraction*. Figure 5.10 shows an example – a pencil in a glass of water. Refraction occurs when light rays pass from one medium to another (for example water and air in Figure 5.10) with a different refractive index. If the light strikes the interface at an angle other than 90°, it changes direction and can distort a view.



a. diffracted ray with $n_2 > n_1$



b. diffracted ray with $n_1 > n_2$

5.11 Light Refraction

When refraction occurs, a light beam bends toward the medium with higher refractive index (where light travels slower) because one side of the beam moves faster than the other. Consider a beam traveling from air into water (Figure 5.11*a*). The side of the beam that reaches the interface first will be slowed as it enters the water. It sort of *stubs its toe*. So the beam bends toward the water. No refraction occurs for beams traveling at 90° to an interface between media with different refractive indices; the beam follows a straight course.

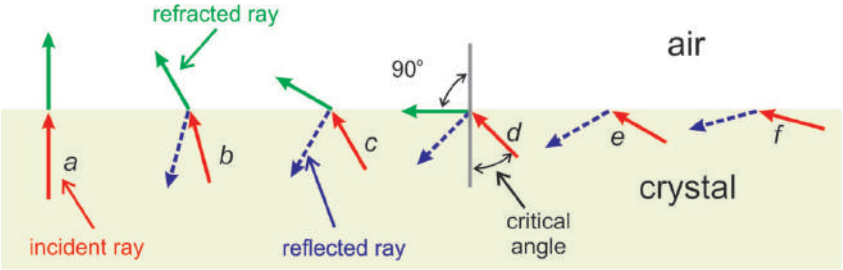
Figures 5.11*b* shows the opposite case: a beam traveling from a medium with a high refractive index (slower light velocity) into another with a lower refractive index (faster light velocity). The beam refracts toward the medium with a higher index, as it did in Figure 5.11*a*.

As seen in Figure 5.11, when light reaches an interface between two different media, the angle between the beam and a perpendicular to the interface is the *angle of incidence (θ_i)*.

After crossing the interface, the angle between the beam and a perpendicular to the interface is the *angle of refraction* (θ_r). The relationship between the angle of incidence (θ_i) and the angle of refraction (θ_r) is

$$\sin(\theta_i) / \sin(\theta_r) = v_i / v_r = n_r / n_i$$

where v_i and v_r are the velocities of light through two media, and n_i and n_r are the indices of refraction of the two media. This relationship, Snell's Law, is named after Willebrod Snell, the Dutch scientist who first derived it in 1621.



5.12 Refraction and the critical angle of refraction

Figure 5.12 shows an incident light ray passing from within a crystal to air outside the crystal. If the incident ray is perpendicular to the crystal-air interface (drawing *a*), all light leaves the crystal. If the angle incidence is small (drawing *b*), most light escapes and is refracted at some angle to the crystal face, but some light reflects back into the crystal. We call this *internal reflection*. As the angle of incidence increases, the proportion of light that is reflected increases. When the angle of incidence becomes large enough (drawing *d*), the refracted ray travels along the crystal-air interface. And for greater incidence angles, no refraction can occur and all light reflects back into the crystal.

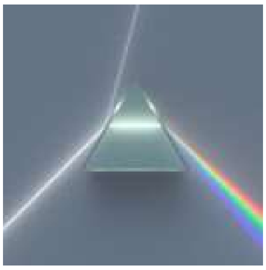
Rearranging Snell's Law tells us that we can calculate the angle of refraction as follows:

$$\theta_r = \sin^{-1}[(n_i/n_r) \text{ x } \sin \theta_i]$$

By definition, sine values can never be greater than 1.0. Suppose a light beam is traveling from a crystal into air. In this situation, $n_i > n_r$, and because the term in square brackets on the right-hand side of the equation above must be less than or equal to 1.0, for some large values of θ_i there is no solution. The limiting value of θ_i is the *critical angle of refraction* (Figure 5.12*d*). If the angle of incidence is greater, none of the light will escape; the entire beam will be reflected inside the crystal as shown in Figures 5.12 *e* and *f*. This is the reason crystals with a high refractive index, such as diamond, exhibit internal reflection that gives them a sparkling appearance. Measuring the critical angle of refraction is a common method for determining refractive index of a mineral. Instruments called *refractometers* enable such measurements.

In Figure 5.12*d*, the critical angle (θ_i) is about 45°. The angle of refraction (θ_r) is 90°. Plugging these values into Snell's law (above) we find that v_i/v_r is 0.7071. In other words, the velocity of light through the crystal is 71% of the velocity through air and, inverting this we find that the crystal has a refractive index of about 1.41. This is on par with many minerals that have low refractive indices.

5.2.2.2 Dispersion and Luster



5.13 Light dispersed by a glass prism

The refractive index of most materials varies with the wavelength of light. In other words, the velocity of light in a crystal varies with the light's color. This variation is *dispersion*. One consequence of dispersion is that different colors of light follow different paths through a crystal because they refract at different angles (according to Snell's Law). We can sometimes see dispersion in thin sections but it is only readily apparent in a few minerals. An excellent but nonmineralogical example of dispersion is the separation of white light into different colors when refracted by a glass prism (Figure 5.13). When a beam of white light enters and exits a prism, different wavelengths (colors) exit at different angles, resulting in the production of colorful rainbows. Note also the reflected beam of white light in Figure 5.13. Reflection and refraction often occur together; their relative intensities depend on the angle at which the light hits an interface.

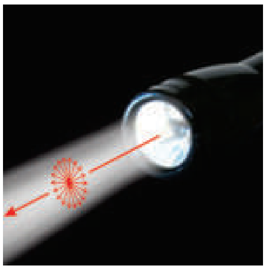
5.14 Play of fire and dispersion in diamond

For a mineralogical example of dispersion, we may consider diamond. Diamond's extreme dispersion accounts, along with its high refractive index, for the *play of colors* (*fire*) that diamonds display (seen in Figure 5.14). If not for dispersion, diamonds might sparkle, but the sparkles would all be the same color. Minerals with low dispersion generally appear dull no matter how well cut or faceted. They may, however, be useful as lenses because dispersion can separate colors and cause unwanted effects.

A mineral’s refractive index and dispersion profoundly affect its luster. Minerals with both very high refractive index and dispersion, such as diamond or cuprite, appear to sparkle and are termed *adamantine*. Minerals with a moderate refractive index, such as spinel and garnet (n = 1.5 -1.8), may appear *vitreous* (glassy) or *shiny*; those with a low refractive index, such as borax, will appear *drab* because they do not reflect or refract as much incident light. Refractive index depends on many things, but a high n-value suggests minerals composed of atoms with high atomic numbers, or of atoms packed closely together.

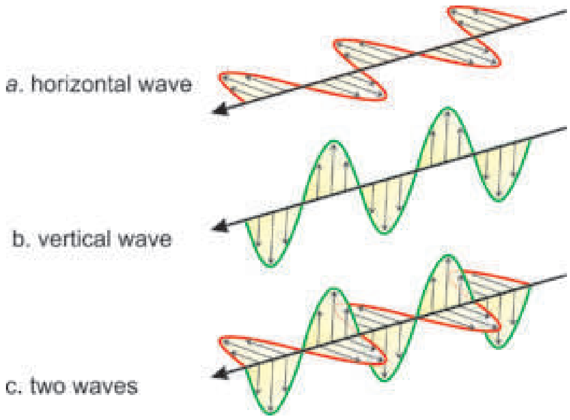
5.3 Polarization of Light

5.3.1 Polarized Light



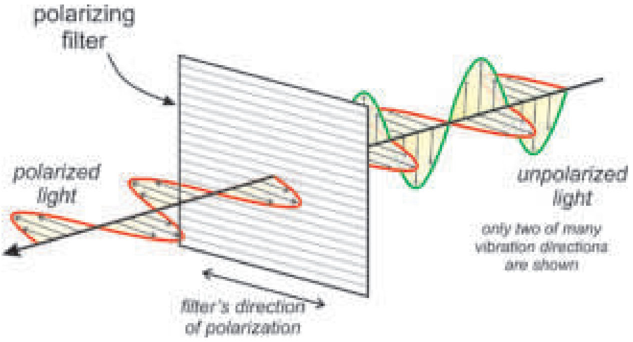
5.15 An unpolarized beam of light

The vibration direction of a light wave (which is the direction of motion of the electric wave) is perpendicular, or nearly perpendicular, to the direction the wave is propagating. In normal *unpolarized* beams of light, waves vibrate in many different directions, shown by arrows in Figure 5.15.



5.16 Polarized light rays

We can filter an unpolarized light beam to make all the waves vibrate in one direction parallel to a particular plane (Figure 5.16). The light is then *plane polarized*, sometimes called just *polarized*. (Unlike the drawings in Figure 5.16, a beam of white light, whether polarized or not, may contain many different wavelengths.) Figure 5.16*a* shows a wave vibrating horizontally and Figure 5.16*b* shows one vibrating vertically. Figure 5.16*c* shows the two polarized rays together. They are in phase but need not be.



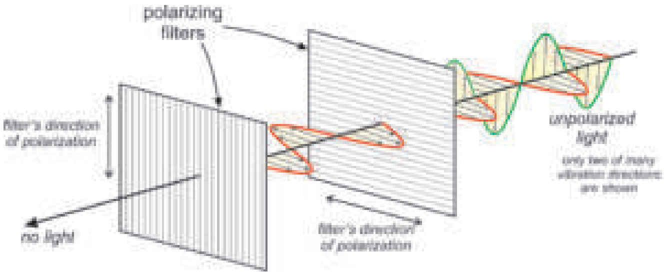
5.17 Filtering unpolarized light to make it polarized

Figure 5.17 shows what happens when a beam of unpolarized light encounter a polarizing filter. Only two vibration directions are shown for the unpolarized light but you should envision light vibrating in all directions before it reaches the filter. After passing through the filter, all light that remains in constrained to vibrate in one plane. It is plane polarized. In this figure, the polarization direction is horizontal, but it could be in any direction if we rotated the filter.

5.18 Looking at fish with and without polarized sunglasses

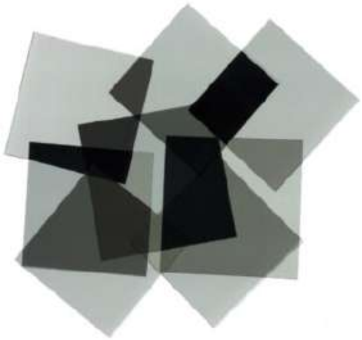
Light becomes polarized in different ways. Reflection from a shiny surface can partially or completely polarize light. Light vibrating in planes parallel to the reflecting surface is especially well reflected, while light vibrating in other directions is absorbed. This is why sunglasses with polarizing lenses help eliminate glare. Figure 5.18 contains two views of a stream containing fish. The view on the left shows lots of glare caused by light reflecting from the water surface. The light is polarized horizontally because the surface is horizontal. The view on the right is through a polarizing filter that only allows us to see light vibrating vertically. Reflections from roads and many other surface cause glare that can be eliminated with polarizing sunglasses.

5.3.2 Crossed Polars



5.19 Polarized light stopped by a polarizing filter

Suppose light passes through a polarizing filter that constrains it to vibrate horizontally (Figure 5.19). (In this figure, we only show two of the many vibration directions in the unpolarized light but think of vibrations occurring in all directions.) On the other side of the first filter, the polarized beam, although perhaps decreased in intensity, appears the same to our eyes because human eyes cannot determine whether light is polarized. If, however, a second polarizing filter, oriented perpendicularly to the first filter, is in the path of the beam, we can easily determine that the beam is polarized. If the second filter allows only light vibrating in a north-south direction to pass, no light will pass through it.

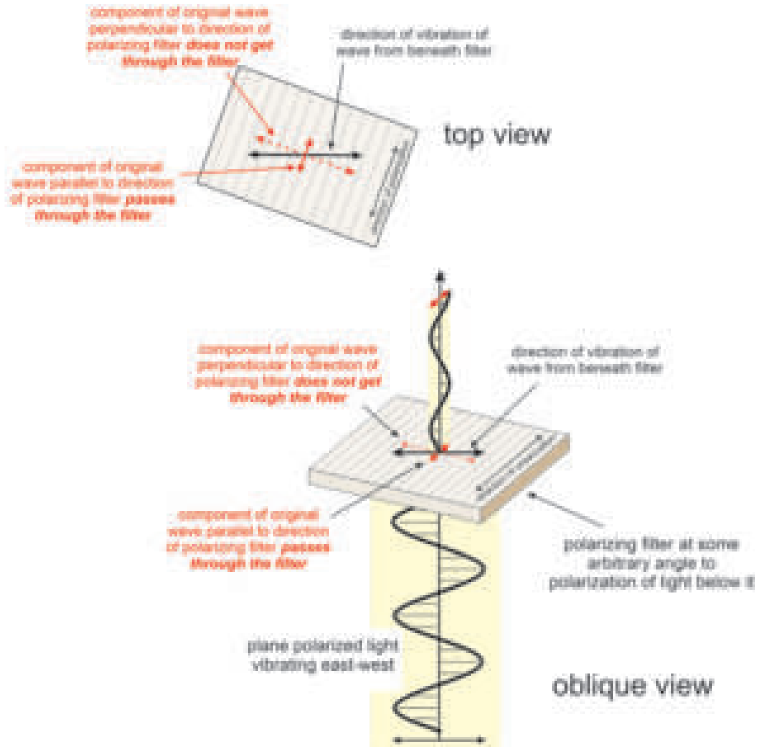


5.20 Overlapping polarizing filters

Figure 5.20 shows some polarizing filters piled randomly on top of each other. In some places the filters are at 90° to each other and no light gets through. In other places they transmit lots of light. (These filters have a gray color and absorb some light, so we do not see any white light being transmitted no matter the orientation of the filters.) But, when the filters are aligned we get maximum light transmission, and when they are perpendicular we get none.

5.3.3 Polarized Light Vibrating at an

Angle to a Polarizing Filter



5.21 Polarized light encountering a polarizing filter

Suppose polarized light hits a polarizing filter at some angle such that the light is vibrating neither parallel, nor perpendicular, to the polarization direction of the filter. In this case, only the component of the light that is vibrating parallel to the filter will pass. The filter absorbs the rest.

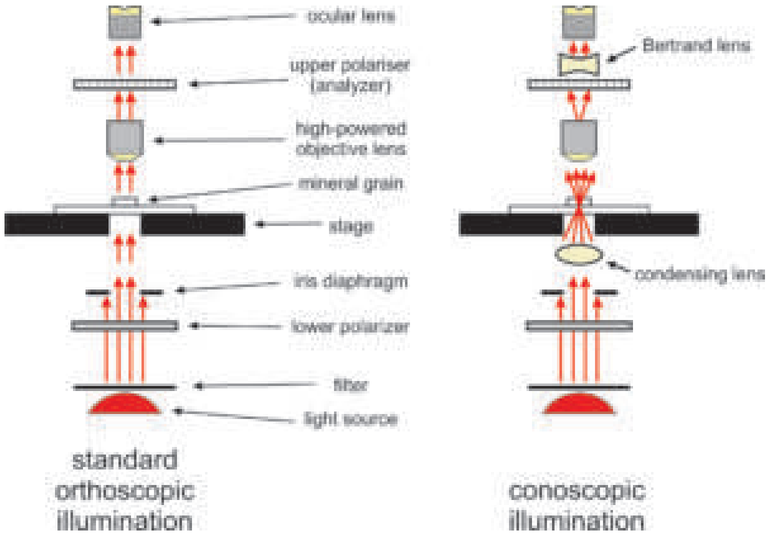
Figure 5.21 shows this happening. An original light beam travels vertically from below and encounters a filter. The light is vibrating nearly perpendicularly to the vibration direction of the filter but a small amount – the component that is vibrating parallel to the filter – gets through. If we rotated the filter, the amount of light transmitted would range from 0 to 100% depending on the orientation of the filter with respect to the polarization direction of the light from below. If the light from below is polarized east-west and the filter is polarized north-south, no light will pass through it (Figure 5.19). If we slowly rotate the filter to an east-west orientation, it will gradually transmit more light, and eventually, all of the light.

5.4 Petrographic Microscopes

5.4.1 The Components of a Microscope

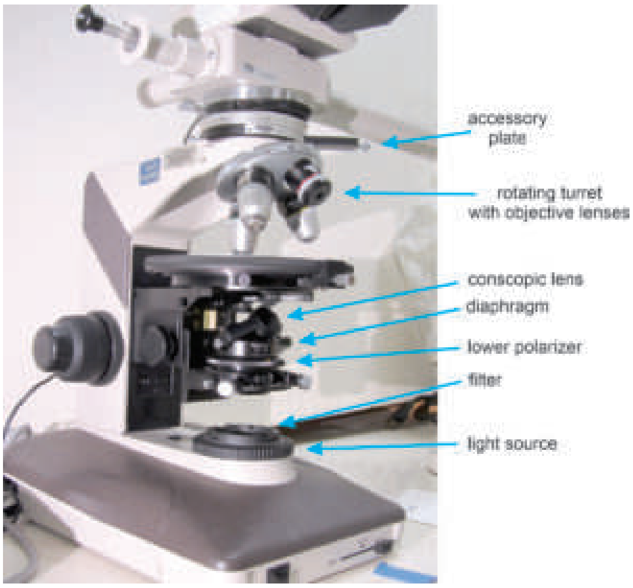
5.22 A standard petrographic microscope

Polarizing microscopes, like the one seen in Figure 5.22, are in many respects the same as other microscopes. They magnify small features in a thin section so we can see fine details. These microscopes include many components. We view thin sections in two modes, depicted in Figure 5.23. *Orthoscopic illumination* is standard and by far the most commonly used method. It involves an unfocused light beam that travels from the substage, through the thin section, and straight up the microscope tube to the ocular lens and our eyes. The light rays travel perpendicular to the stage and perpendicular to a thin section on the stage.



5.23 Components of a petrographic microscope

For some purposes, we insert a special lens called, a *conoscopic lens*, between the lower polarizer and stage to produce *conoscopic illumination* (shown in Figure 5.23). The conoscopic lens, also called a *condenser lens*, causes the light beam to converge (focus) on a small spot on the sample. So, light illuminates the sample with a cone of nonparallel rays. The light then travels up the microscope tube in many directions instead of only vertically. Above the upper polarizer, most microscopes have a *Bertrand lens* that causes light to again travel vertically before it reaches the ocular.



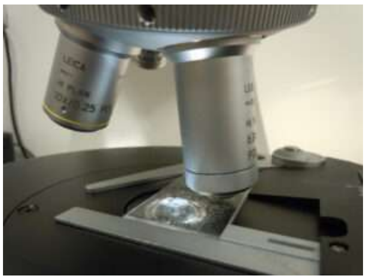
5.24 Another view of a petrographic microscope

Figures 5.22 and 5.24 show the most important microscope components. A bulb beneath the microscope stage provides a white light source. The light passes through several filters, the lower polarizer, and a diaphragm that can limit the size of the light beam. When polarized white light reaches the stage, it interacts with the material being observed. Ultimately, the light reaches our eye(s) and we see the sample.

The most important filter below the stage is the *lower* (substage) *polarizer*, which ensures that all light striking the sample is plane polarized (vibrating, or having wave motion, in only one plane). The presence of a substage polarizer sets petrographic/polarizing microscopes apart from other microscopes. In most modern polarizing microscopes, the lower polarizer only allows light vibrating in an east-west direction to reach the stage. Older microscopes, however, may have the lower polarizer oriented in a north-south direction. Above the polarizing filter, a diaphragm helps concentrate light on the sample.

5.25 Angular scale on a microscope stage

Because most minerals are anisotropic, the interaction of the light with a mineral varies with stage rotation. We can rotate the microscope stage to change the orientation of the sample relative to the polarized light. A calibrated angular scale around the outside of the stage allows us to make precise measurements of crystal orientation (Figure 5.25). The scale is also useful for measuring angles between cleavages, crystal faces, and twin orientations, and for measuring other optical properties.



5.26 Microscope turret and objective lenses

A rotating turret above the microscope stage holds several objective lenses (Figure 5.26). Typically, they range in magnification from 4*x* to 64*x*. Different objective lenses can have different numerical apertures (*NA*), a value that describes the angles at which light can enter a lens, which is an important consideration when making some kinds of measurements. In the discussion of interference figures later in this chapter, we have assumed that the objective lens being used has an *NA* of 0.85, since this is by far the most common today. (For lenses with a different *NA*, some angular values in the discussion of interference figures later in this chapter will be in error.)

5.27 Microscope eyepieces that contain ocular lenses

Microscope eyepieces contain additional lenses, called oculars, usually providing 8*x* or 10*x* magnification. (The eyepieces shown in Figure 5.27 have 10*x* magnification written on them.) Older microscopes only had one eyepiece but today most are *binocular microscopes* with two eyepieces and two oculars. Oculars have crosshairs that aid in making measurements when we rotate the stage. The total magnification, which is the product of the objective lens magnification and the ocular magnification, varies from about 16*x* to 500*x*, depending on the lenses used.

Petrographic microscopes have other filters and lenses between the objective lens and the ocular (shown and labeled in Figures 5.22, 5.23, and 5.24). The *upper polarizer*, sometimes called the *analyzer*, is a polarizing filter oriented at 90° to the lower polarizer. We can insert or remove it from the path of the light beam. If no sample is on the stage, light that passes through the lower polarizer cannot pass through the upper polarizer. If a sample is on the stage, it usually changes the polarization of the light so that some can pass through the upper polarizer.

5.28 A quartz wedge (A) and two examples of accessory plates (B)

We can also insert a *quartz wedge* or an *accessory plate* above the upper polarizer. (A quartz wedge is exactly what it sounds like – a sliver of quartz that is thicker at one end than at the other.) The most common kind of accessory plate used today is a *full wave plate*. In the past, all full-wave plates were made of gypsum but today they are made of quartz. A wedge or an accessory plate modify light properties for making some specific kinds of observations.

5.4.2 Plane (PP) Polarized Light and Cross Polarized (XP)Light

For routine viewing, petrologists and mineralogists use polarizing microscopes with orthoscopic illumination, and with, or without, the upper polarizer inserted. Without the upper polarizer, we see a sample in *plane polarized light* (PP light); with the upper polarizer, we see it in *crossed polars* (XP light). Grain size, shape, color, cleavage, and other physical properties are best revealed in PP light. The optical properties refractive index and pleochroism are also determined using PP light. We use XP light, sometimes focused with conoscopic and Bertrand lenses, to determine other properties including retardation, optic sign, and *2V*. To see examples of all of these properties and many views of the most common minerals in thin section go to our Optical Mineralogy website. We will discuss mineral properties in XP light later in this chapter. For now, we will concentrate on plane polarized light.

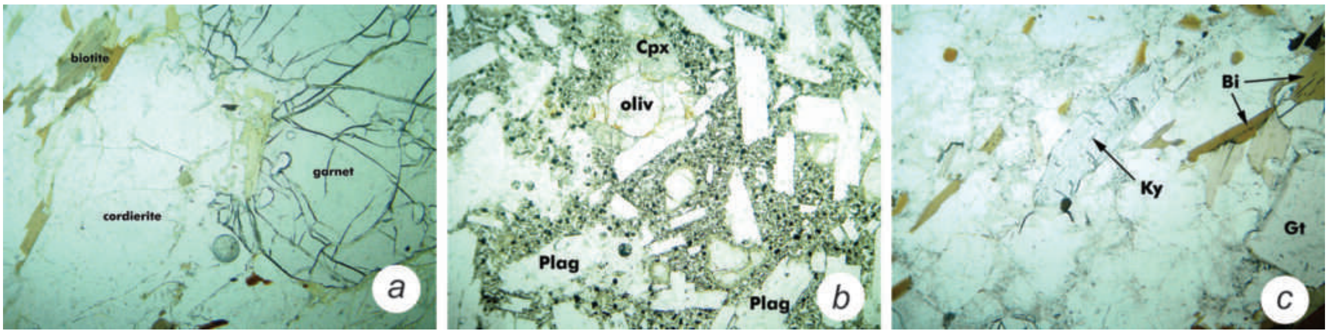
5.4.2.1 Characteristics Seen in Plane Polarized (PP) Light

Opaque and Nonopague Minerals

Opaque minerals, in contrast with nonopaque minerals, do not allow any light to pass through them. So, opaque grains appear black in both PP and XP light, even if we rotate the stage. The most common opaque minerals include graphite, oxides such as magnetite or ilmenite, and sulfides such as pyrite or pyrrhotite. It is sometimes possible (especially if a thin section does not have a cover slip) to remove a slide from the microscope stage, hold it up and turn it around, and reflect light off mineral grains to see the reflected color. A silver color suggests the grains are graphite or oxides and a golden color suggests they are sulfides.

Crystal Shape and Habit

When viewing minerals in PP light, we can pick out different minerals based on their grain shapes and habit. For example, Figure 5.29*a* below shows a large rounded grain of garnet containing many sharp fractures. Figure 5.29*b* contains lathes of clear plagioclase (Plag), an equant grain of olivine (oliv) and an almost rectangular grain of clinopyroxene (Cpx). Figure 5.29*c* has a large blade of light blue kyanite in the center of the view. Both Figures 5.29*a* and *c* contain flakes of brownish biotite (Bi).



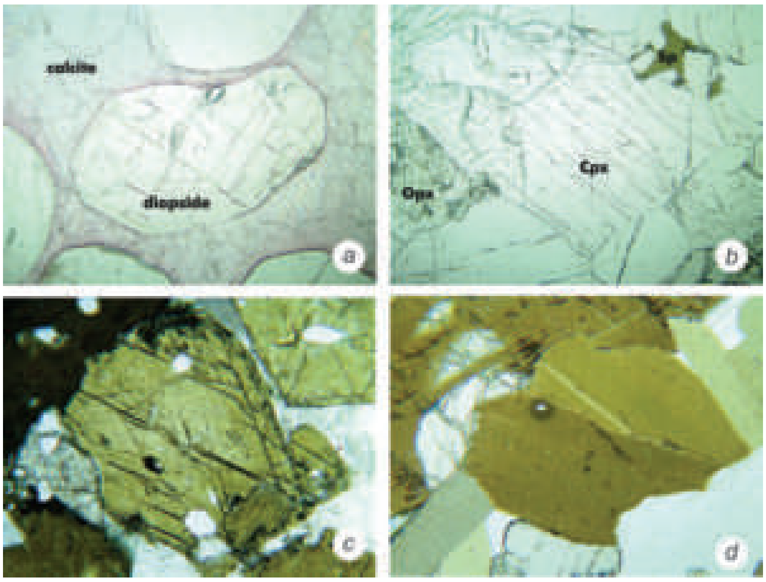
5.29 Mineral habits seen in thin section (PP light)

Cleavage

The garnet, cordierite, and olivine seen in Figure 5.29 show no cleavages (although the garnet does display many fractures). Many minerals, however, exhibit cleavage, usually appearing as straight parallel cracks through a grain. When we can see cleavage with a microscope, it can be an important diagnostic tool. We use qualitative terms such as *perfect*, *good*, *fair*, and *poor* to describe the ease with which a mineral cleaves in different directions. Minerals with one or more good or perfect cleavages show cleavage most of the time, while those with only poor cleavage may not. Additionally, minerals with low relief do not show cleavage as readily as those with high relief. We can overcome this problem sometimes by closing down the substage diaphragm, which narrows the cone of light hitting the thin section and increases contrast.

Minerals may have zero, one, two, three, four, or even more cleavages, but because thin sections provide a view of only one plane through a mineral grain, we rarely see more than three at a time. And minerals that have elongate habits exhibit different cleavage patterns when viewed in a cross section than they do when viewed in a longitudinal section.

When we look at a mineral grain in thin section we are looking in a singular direction through the mineral. But cleavage planes are oriented in three dimensions (3D). So observed cleavage angles depend on grain orientation. If a mineral has two cleavages that intersect at 60°, the cleavages will appear to intersect at any angle from 0° to 60° depending on grain orientation. So we must often examine many grains (or one with a known orientation determined by examining an interference figure) to learn the maximum, and true, 3D cleavage angle.



5.30 Cleavage seen in thin section (PP light)

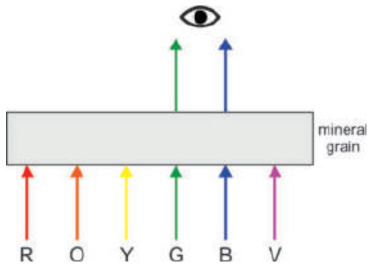
Figure 5.30*a* shows a grain of diopside with two perpendicular cleavages. Figure 5.30*b* shows augite, a pyroxene closely related to diopside, but the grain is at a different orientation and shows only one direction of cleavage. Figure

5.30*c* shows a brown amphibole grain with two cleavages that intersect at about 60° and 120°. If the grain were oriented differently, only one cleavage might be visible. Figure 5.30*d* shows several grains of biotite. The tilted greenish rectangular grain near the lower left corner shows good mica cleavage (cleavage in one direction). The large darker brownish grain that fills most of the view does not because the view is looking down on top of a flake.

Color and Pleochroism

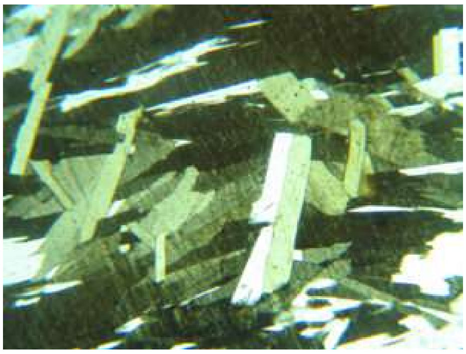
When we talk about the color of a mineral in thin section, we are talking about its color when viewed with PP light, not when viewed with XP light. Many minerals appear colored in hand specimen, and some show color when viewed with a microscope. But it is rare for the reflected color of a hand specimen to have any resemblance to the transmitted color seen in thin section.

The difference is due to several things. Most importantly, when we see color in a hand sample, we are seeing the color of light reflected by the sample. If all colors reflect, the sample appears white. If none reflect, it is black. And if only some wavelengths reflect we see various colors. This is not what happens when we view minerals in thin section.



5.31 Absorption of some colors means that other colors reach our eye

When we see color in thin section (using PP light) we are seeing transmitted colors. These are the colors of light passing through a mineral grain (Figure 5.31). Crystals absorb some wavelengths and transmit others. If all colors are transmitted, we see white. If none are transmitted, we see black. And in other cases we see colors of different hues depending on the mineral’s absorption. But many minerals in thin section are not thick enough to significantly absorb specific wavelengths of light. So minerals in thin section often appear light colored even if the mineral has strong coloration in hand specimen.

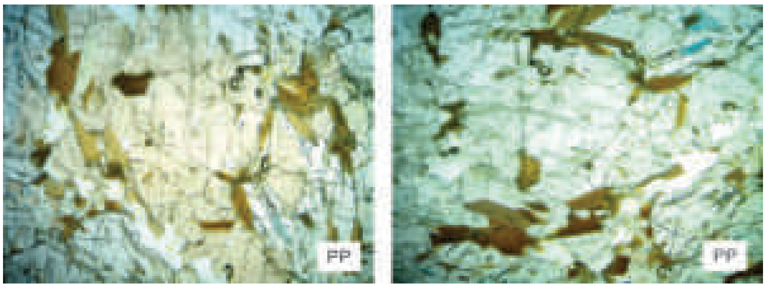


5.32 Thin section view of a rock containing (mostly) biotite, muscovite, and quartz (PP light)

Figure 5.32 shows a mica schist, viewed with PP light. The minerals present include biotite in various shades of greenish brown and tan, clear elongated clear crystals of muscovite and somewhat equant quartz (on the lower right edge). Biotite is generally black when viewed in hand specimen but always is lighter colored in thin section, like the biotite seen here. Different grains of biotite have different colors because they have different atomic orientations with respect to the light vibration direction. In this thin section, the few grains of muscovite (white mica) have the same shape as the biotite (because they are both micas) but show no coloration.

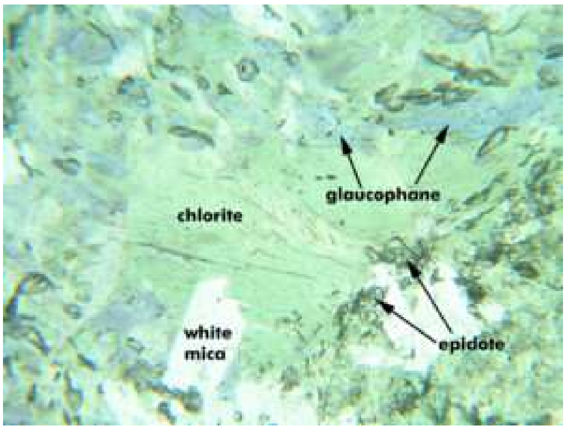
Many minerals absorb different wavelengths of light depending on light vibration direction. So colors we see in thin section generally change when we rotate the microscope stage. This is because rotating the stage changes the orientation of the mineral’s crystal structure with respect to the polarized light passing through the lower polarizer. We call this property (changing colors with stage rotation) *pleochroism*. Biotite is an example of a mineral that normally displays marked pleochroism. If we rotated the sample seen in Figure 5.32, biotite colors would vary between various shades of brown or tan. The exact colors depend on the biotite composition. For a typical grain, color varies between two hues. The range of color, however, depends on grain orientation in the thin section.

▶ Video 2: Explanation of color and pleochroism (3 minutes)



5.33 Two views (differing by 90° stage rotation) of the same grain of orthopyroxene (PP light)

Pleochroism is an especially useful diagnostic property when identifying some minerals, but it can be overlooked because it may be subtle. For example orthopyroxenes are nearly colorless in thin section, but some show a faint pleochroism from (what mineralogists call) pink to green. The photos in Figure 5.33 show the same large grain of orthopyroxene but the orientation of the grain is 90° different in the two views. Light pinkish color can be seen in the photo on the left, and light green color in the photo on the right. Pleochroism of pyroxenes is an important property because it sometimes distinguishes the two major pyroxene subgroups: *orthopyroxenes* and *clinopyroxenes*.



5.34 Glaucophane, epidote, white mica, and chlorite in a blueschist from Panoche Pass, California (PP light)

In contrast with orthopyroxenes, many amphiboles display strong colors and a very noticeable pleochroism in thin section. For minerals, such as amphiboles, that have noticeable pleochroism, reference tables give *pleochroic formulas* that describe the colors seen when looking at grains in different directions through the crystal's atoms. The hornblende in Figure 5.4, for example, is pleochroic in various shades of green. And the biaxial mineral glaucophane (an amphibole shown in Figure 5.34) has pleochroism described by the pleochroic formula:

- X = colorless or pale blue
- Y = lavender-blue or bluish green
- Z = blue, greenish blue, or violet

X, Y, and Z refer to light vibrating parallel to each of three mutually perpendicular vibration directions in a crystal. In thin sections, glaucophane's colors vary within the limits described for X, Y, and Z, depending on the crystal orientation, as we rotate the microscope stage. Figure 5.34 shows blue glaucophane in a rock from Panoche Pass, California. Different grains of glaucophane show different hues due to different grain orientations. Figure 6.88 (Chapter 6) shows a hand sample of glaucophane; it is one of a small number of minerals that have colors in thin section that are quite similar to those seen in hand sample.

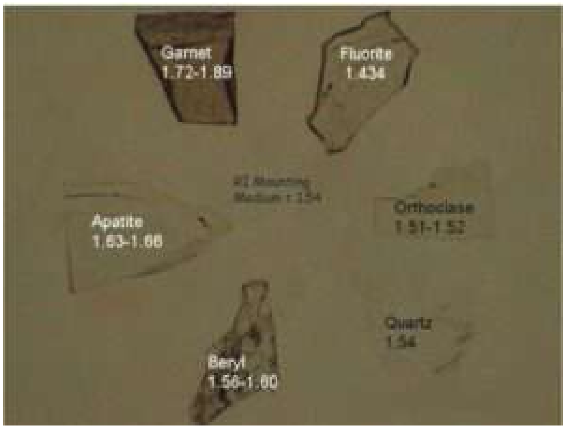
For another example of pleochroism, consider the biotite in Figure 5.32. It is pleochroic in browns, and a standard pleochroic formula for biotite might be:

- X = colorless, light tan, pale greenish brown, or pale green
- Y ≈ Z = brown, olive brown, dark green, or dark red-brown

Relief and Becke Lines

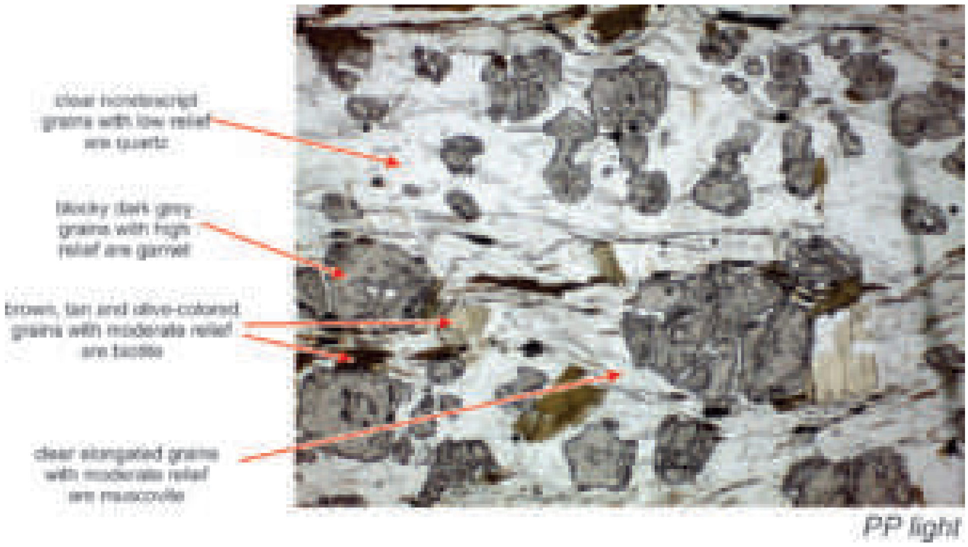
5.35 (A) Garnet showing high relief, and (B) halite showing low relief (PP light)

If epoxy or some other material with significantly different refractive index surrounds mineral grains, the grains will stand out. This is the case for the garnet in epoxy in Figure 5.35*A*. But, if mineral grains are surrounded by material that has a similar refractive index to the mineral, they may be almost invisible unless the mineral is one of the few minerals with very strong coloration. This is the case for the halite grains seen in a grain mount in Figure 5.35*B*. As the difference between the index of the surrounding material and the mineral decreases, the boundary between the two becomes less easily distinguished. The term *relief* describes the contrast between the mineral and its surroundings.



5.36 View of six minerals with different refractive indices (PP light)

In grain mounts, we often look at mineral fragments surrounded by *immersion oil* with a specific refractive index. Figure 5.36 shows how relief changes depending on the difference between refractive index of a mineral and surrounding oil. The oil has refractive index of 1.54, but the minerals mostly do not. The garnet and fluorite both have high relief. The other minerals have variable relief, and the quartz almost disappears because quartz and the surrounding oil have the same refractive index.



5.37 Minerals with high, medium, and low relief in thin section. The field of view is about 2.5 mm across.

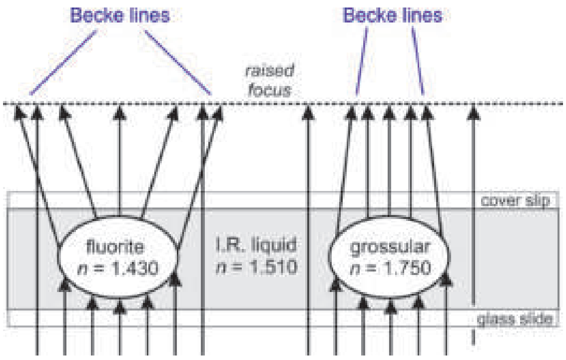
Grains mounts show relief well, but minerals in thin sections also show relief. The relief depends on the difference in the indices of refraction of the mineral and the material (today usually a special type of epoxy) in which it is mounted. Thin section epoxy typically has an index of refraction of 1.54-1.56. As the difference in indices increases, relief becomes more noticeable. We can see relief with either a monocular or a binocular microscope, but more easily with the latter. Some, not all, people see relief in three dimensions when viewing a thin section with a binocular microscope.

Minerals with high refractive indices show high *positive relief* because their index of refraction is greater than that of the epoxy. They also show structural flaws, such as scratches, cracks, or pits, more than those with low refractive indices. The thin section in Figure 5.37 contains very high relief garnet, moderate relief biotite and muscovite, and low relief quartz. A few minerals (such as calcite) display *variable relief* with stage rotation; variable relief is a useful diagnostic property for calcite.

Most minerals that appear to have high relief have high refractive indices. But some minerals (fluorite, for example) with very low refractive indices show high relief (termed *negative relief*) in thin section because their index of refraction is much lower than that of the epoxy. We do not differentiate between positive and negative relief in this book; for most purposes, we need only to know whether a mineral displays high, medium, or low relief – which really means whether it stands out in thin section.

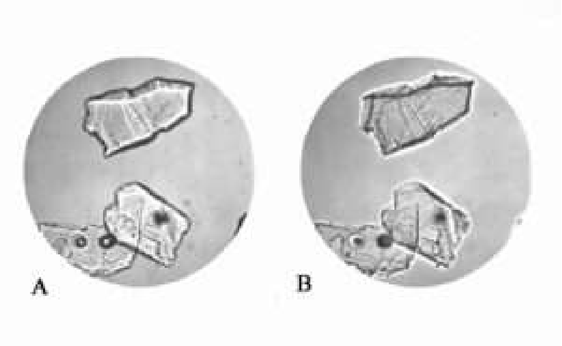
When we immerse a mineral grain in liquid that has refractive index different from the mineral’s, refraction occurs and some light rays bend toward the medium with the higher refractive index. Other light rays are completely reflected because they hit the mineral-liquid interface at an angle greater than the critical angle of refraction. But overall, light interacts with a mineral grain as if the grain were a small lens (Figure

5.38).



5.38 Becke lines of two sorts

If $n_{mineral} < n_{liquid}$, light rays are refracted and diverge after passing through the grain. If $n_{mineral} > n_{liquid}$, light rays are refracted and converge after passing through the grain. If we slowly lower the microscope stage, shifting the focus to a point above the mineral grain, a bright narrow band of light called a *Becke line* appears at the interface and moves toward the material with higher refractive index. A complementary but more difficult to see dark band moves toward the material with lower refractive index.



5.39 In photo A, the oil around the grains has lower refractive index than the grains. In photo B, we have chosen a different oil that has index greater than the grains. In both images we have lowered the stage.

Figure 5.39 shows fragments of a mineral in a refractive index oil significantly different from the mineral. In Figure 5.39*A*, the microscope focus has been raised (the stage has been lowered), and a white line moved into mineral grains that have higher refractive index than surrounding oil. In Figure 5.39*B*, the focus was raised (the stage was lowered) and the white line moved outward into oil that has higher refractive index than the mineral grains.

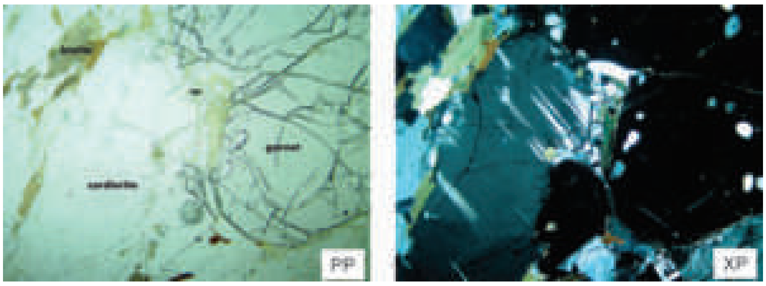
Although not as straightforward, we can also use Becke lines to compare the relief of minerals in thin sections by purposely focusing and defocusing the microscope while we examine a grain boundary. We also compare relief by noting how well a mineral appears to stand out above another.

▶ Video 3: a good video about Becke lines (5 minutes)

5.4.2.2 Characteristics Seen in Cross Polarized (XP) Light

Anisotropic vs Isotropic Minerals

Most minerals are anisotropic. For example, you do not have to look very long at the atomic structures of sheet silicates (Figure 13.30 in Chapter 13) to see that the atom order is different in different directions; they are anisotropic. Because atomic order is not the same in different directions through an anisotropic crystal, refractive index varies with direction. In contrast, a glass, such as window glass or obsidian, is isotropic because it has a random atomic arrangement. Randomness means that, on the average, the structure and refractive index are the same in all directions. Minerals whose crystals belong to the cubic system are isotropic because their atomic arrangement is the same along all crystallographic axes. Minerals belonging to other crystal systems are anisotropic.



5.40 Cordierite-garnet-biotite gneiss in PP and XP light. The view is 3 mm across and the sample comes from just south of Kazabazua, Quebec.

Isotropic minerals are easy to spot in thin sections. When viewed with a polarizing microscope and XP light, they are always extinct, which means they remain black as the stage rotates, no matter what their orientation is on the stage. For example, Figure 5.40 shows PP and XP views of a gneiss containing cordierite and garnet. In the XP view on the right, the garnet is black (isotropic) but the cordierite, which shows stripes due to twinning, is not (anisotropic). There are few common isotropic minerals, but the most common are garnet, sphalerite, and fluorite. Usually we can tell these and the few other isotropic minerals apart by looking at color, relief, habit, and cleavage. Sometimes (poorly made) thin sections contain holes, places with no mineral and only epoxy. The holes appear isotropic and can occasionally be mistaken for isotropic minerals.

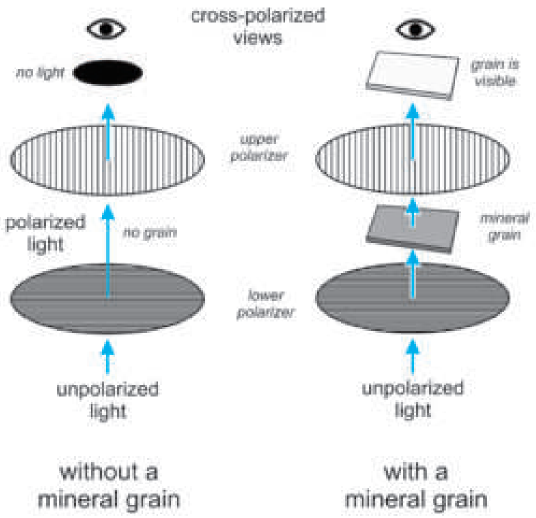
In contrast with isotropic minerals, randomly oriented anisotropic mineral crystals do not normally appear extinct when viewed in XP light. But if we rotate the microscope stage, they go extinct briefly every 90°. There is, however, a complication. If an anisotropic crystal is oriented so that light passes through it parallel to a special direction called an *optic axis*, it will appear to be isotropic. (This occurs when the optic axis is perpendicular to the microscope stage.) In this special orientation the mineral will remain extinct as we rotate the stage.

Fortunately, the number of optic axes in anisotropic minerals is limited to one (in *uniaxial* minerals) or two (in *biaxial* minerals). In thin sections, the odds of the optic axis being vertical and parallel to the light beam are small, and confusing isotropic and anisotropic minerals is rarely a problem. When in doubt, we can distinguish them most easily by looking at multiple grains of the same mineral (they cannot all be oriented with their optic axes perpendicular to the stage). We can also distinguish isotropic from anisotropic crystals using conoscopic illumination because anisotropic minerals transmit some conoscopic light and display interference figures (discussed later), while isotropic minerals do not.

Views Using Crossed Polars

5.41 Two perpendicularly polarizing filters sandwiching a large flake of muscovite

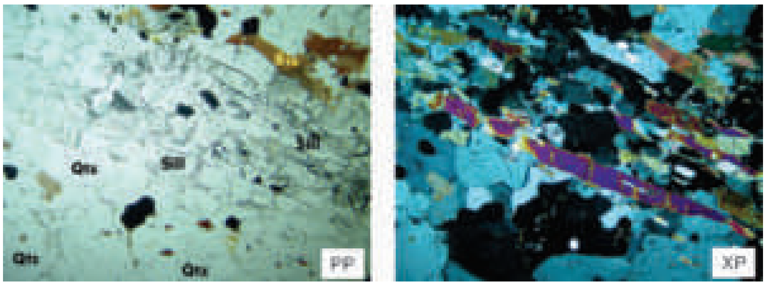
Figure 5.41 shows a ragged flake of muscovite (white mica) with one rectangular polarizing filter below it and another above it. We oriented the filters perpendicularly. So we see black where they overlap and there is no mica. But, where it is present, the mica changes the vibration direction of the light so it can pass through the top polarizer.



5.42 Mineral crystals change light polarization and color

Besides changing direction of polarization, when viewed with XP illumination, crystals also change white light to different colors. These are *interference colors* and, in Figure 5.41, they do not match the color of the mica at all. They appear as various shades of blue, red, orange, and purple. These colors do not result from absorption of different wavelengths by the mineral (which is how minerals get their color when viewed in PP light). Instead, the colors are artifacts of polarized light passing through two polarizers and a crystal. The interference colors in this figure are blotchy and variable because the flaky mica is thicker in some places than in others.

Figure 5.42 shows the origin of the phenomena seen in the previous figure, but with geometry more similar to what happens with a microscope. When no mineral grain is in the path of the light, east-west polarized light encounters a north-south polarizing filter. So, no light is transmitted and only a black color is seen. But, when a flake of mica is present, the grain changes light polarization, so some light gets through the upper polarizer. During this process double refraction occurs (discussed later in this chapter) and the result is interference colors.



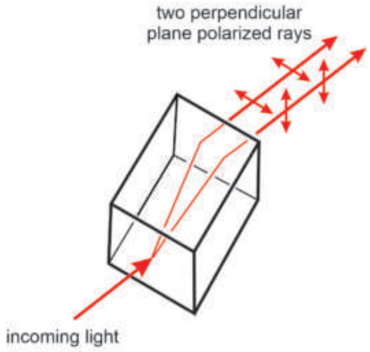
5.43 Sillimanite gneiss from Kazabazua, Quebec

We only see interference colors if we insert the upper polarizer and view a thin section in XP light. For example, the photos in Figure 5.43 show PP and XP views of the same area on a thin section. In the PP view, brown-tan biotite and opaque magnetite (black and unlabeled) are easily seen. But quartz and sillimanite are clear and uncolored.

The XP view in Figure 5.43 is more colorful because it shows interference colors. Interference colors for quartz vary with crystal orientation and would change from white to black if we rotated the microscope stage. Feldspars, and many other minerals have similar white to black interference colors. But most minerals display colors of some sort that may be brighter and more pronounced than colors seen when we view the same mineral in PP light. For example, the long needle of sillimanite in this thin section is clear in PP light. It shows bright purplish-blue colors (that are not completely uniform because the needle is thicker in some places than in other) in XP light. Other grains of sillimanite, which are blocky end-views of needles, show gray or yellow interference colors.

Interference colors are unrelated to the true color of a mineral. And interference colors depend on grain orientation, so different grains of the same mineral in one thin section normally display a range of interference colors. Different minerals display different ranges of interference colors, so color variation is a useful tool for mineral identification. Colors also vary with the thickness of grains, so it is important that thin sections be of uniform thickness. Additionally, the edges of some grains, grains near the edge of a thin section, or grains next to holes in a thin section (places where the sample is thin), may display abnormal interference colors.

Q. What is the Origin of Interference Colors? A. Double Refraction



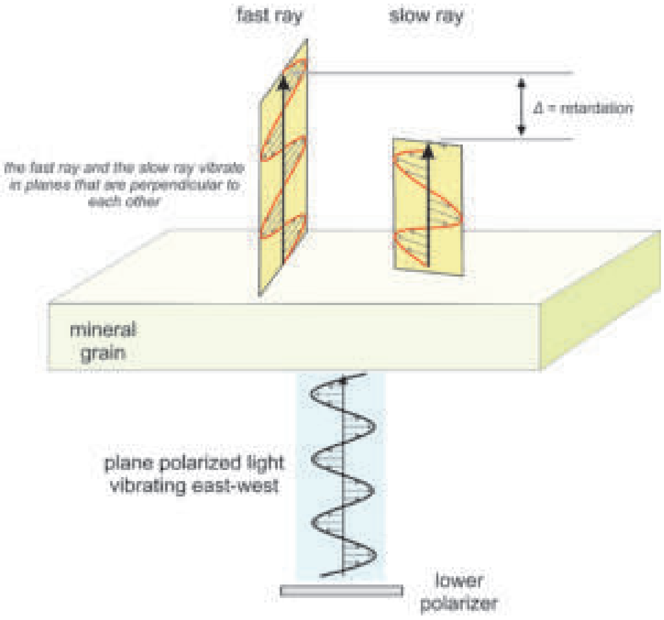
5.44 Double refraction produces two rays that vibrate perpendicularly

When polarized light encounters an isotropic mineral, it slows as it passes through the mineral, but maintains its character when it emerges. Upon entering an anisotropic crystal, however, light is normally split into two polarized rays, each traveling through the crystal along a different path with a slightly different velocity and refractive index (Figure 5.44). For uniaxial minerals, we call the two rays the *ordinary ray* (O ray), symbolized by ω, and the *extraordinary ray* (E ray), symbolized by ε′. The O ray travels a path predicted by Snell’s Law, while the E ray does not. The directions of the O-ray and E-ray vibrations depend on the direction the light is traveling through the crystal structure, but as seen in Figure 5.44 the vibration directions of the two rays are always perpendicular to each other when they emerge from the crystal.

Things are a bit more complicated for biaxial minerals. But, as with uniaxial minerals, a polarized ray encountering a biaxial crystal normally splits into two rays vibrating perpendicularly to each other. One ray emerges from the crystal before the other, so we call the two rays the *fast ray* and the *slow ray*. (We also sometimes use the same terms, fast and slow, for the O ray and the E ray of uniaxial minerals, but sometimes the O ray is the fastest and sometimes the E ray is.)

5.45 Double refraction by calcite causes one line to appear as two

We call the splitting of a light beam into two perpendicularly polarized rays *double refraction*. All randomly oriented anisotropic minerals cause double refraction. We can easily observe it if we place clear calcite over a piece of paper on which a line, dot, or other image has been drawn (as in Figure 5.45). Two images appear, one corresponding to each of the two rays. A thin piece of polarizing film placed over the calcite crystal would verify that the two rays are polarized and vibrating perpendicular to each other. If we rotate either the film or the crystal, every 90° one ray becomes extinct, and we will see only one image. Calcite is one of a few common minerals that exhibits double refraction easily seen without a microscope, but even minerals that exhibit subtler double refraction can be tested using polarizing filters. Gemologists use this technique to tell gems from imitations made of glass. Glass, like all isotropic substances, does not exhibit double refraction.



5.46 Double refraction causes plane polarized light to be split into two rays vibrating at 90° to each other

Consider a thin section and light entering an anisotropic crystal (Figure 5.46). Double refraction occurs, and as the two rays pass through the crystal (uniaxial or biaxial), they travel at different velocities unless they are traveling parallel to an optic axis. Because the rays travel at different velocities, their refractive indices must be different. The difference in the indices of the fast ray and the slow ray ($n_{slow} - n_{fast}$) is the *apparent birefringence* (δ'). It varies depending on the atomic orientation in the crystal and the direction light is traveling. δ' ranges from zero to some maximum value (δ) controlled by the crystal structure. The maximum birefringence (δ) is a diagnostic property of minerals.

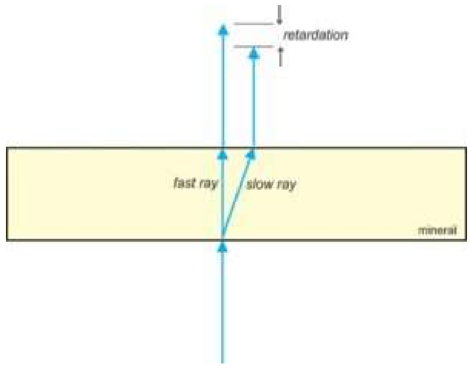
When the slow ray emerges from an anisotropic crystal, the fast ray has already emerged and traveled some distance. This distance is the *retardation* (Δ), labeled in Figure 5.46. Retardation is proportional to both the thickness (t) of the crystal and to the birefringence in the direction the light is traveling (δ'):

$$\Delta = t \times \delta' = t \times (n_{slow} - n_{fast})$$

Most anisotropic minerals have birefringence between 0.01 and 0.20. The birefringence and retardation of isotropic crystals are always zero. No double refraction occurs, and all light passes through isotropic crystals with the same velocity because the refractive index is equal in all directions.

Crystals Between Crossed Polars

As pointed out previously, when viewing with the upper polarizer in place – under crossed polar (XP) light – we can differentiate isotropic and anisotropic crystals. If we are looking at an isotropic crystal using XP light, it will remain extinct (dark) through 360° of stage rotation. This is because the light emerging from the mineral retains the polarization it had on entering and will always be east-west polarized. It cannot pass through the upper polarizer, oriented at 90° to the lower polarizer. The effect is the same as if no mineral were on the stage.



5.47 Retardation is the distance that the slow

ray lags behind the
fast ray

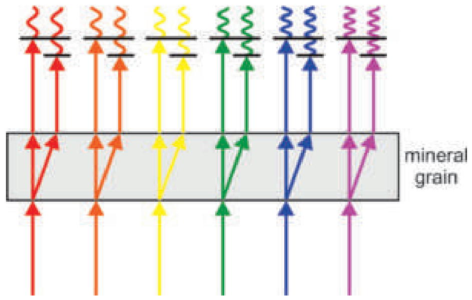
But when we view an anisotropic crystal with XP light, light is split into two rays – a fast ray and a slow ray – unless we are looking down an optic axis (Figure 5.47). The two rays, after emerging from the crystal, travel on to the upper polarizer where they are resolved into one ray with north-south polarization. Because the vibration directions of the fast and slow rays are normally not perpendicular to the upper polarizer, only some components of both pass through the upper polarizer and combine to produce the light reaching our eye. As we rotate the microscope stage, however, the relative intensities of the two rays emerging from the crystal vary. Every 90°, the intensity of one is zero, and the other is vibrating perpendicular to the upper polarizer. Consequently, no light passes through the upper polarizer and the crystal appears extinct every 90°.

If we used a monochromatic light (one wavelength) source in our microscope and looked at an anisotropic crystal under XP light, it would go from light to complete darkness as we rotate the stage. Extinction would occur every 90°, and maximum brightness would be at 45° to the extinction positions. However, most polarizing microscopes use polychromatic light. Because of dispersion, double refraction is slightly different for different wavelengths. Minerals with high dispersion may never appear completely dark, but most come close.

▶ Video 4: Explanation of double refraction with animation (2 minutes)

▶ Video 5: What Happens at the Upper Polarizer? (3 minutes)

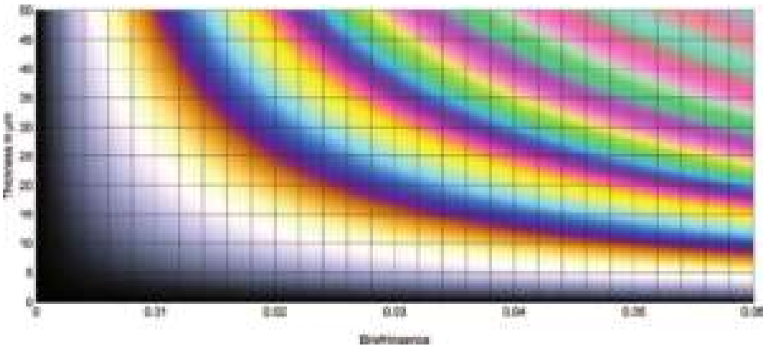
Interference Colors



5.48 After double refraction, some light waves for different colors may be in phase; others may be out of phase

When white light passes through an anisotropic mineral, all wavelengths are split into two polarized rays vibrating perpendicularly. The slow ray lags behind the fast ray by a distance equivalent to the retardation. Different colors have different wavelengths, so when the rays leave the crystal, the fast and slow rays for any color may be in phase, completely out of phase or somewhere between depending on the retardation compared with wavelength (Figure 5.48). The waves will not initially interfere because they are vibrating in perpendicular directions and are not following the same paths. But when the north-south components of the two rays are combined at the upper polarizer (where the filter constrains them to vibrate north-south), constructive interference occurs for some colors, and destructive interference for others. Most wavelengths will not be completely in phase or out of phase, so some intermediate amount of interference will occur.

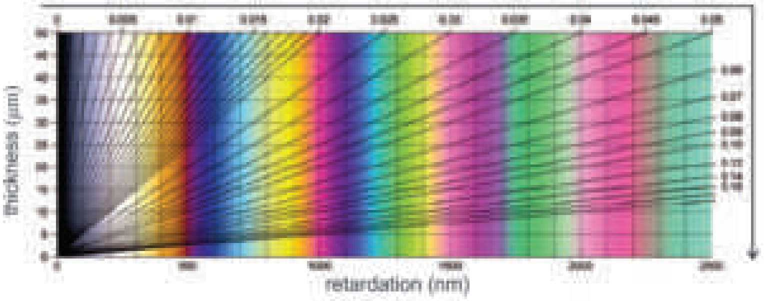
When we look at a mineral under XP light, we see one color. It is mostly a combination of those wavelengths that are in phase or partially in phase, and is missing wavelengths that are out of phase or mostly out of phase. Interference colors depend on the retardation of different wavelengths, which in turn depends on the orientation, birefringence, and thickness of a crystal. Interference colors change intensity and hue as we rotate the stage; they disappear every 90°, when the mineral goes extinct.



5.49 A Raith–Sørensen chart showing interference colors as a function of birefringence and mineral thickness

Retardation, and thus interference colors, vary with mineral birefringence and thickness. The *Raith–Sørensen chart* seen in Figure 5.49 shows the relationships. Retardation increases diagonally from zero in the bottom left corner to about 3,000 nm in the upper right corner.

Interference colors vary in hue and intensity with stage rotation, but this chart shows "maximum" interference colors that we may see halfway between extinctions. Grains that are very thin or that have very low birefringence display up to white interference colors. Those that are thicker and have greater birefringence display other colors. Overall, the colors become less pronounced as retardation increases.



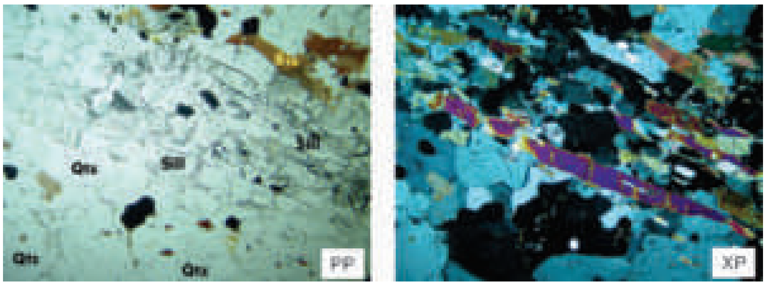
5.50 A Michel-Lévy color chart showing interference colors for different values of retardation

Figure 5.50 shows the same information as the previous figure but the axes have been changed. This kind of chart, called a *Michel-Lévy Color Chart*, is more commonly used by mineralogists than the Raith–Sørensen chart above. In a Michel-Lévy chart, the horizontal axis is retardation; it directly correlates with interference color (shown as vertical color swatches). The vertical axis is grain thickness. The diagonal lines and numbers on the top and right side of the chart show birefringence.

Very low-order interference colors, corresponding to a retardation of less than 200 nm, are gray and white. If retardation is slightly greater, yellow, orange, or red interference colors will appear when we rotate the stage. These colors, corresponding to retardation of 200 nm to 550 nm, are called *first-order colors*. As retardation increases further, we see blue, and then colors repeat every 550 nm, the average wavelength of white light. This is because it does not matter if a wave is 1 wavelength, 2, or 3, behind another – it will still be in phase. And the same holds true for out-of-phase waves – it does not matter if they differ by 1.5, 2.5, etc., wavelengths, they are still out of phase.

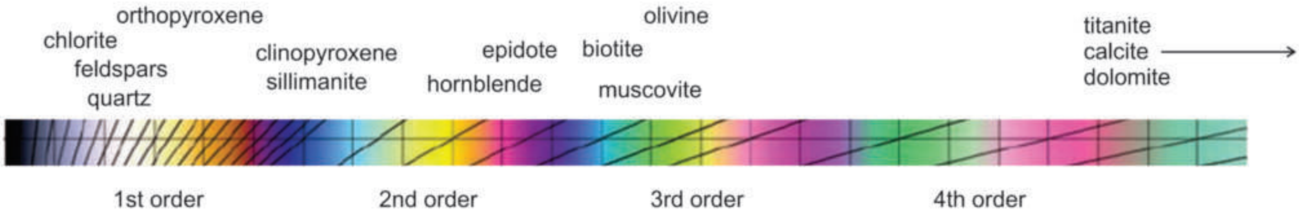
Colors go from violet to red (*second order*) and then from violet to red again (*third order*). They become more pastel (washed out) in appearance as order increases. Fourth-order colors are often so weak that they appear “pearl” white (because they have a play of color like pearls) and may occasionally be confused with first-order white. So, when describing an interference color, stating both the color and the order is important. For mineral identification, the order is often more important than the color.

Birefringence can be a good tool for mineral identification. Standard thin sections are 30 µm (0.03 mm) thick but sometimes thin sections are poorly made, and often grains are thinner around their edges than in their centers. This chart reminds us that retardation, and thus interference colors, are a product of both thickness and birefringence. Additionally, birefringence depends on mineral orientation. If a mineral is oriented with an optic axis vertical, its birefringence will be zero. And if the optic axis is close to vertical, birefringence may be much less than the maximum it could be. Consequently, when estimating birefringence from interference colors seen in thin section, we must look at multiple grains of the same mineral to make sure we know what the maximum birefringence is.



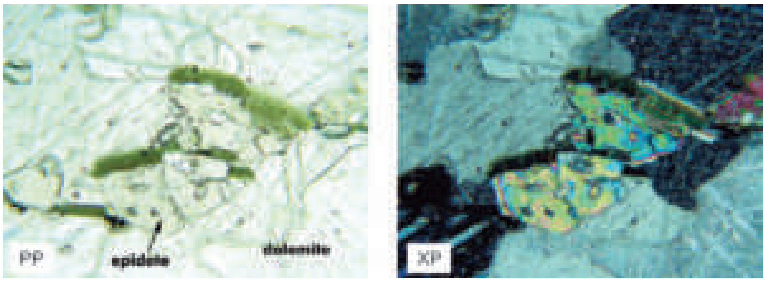
5.51 PP and XP views of a sillimanite gneiss from near Kazabazua, Quebec

Figure 5.51 shows PP and XP views of a thin section we saw earlier in this chapter. The rock contains mostly quartz, sillimanite and biotite. A few grains of opaque magnetite (black and unlabeled) are apparent in the PP view. Quartz has birefringence of about 0.01, biotite and sillimanite have greater birefringence. So the quartz shows only white and gray interference colors; the other minerals display bright blues, violets, yellows, and other hues.



5.52 Maximum interference colors for some common minerals

Figure 5.52, a slice through the Michel-Lévy chart in Figure 5.50, shows normal interference colors for some common minerals. If thin sections are of uniform thickness (30 μm) and minerals have normal compositions, these are the maximum interference colors that will be seen. Many complicating factors, including how well a thin section was made and the nature of the substage light source, can cause aberrations. Note that some relatively common minerals (titanite, calcite, and dolomite) plot way off-scale to the right on this diagram.



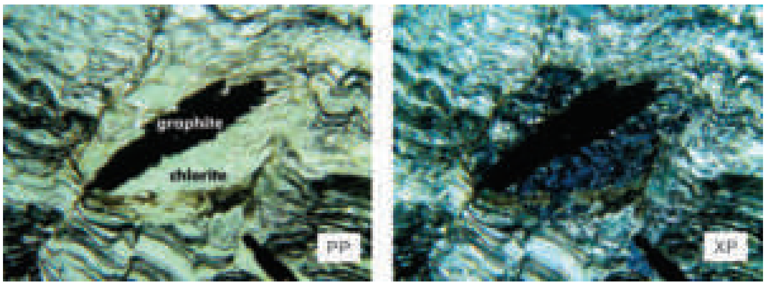
5.53 PP and XP views of a marble from Essex County, New Jersey

Minerals with very low birefringence that display first-order white, gray, or yellow interference colors include quartz, leucite, nepheline, apatite, beryl, and feldspar. Biotite and sillimanite have intermediate birefringence and display third order colors. But, birefringence can be much greater.

The epidote seen in Figure 5.53 (XP view) shows blotchy 2nd and 3rd order colors. Most of this specimen, however is dolomite. Dolomite has birefringence of about 0.2, which means its interference colors are off the chart – they are very high-order pearly pastels that appear almost white. Minerals including dolomite, titanite (sphene), and calcite have very high birefringence. So they commonly show such weak colors that it is impossible estimate retardation and birefringence with any certainty.

Anisotropic minerals have different refractive indices that vary depending on the path light travels when passing through them. Their optical properties, including birefringence, and thus interference colors, depend on their orientation. For identification purposes, the maximum birefringence (δ), corresponding to the highest-order interference colors, is diagnostic. This may be hard to estimate in grain mounts because mineral thickness varies, making it difficult or impossible to estimate birefringence from interference colors. In thin sections, the task is easier because thickness is known (30 µm) so we can use the Michel-Lévy Chart to determine birefringence from interference color.

Randomly oriented mineral grains may not show maximum interference colors. If minerals are oriented with an optic axis close to vertical, their birefringence may be much less than the maximum it could be. If the optic axis is vertical, the grain will appear extinct. Consequently, when estimating birefringence from interference colors seen in thin section, we must look at multiple grains of the same mineral to make sure we know what the maximum birefringence is. Because we cannot be exact, we normally use qualitative terms such as “low,” “moderate,” “high,” or “extreme” to describe retardation and birefringence.



5.54 PP and XP views of a phyllite from Poughkeepsie, New York

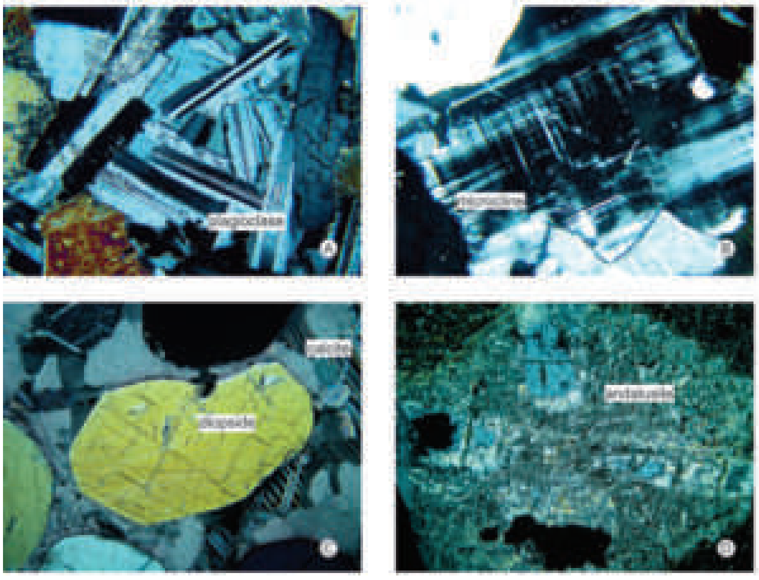
Some minerals display *anomalous interference colors*. These are colors not represented on the Michel-Lévy Color Chart. Anomalous interference colors may result if minerals have highly abnormal dispersion, if they are deeply colored, or for several other reasons. Minerals that commonly display anomalous inference colors include chlorite, epidote, zoisite, jadeite, tourmaline, and sodic amphiboles. Figure 5.54 shows a phyllite collected from near the Hudson River in Poughkeepsie, New York. In the PP view, chlorite appears drab and green, but in the XP view it displays inky blue interference color. Inky blue color, although not on the Michel-Lévy Chart, is often a key to identifying chlorite in thin section. Some chlorite, however, shows interference colors in other hues.

▶ Video 6: Examples of low, medium, and high-order interference colors in thin section (3 minutes)

▶ Video 7 summarizes fundamental information about interference colors (5 minutes)

Twinning, Zoning, and Undulatory Extinction

Many minerals twin, and sometimes we can see the twins with a microscope. The dolomite in Figure 5.53, for example, shows stripes due to twinning in both the PP and the XP view. But normally we only see twinning when we cross the polars. Twins show in XP light because different twin domains have different crystallographic orientations. So the domains do not go extinct simultaneously when we rotate the microscope stage.



5.55 Examples of twinning in thin section

Figure 5.55 shows more examples of twinning. These are XP views of plagioclase, microcline, diopside, calcite, and andalusite. The plagioclase and diopside have lamellar twins (parallel with a long direction) and sharp twin boundaries (although the twins in the diopside are hard to see because they are so thin.) These are examples of *contact twins*. The calcite, microcline and andalusite grains contain *penetration twins* that cut across each other.

Twinning is often an excellent way to distinguish different minerals in thin section. Sometimes we describe plagioclase twinning (Figure 5.55*a*) as *zebra stripes*, for obvious reasons. The microcline (Figure 5.55*b*) shows two types of lamellar twins with different orientations. They combine to produce what we call *microcline twinning* or *Scotch plaid twinning*. Orthoclase (not shown) often contains simple contact twins. Calcite (Figure 5.55*c*) is characterized by polysynthetic twins parallel to the long diagonal of its rhombohedral shape. Other carbonates have no twins or have twins parallel to the short diagonal. The andalusite seen above (Figure 5.55*d*) contains a cross made by two twin domains – few minerals twin this way. Thus, for the feldspars, the carbonates, and for some other minerals, twinning can be a key to identification.

5.56 A zoned and twinned plagioclase crystal in a rhyolite

Some mineral grains, most notably those that crystallize from magma over a range of temperature, are heterogeneous. So different parts of grains have different optical properties, producing *compositional zonation*, commonly just called *zoning*. Feldspars and other minerals that commonly twin, often show zoning. Figure 5.56 is an example – a zoned plagioclase in rhyolite. The zoning appears as concentric rings that parallel the outside of the crystal, somewhat like tree rings. The rings developed as the grain crystalized from melt. Subsequently the mineral twinned, producing the long lathes parallel to the grain's long dimensions. Many other minerals, besides plagioclase, can show zoning in thin section.

5.57 Quartz in thin section displaying undulatory extinction

Quartz and some feldspars are known for displaying *undulatory extinction* when viewed under XP light. This kind of extinction is sometimes confused with compositional zonation. When a grain shows undulatory extinction, it means that different parts of a crystal go to extinction at different times with stage rotation. This gives an overall patchy or blotchy appearance. This property derives from strain imposed on a crystal after it formed. Undulatory extinction is so common in quartz that it is considered a diagnostic property. Figure 5.57 shows several large quartz grains. Portions of each are at extinction but most of the grains are not.

▶️ Video 8: twinning and zoning with some great photos (4 minutes)

5.5 More About Uniaxial and Biaxial

Minerals

[In the discussion below, references are made to crystal systems and to crystallographic axes. But we do not talk about them in detail until later in this book. The interested reader will come back and read this section after having read Chapter 11.]

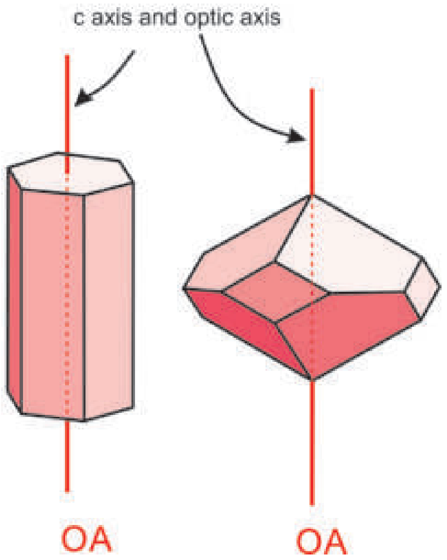
As described earlier in this chapter, if a crystal is oriented so that the optic axis is perpendicular to the microscope stage, light passing through the crystal travels parallel to the optic axis and behaves as if the crystal were isotropic. There is no double refraction and the polarization direction of the light is not changed by interaction with the crystal. If we view the crystal with the upper polarizer inserted (XP light) the grain will remain extinct even if we rotate the stage.

Most crystals in thin section, however, will not have optic axis vertical and we will see optical properties that relate to the crystal system of the mineral. For example, all minerals that have crystals belonging to the cubic crystal system are isotropic. They have the same light velocity and therefore the same refractive index (*n*) in all directions. The table below compares optical parameters and properties for isotropic, uniaxial, and biaxial minerals. Isotropic crystals have a single index of refraction (*n*) and their birefringence is zero.

Indices of Refraction and Birefringence in Isotropic and Anisotropic Crystals

	principle indices of refraction	**index of refraction parallel to an optic axis**	**indices of refraction in a random direction**	**birefringence in a random direction**	**maximum possible birefringence**

isotropic crystals	n	n	n	0	0
uniaxial crystals	ω, ε	ω	ω, ε'	$\delta' = \lvert\omega - \varepsilon'\rvert$	$\delta = \lvert\omega - \varepsilon\rvert$
biaxial crystals	α, β, γ	β	α', γ'	$\delta' = \lvert\gamma' - \alpha'\rvert$	$\delta = \lvert\gamma - \alpha\rvert$

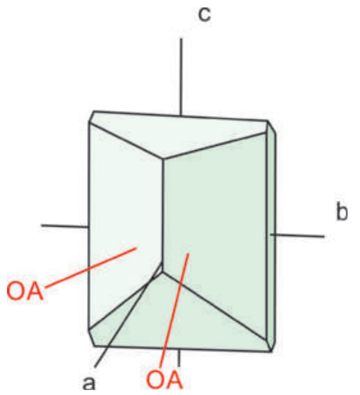


5.58 Hexagonal and tetragonal uniaxial crystals

All minerals with crystals that belong to the tetragonal or hexagonal crystal systems are uniaxial, meaning that they have only one optic axis. In these crystals, the optic axis is coincident with the c crystallographic axis (Figure 5.58), and in many uniaxial minerals, the optic axis is parallel or perpendicular to crystal faces. In uniaxial crystals, refractive index varies between two limiting values, that we designate epsilon (ε) and omega (ω). The maximum value of birefringence in uniaxial crystals is the absolute value of the difference between ω and ε (see the table above): $\delta = |\omega - \varepsilon|$. We can only see maximum birefringence (which corresponds with maximum retardation) if the optic axis is parallel to the microscope stage.

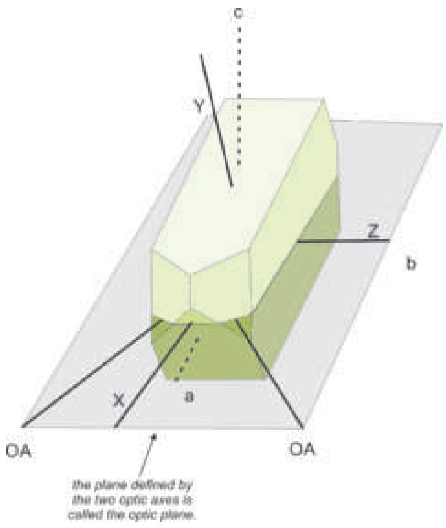
Light traveling parallel to the single optic axis of a uniaxial mineral travels as an ordinary ray and has refractive index *ω*. Light traveling perpendicular to the optic axis has refracted index *ε*. Unless traveling parallel to the optic axis, light is doubly refracted, splitting into two rays with one having refractive index *ω*. The other ray has refractive index *ε′*, which varies depending on the direction of travel. ε′ may have any value between *ω* and *ε*.

We divide uniaxial minerals into two classes: if $\omega < \varepsilon$, the mineral is uniaxial positive (+). If $\omega > \varepsilon$, the mineral is uniaxial negative (-). We can use the mnemonic *POLE* (positive = omega less than epsilon) and *NOME* (negative = omega more than epsilon) to remember these relationships. Positive minerals are often described as having a positive optic sign; negative minerals have a negative optic sign.



5.59 A biaxial crystal

Biaxial minerals include all minerals that have crystals belonging to the orthorhombic, monoclinic, or triclinic systems. Biaxial crystals, such as the one shown in Figure 5.59, have two optic axes, and the axes are not coincident with crystallographic axes (a, b, or c). Like uniaxial crystals, biaxial crystals have refractive indices that vary between two limiting values. But, unlike uniaxial minerals, both limiting values change with changes in crystal orientation relative to the light source.



the plane defined by the two optic axes is called the optic plane.

5.60 An orthoclase crystal with crystallographic (a, b, c) and optical (X, Y, Z) axes labeled

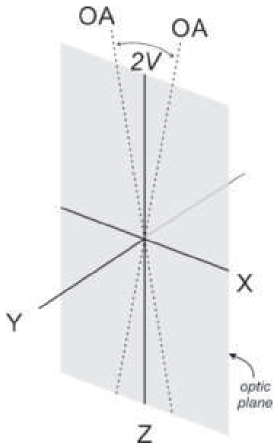
As with uniaxial crystals, light passing through a biaxial crystal experiences double refraction unless it travels parallel to an optic axis. We describe the optical properties of biaxial minerals in terms of three mutually perpendicular directions: X, Y, and Z (Figure 5.60).

The vibration direction of the fastest possible ray is designated X, and that of the slowest is designated Z. The indices of refraction for light vibrating parallel to X, Y, and Z are α, β, γ. α is therefore the lowest refractive index, and γ is the highest. β, having an intermediate value, is the refractive index of light vibrating perpendicular to an optic axis.

We divide biaxial minerals into two classes based on their refractive indices. In biaxial positive minerals, the intermediate refractive index β is closer in value to α than to γ. In biaxial negative minerals, it is closer in value to γ. Retardation and apparent birefringence vary with the direction light travels through a biaxial crystal, but the maximum value of birefringence (δ) in biaxial crystals is always $\gamma - \alpha$. See the table above for descriptions of other parameters.

In orthorhombic crystals the optical directions X, Y, and Z correspond to crystal axes (a, b or c). But, it is not a one-to-one correspondence because the X direction can be either a, b, or c. The same holds for Y and Z. In monoclinic crystals either X, Y, or Z are the same as the b axis. For example, Figure 5.60 shows a monoclinic orthoclase crystal where z is equivalent to b. The other two optical directions do not correspond to crystal axes – but in many monoclinic crystals are close. In triclinic crystals there is no correspondence between optical axes and crystallographic axes.

Normally, light passing through a randomly oriented biaxial crystal is split into two rays, neither of which is constrained to vibrate parallel to X, Y, or Z, so their refractive indices will be some values between α and γ. However, if the light is traveling parallel to Y, the two rays have refractive indices equal to α and γ, vibrate parallel to X and Z, and the crystal will display maximum retardation. If the light travels parallel to an optic axis, no double refraction occurs, and it has a single refractive index, β. There is no birefringence or retardation and the mineral appears extinct.



5.61 The optic plane and *2V* in a biaxial mineral

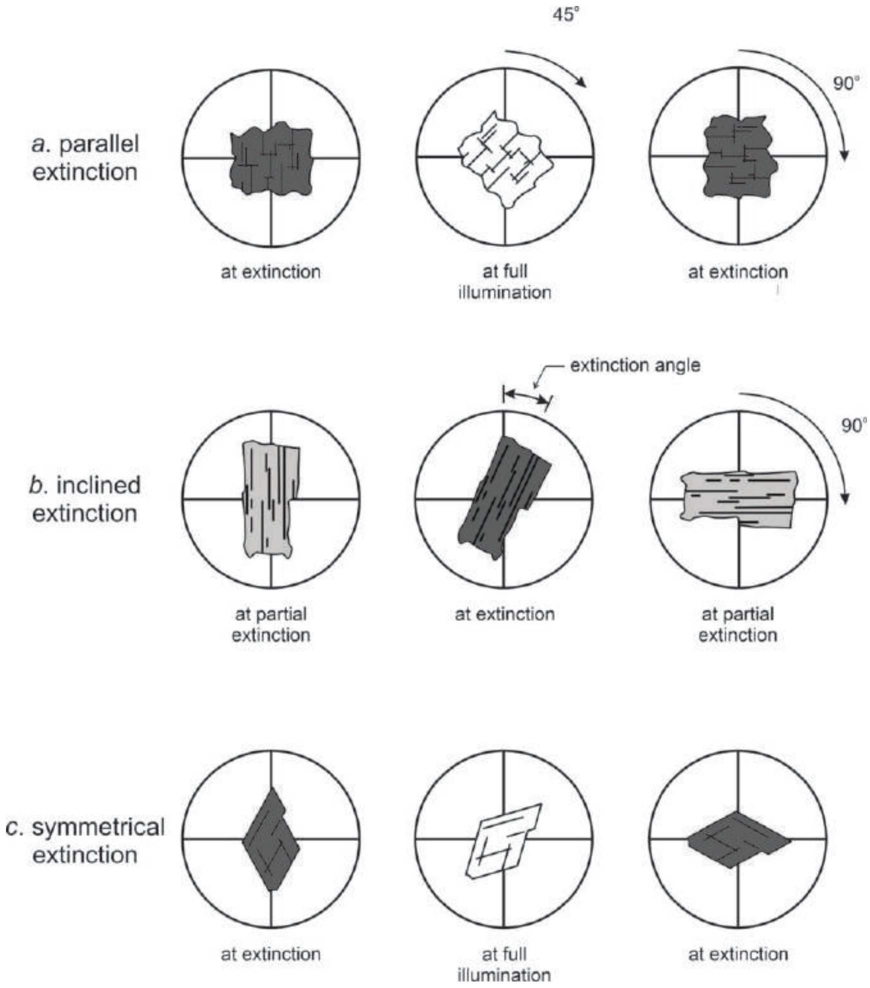
In biaxial minerals, we call the plane that contains X, Z, and the two optic axes the *optic plane* (Figures 5.60 and 5.61). The acute angle between the optic axes is *2V*. A line bisecting the acute angle must parallel either Z (in biaxial positive crystals) or X (in biaxial negative crystals). We can measure *2V* with a petrographic microscope and it can be an important diagnostic property. The feldspar in Figure 5.60 is biaxial negative but the drawing in Figure 5.61 is for a positive crystal.

5.5.1 Accessory Plates and Extinction Angles

We use accessory plates to make some measurements. When inserted, the slow and fast vibration directions of the plate are at 45° to the lower and upper polarizers. A double-headed arrow on accessory plates usually marks the slow direction. A standard full-wave plate has a retardation of 550 nm (equal to the average wavelength or visible light), equivalent to first-order red interference colors. A quartz wedge is sometimes a useful alternative to a full-wave plate. The wedge has a variable thickness, with retardation ranging from 0 nm to 3,500 nm. By inserting a plate or quartz wedge we add or subtract to the retardation of mineral grains.

Accessory plates make it possible to learn which vibration direction in a crystal permits polarized light to travel the fastest. If crystals have a long dimension, we can learn whether the mineral is *length fast* (also sometimes called *negative elongation*) or *length slow* (*positive elongation*). Determining the sign of elongation is often straightforward and can be helpful for identifying minerals.

Viewed with crossed polars, anisotropic grains go extinct every 90° as we rotate the microscope stage. We can measure the extinction angle, the angle between a principal cleavage or direction of elongation (if the grain has a long dimension) and extinction by rotating the stage and using the angular scale around the stage perimeter.



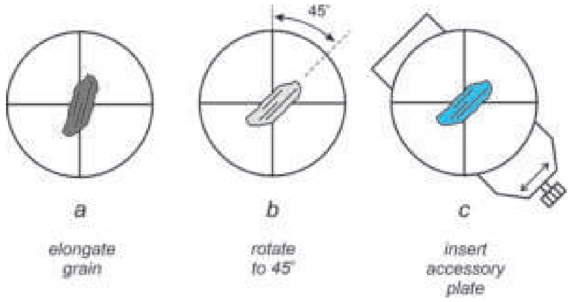
5.62 Different kinds of extinction

Some hexagonal, tetragonal, and orthorhombic minerals exhibit *parallel extinction*; they go extinct when their cleavages or directions of elongation are parallel to the upper or lower polarizer (Figure 5.62*a*). Many monoclinic and all triclinic crystals exhibit *inclined extinction* (Figure 5.62*b*) and go extinct when their cleavages or directions of elongation are at angles to the upper and lower polarizer. Some minerals exhibit *symmetrical extinction*; they go extinct at angles symmetrical with respect to cleavages or crystal faces (Figure 5.62*c*). These different kinds of extinction result from different kinds of atomic arrangements and so are diagnostic for mineral identification.

For any given mineral, the extinction angle seen in thin section depends on grain orientation. (This is because the apparent angle at which planes intersect depends on the direction of viewing.) But there is always some maximum value for any mineral. To determine this maximum value requires measurements on multiple grains, or on one grain in the correct orientation (determined by looking at interference figures, discussed later). If the grains are randomly oriented in a thin section and if the sample size is large enough, determining the maximum value is straightforward although, perhaps, a bit tedious.

5.5.2 Accessory Plates and the Sign of Elongation

Some anisotropic crystals have a prismatic or elongate habit, or a well-developed cleavage, that causes them to occur in elongated grains. Polarized light passing through a crystal with polarization parallel to the long dimension will not travel at the same velocity as light polarized in other directions. This distinction allows the minerals to be assigned a *sign of elongation*: *length fast* (faster light vibrates parallel to the long dimension) and *length slow* (slower light vibrates parallel to the long dimension). We cannot measure a sign of elongation for crystals that crystallize or cleave to produce equidimensional grains.



5.63 Determining the sign of elongation

Determining the sign of elongation (length fast or length slow) is usually straightforward for tetragonal and hexagonal prismatic crystals (all of which are uniaxial) and some orthorhombic crystals. We orient the long dimension of a grain in a southwest-northeast direction (45° to the polarizers) and note the interference colors (Figure 5.63). We then insert a full-wave accessory plate (having a retardation of 550 nm, equivalent to first-order red interference colors).

After insertion, the slow direction of most accessory plates will be oriented southwest-northeast. If the retardation of the accessory plates adds to the retardation of the grain, we get higher order interference colors, and the grain must be length slow. If retardation decreases, and we get lower-order colors, the grain must be length fast. Many minerals, especially if grains are small, exhibit low first-order interference colors (grays). If gray interference colors are added to first-order red, first-order blue results (Figure 5.63*c*). If gray interference colors are subtracted from first-order red, first-order yellow results. So, addition or subtraction is often just a matter of looking for blue or yellow. If we see blue or other higher-order interference colors when we insert the plate, the mineral is length slow (as in Figure 5.63*c*). If we see yellow or other lower-order colors, it is length fast.

If the interference colors for a mineral grain are not mostly gray, determining addition or subtraction may not be quite so simple. Sometimes we must rotate the stage to see the colors that appear when the mineral is oriented northwest-southeast. The effects in that orientation will be opposite to those seen when the mineral is oriented southwest-northeast. When oriented northwest-southeast, higher-order colors correspond to length fast, lower-order to length slow. A quartz wedge can be useful in determining the sign of elongation if a grain contains several color bands rather than just gray. If we insert the wedge in the accessory slot, the color bands on a southwest-northeast-oriented grain will move toward the thicker portions of the grain (usually the center of the grain) if the retardation is being subtracted (length fast). If the bands move away from the thicker portions of the grain, the retardation is being added (length slow).

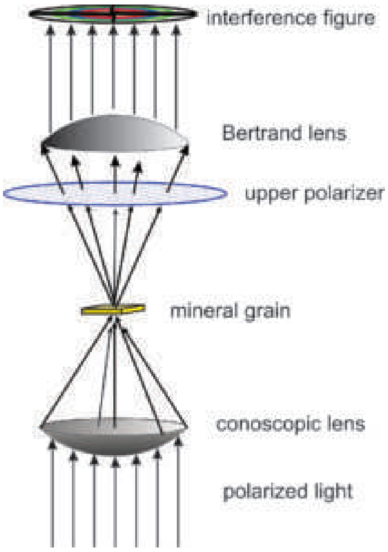
Determining the sign of elongation for an orthorhombic, monoclinic, or triclinic mineral can be problematic or impossible. We can sometimes determine it for orthorhombic or monoclinic minerals with parallel extinctions, but it may vary with the orientation of the mineral. Mineral identification tables commonly list whether a given mineral is likely to provide a sign of elongation and whether the sign may vary with the mineral’s orientation. If the extinction angle of the monoclinic or triclinic grain is only a few degrees, we can often determine a sign of elongation. If they have inclined extinction, we often cannot make the determination because the sign may vary in a complicated way with the orientation of the grain, and because determining the orientation of the grain on the microscope stage is difficult.

5.6 Interference Figures

To determine whether an anisotropic mineral is uniaxial or biaxial, and whether it is optically positive or negative, requires obtaining an interference figure. Measuring *2V*, for biaxial minerals, also requires an interference figure. We obtain these figures using a conoscopic lens below the microscope stage, and a Bertrand lens above the upper polarizer, when looking at a grain with XP light. Figure 5.23 shows this arrangement.

Any uniaxial or biaxial mineral (whether in a grain mount or a thin section) will, in principle, produce a visible interference figure; isotropic minerals will not. We must take care to choose grains without cracks or other flaws so light can pass through without disruption. In addition, for some purposes, we need grains with a specific orientation.

Having chosen an appropriate grain, obtaining an interference figure is relatively straightforward. We focus the microscope using PP light and high magnification. (If perfect focus is ambiguous, it often helps to focus first at low magnification.) Then we insert the upper polarizer to get XP light. If the microscope is properly aligned, the grain will still be in focus. Next, we fully open the substage diaphragm, insert the substage conoscopic lens (if it is not already in place), and then insert the Bertrand lens above the upper polarizer.

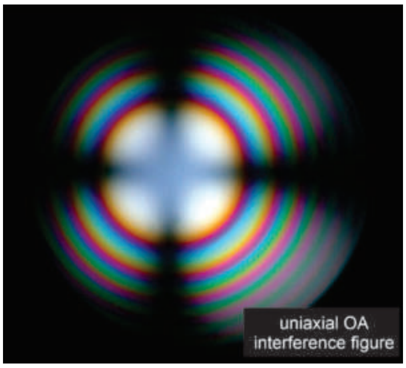


5.64 Conoscopic light and interference figures

As seen in Figure 5.64, the conoscopic lens focuses polarized light so it enters a mineral grain from many different angles simultaneously and focuses on a small area. Double refraction occurs for all rays and different wavelengths have different retardations. At the upper polarizer, slow rays and fast rays combine to produce interference colors. And above that polarizer, the Bertrand lens focuses the light so it is parallel again. The Bertrand lens also magnifies the image.

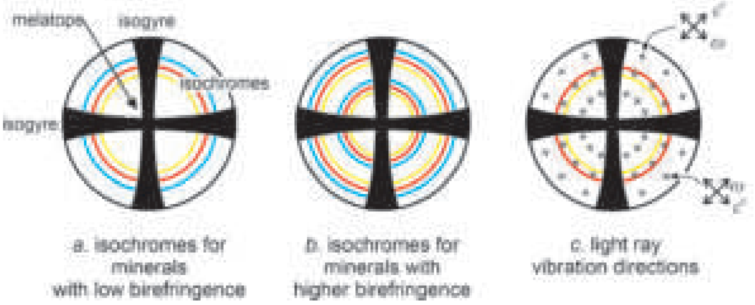
So, the two special lenses together permit us to see an interference figure and examine light traveling through a crystal by many paths in a single view. Without the lenses, we would have to look at many different crystals to obtain the same information. (Some older microscopes do not have Bertrand lenses, but we can still see an interference figure by removing an ocular and inserting a peep sight, or by just peering down the tube. The figures, however, will be quite small.)

5.6.1 Uniaxial Interference Figures



5.65 A uniaxial optic axis figure

The best way to learn the optic sign of a uniaxial mineral, is to obtain an interference figure looking down, or nearly down, a crystal's optic axis. The figure obtained is an *optic axis* (OA) *figure*; Figure 5.65 shows an example. Finding a grain that gives an OA figure is normally not difficult. Grains oriented with the optic axis vertical appear isotropic (when viewed under normal XP light) because they produce no double refraction. Grains oriented with the optic axis close to vertical have low retardation and, therefore, low-order interference colors.



a. isochromes for minerals with low birefringence

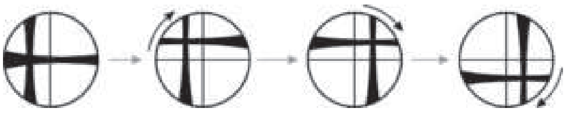
b. isochromes for minerals with higher birefringence

c. light ray vibration directions

5.66 Uniaxial interference figures

A centered uniaxial OA figure contains a black cross, like the one seen in the photo above (Figure 5.65), and depicted in Figure 5.66*a, b* and *c*. The cross will not move much if we rotate the stage. The center of the cross, called the *melatope*, corresponds to the direction of emergence of the optic axis. We call the dark bands forming the cross *isogyres*. The surrounding colored rings, if present, are *isochromes*. They are bands of equal retardation caused by the light entering the crystal at different angles (because of the conoscopic lens). Interference figures for minerals with very low birefringence, like quartz and feldspars, may not show any colored isochromes but most minerals do. Minerals with low to moderate birefringence typically show a few isochromes (Figure 5.66*a*), and interference figures for minerals with high birefringence commonly show many (Figure 5.65 and Figure 5.66*b*).

As shown in Figure 5.66*c*, in all parts of a uniaxial optic axis interference figure ε′ vibrates radially (along the radius of the interference figure) and ω vibrates tangent to isochromes. One way to remember these relationships is with the acronym *WITTI* for the mnemonic “*ω* is tangent to isochrome.”



5.67 Precession of the melatope and isogyres for an off-center optic axis figure

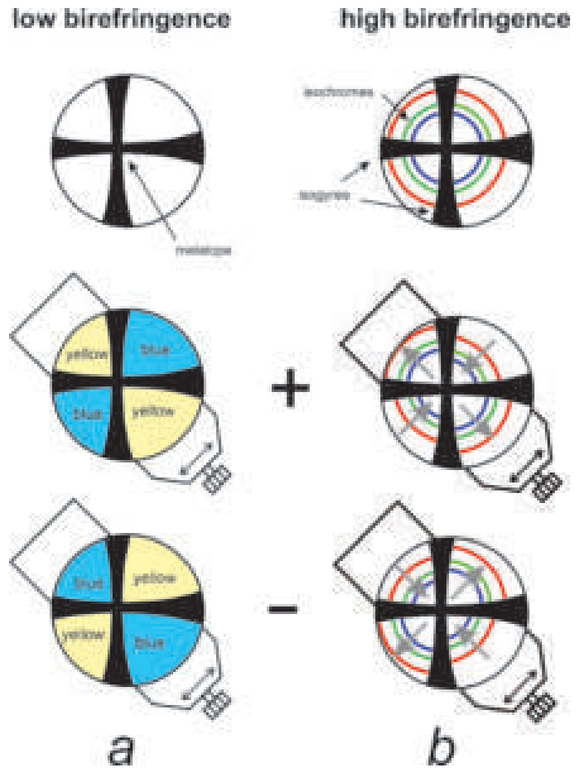
Sometimes, we obtain an optic axis figure but the optic axis is not perfectly vertical. If so, the black cross will be off center. As we rotate the stage the cross will precess as the melatope follows a circular path (Figure 5.67). But, even if the cross is somewhat off center, we can use it to learn the optic sign. And once we have an OA figure, perfectly centered or not, we use an accessory plate to learn whether a mineral is positive or negative. This procedure is described below.

Most randomly oriented uniaxial mineral grains do not exhibit a centered OA figure. The optic axis is only one direction in the crystal and grains are unlikely to have their optic axis vertical. If the optic axis of a grain lies parallel to the stage of the microscope, we get an *optic normal figure*, also called a *flash figure*. The flash figure appears as a vague cross or blob that nearly fills the field of view when the grain is at extinction (when the optic axis is perpendicular to a polarizer). Upon stage rotation, it splits into two curved isogyres flashing in and out of the field of view with a few degrees of stage rotation. Biaxial flash figures have the same general appearance.

▶ Video 9: Short video showing an optic axis figure for calcite changing during stage rotation (15 seconds)

▶ Video 10: Short video showing and optic axis figure for benitoite changing during stage rotation (30 seconds)

5.6.1.1 Determining the Optic Sign of a Uniaxial Mineral



5.68 Determining optic sign for a uniaxial mineral

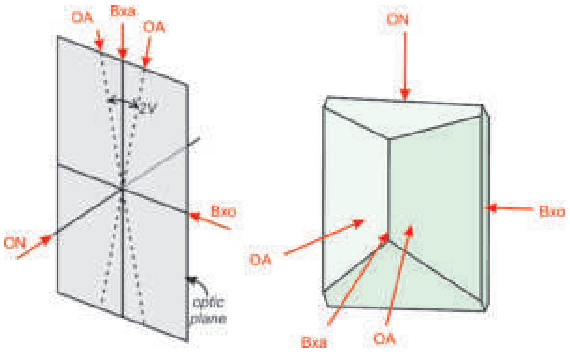
To know the optic sign of a uniaxial mineral, we must determine whether $\omega > \varepsilon$ or $\varepsilon > \omega$. We make this determination by examining an optic axis figure and using an accessory plate with known orientation of the fast and slow rays. Standard accessory plates have their slow direction oriented southwest-northeast at 45° to both polarizers. We insert the plate, and we observe interference color changes or isochrome (color ring) movements in the southwest and northeast quadrants of the interference figure (Figure 5.68).

If the slow direction of the accessory plate corresponds to the slow direction of the mineral, retardation will add and we will see higher order interference colors. If they do not correspond, retardation will, in part, cancel and we will see lower order colors. In a uniaxial optic axis figure, ε' vibrates radially. So, if interference colors in the southwest and northeast quadrants shift to higher orders when we insert the plate (or wedge), addition of retardation has occurred. So, ε' is the slow ray and the crystal is uniaxial positive. Subtraction (lower-order interference colors) in the southwest and northeast quadrants indicates that *ε′* is the fast ray, and the crystal is optically negative. Because *ε′* vibrates parallel to the prism axis (c-axis) in prismatic uniaxial minerals, the optic sign is the same as the sign of elongation.

Although we could use a quartz wedge, we normally use a full-wave accessory plate when the optic axis figure shows low-order interference colors. In positive crystals, addition produces light blue in the southwest and northeast quadrants of the interference figure (Figure 5.68*a*), while subtraction produces light yellow in the northwest and southeast quadrants. In negative crystals, the effect is the opposite. If several different color rings (isochromes) are visible, the blue and yellow colors will only appear on the innermost rings near the melatope (the center of the black cross).

We can sometimes use a full-wave plate, but normally use a quartz wedge, to learn an optic sign for minerals that exhibit high-order interference colors. The retardation of the quartz will add to the retardation of the unknown mineral in two quadrants as we insert the wedge. It will also subtract from the retardation in the other two. The result will be color rings (isochromes) moving inward in quadrants where addition occurs, and outward in quadrants where subtraction occurs (Figure 5.68*b*). For positive minerals, this means that colors move inward in the southwest and northeast quadrants and outward in the northwest and southeast quadrants. For negative minerals, the motion is opposite.

5.6.2 Biaxial Interference Figures



5.69 Perspectives corresponding to different kinds of biaxial interference figures

We obtain biaxial interference figures in the same way as uniaxial interference figures. However, complications arise with biaxial minerals because it is more difficult to find and identify grains oriented in a useful way. We can get interference figures from all grains, but interpreting them can be difficult or impossible.

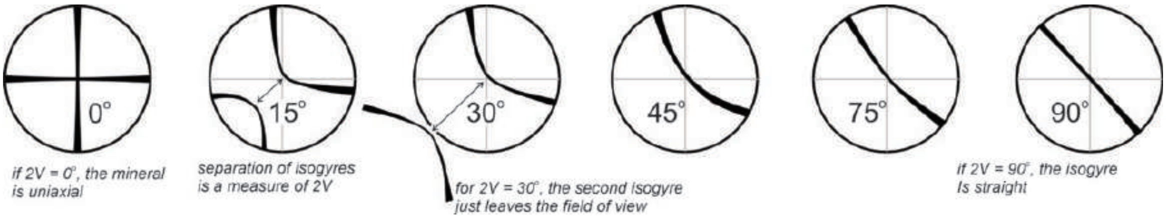
With care, however, we can identify three different kinds of useful figures: *optic axis figures* (OA), *acute bisectrix figures* (Bxa), and *optic normal figures* (ON). Each corresponds to a different light path through the crystal, relative to the orientation of the optic axes. A fourth type of figure – a *Bxo figure* (Bxo) – is generally of limited use but we discuss it briefly in the interests of thoroughness.

Figure 5.69 shows the orientations of the different views for a typical biaxial mineral. The optic plane is vertical in the drawing on the left, but is horizontal in the drawing on the right. You can compare these drawings with ones seen earlier in which the crystallographic (a, b, c) and optical axes (X, Y, and Z) were labeled (Figures 5.60 and 5.61).

▶ Video 11: Biaxial interference figures with good photos (5 minutes)

5.6.2.1 Optic Axis Figure

We obtain an OA figure by looking down an optic axis (Figure 5.69). We can find grains oriented to give an OA figure because they have zero or extremely low retardation. Under normal XP light, they remain dark even when we rotate the microscope stage. An interference figure will show only one isogyre unless *2V* is quite small (less than 30°).



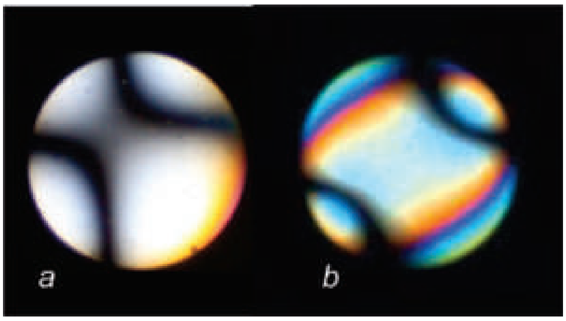
5.70 Optic axis figures for different values of *2V*

Figure 5.70 show depictions of isogyres for different values of *2V*. (In these drawings, the isogyres are narrow with sharp boundaries but in thin section they are commonly quite diffuse.) No matter the *2V* value, if the figure is perfectly centered, the cross will remain centered with stage rotation. If *2V* = 0° it means we are looking at a uniaxial mineral and we see a black cross. If *2V* is very low (< 30°) We may see two isogyres, shown in the 15° drawing above. The two isogyres will come together and separate with stage rotation. If *2V* > 30° the second isogyre no longer enters the field of view. As *2V* approaches 90°, the single isogyre becomes straighter, and at 90° the isogyre is completely straight. So, the curvature allows us to estimate *2V*.

For any value of *2V*, stage rotation causes isogyre rotation. For some purposes, discussed later, we may wish to know which side of the isogyre is concave and which is convex; this can be difficult to discern if *2V* is very large because the isogyre will be nearly straight. In part also, the difficulty arises because a straight biaxial isogyre (unlike a uniaxial isogyre) does not have to be parallel or perpendicular to the microscope crosshairs.

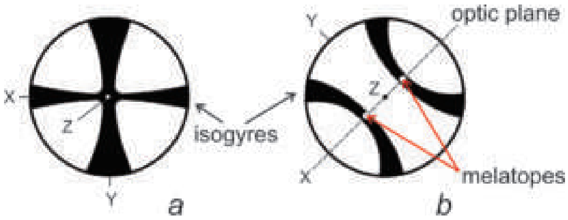
▶ Video 12: Link to an optic axis figure for betrandite (biaxial) (30 seconds)

5.6.2.2 Bxa and Bxo Figures



5.71 Two Bxa interference figures

We obtain Bxa figures, such as those in Figure 5.71 by looking down the *acute bisectrix*, the line bisecting the acute angle between the two optic axes (Figure 5.69). We obtain a Bxo figure by looking down the *obtuse bisectrix*, the line bisecting the obtuse angle between the two optic axes (Figure 5.69). In biaxial positive crystals, Bxa corresponds to a view along Z; in biaxial negative crystals, it corresponds to a view along X. The opposite is true for Bxo figures. Generally, however, we do not seek a Bxo figure because it is of less use than a Bxa. So the discussion below focuses mostly on Bxas.



5.72 Two views of Bxa interference figures for a biaxial positive crystal

When we observe an acute bisectrix figure (Bxa) for a grain in an extinction orientation (which occurs when Y is perpendicular to a polarizer), it appears as a black cross, similar in some respects to a uniaxial interference figure (Figure 5.72*a*). When we rotate the stage, the cross splits into two isogyres that move apart and may leave the field of view (Figure 5.72*b*). After a rotation of 45°, the isogyres are at maximum separation; they come back together to reform the cross every 90°.

The points on the isogyres closest to the center of a Bxa (or a Bxo), the *melatopes*, are points corresponding to the orientations of the optic axes (Figure 5.72*b*). (Figure 5.72*b* is for a biaxial positive crystal; X and Z will switch places for a biaxial negative crystal.) If the retardation of the crystal is large enough, isochromes circle the melatopes. Some colorful isochromes are apparent in Figure 5.71*b*, above. Isochrome interference colors increase in order moving away from the melatopes because retardation is greater as the angle to the optic axes increases.

In Figure 5.71*a*, the isogyres are just beginning to separate; in Figure 5.71*b* they are at maximum separation. The maximum amount of isogyre separation depends on *2V*; the greater the separation, the larger the *2V*. If *2V* is less than about 60°, the isogyres of a well-centered figure stay in the field of view as we rotate the stage. If *2V* is greater than 60°, the isogyres completely leave the field of view

Finding a grain that yields a Bxa is easiest for minerals with a small *2V*. We begin by searching for a grain that has minimal retardation. Such a grain will be oriented with an optical axis near vertical. Then we obtain an interference figure. We rotate the stage, and note how the isogyres behave. After checking several grains, we will find a Bxa. For minerals with low-to-moderate *2V*, both isogyres will stay in the field of view, but the interference figure may not be perfectly centered. If an isogyre leaves the field of view, we check other grains until we are sure we are looking at a nearly centered Bxa. Getting a perfectly centered Bxo or Bxa figure is difficult and, sometimes for off-centered figures, we may only see one isogyre clearly.

For minerals with high *2V*, the search for a Bxa sometimes becomes frustrating. Distinguishing a Bxa from a Bxo may be difficult or impossible. If we mistake one for the other, we may get some properties, *2V* for example, wrong if we make measurements. But, the isogyres in a Bxo figure always leave the field of view because, by definition, an obtuse angle separates the optic axes in the Bxo direction. Thus, if the isogyres remain in view, the figure is a Bxa figure. For standard lenses, if the isogyres leave the field of view, the figure may be a Bxo or a Bxa for a mineral with high *2V* (greater than about 60°). Expert optical mineralogists can tell a Bxa from a Bxo figure by the speed with which the isogyre leaves the field of view on stage rotation. For the rest of us, it is probably best to search for another grain with a better orientation.

▶ Video 13: Link to off-center Bxa figure for titanite (30 seconds)

▶ Video 14: Link to Bxa video for phlogopite (30 seconds)

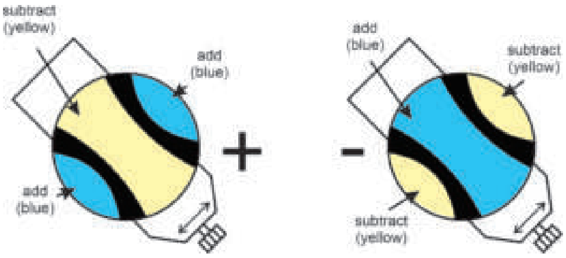
5.6.2.3 Optic Normal Figure (ON)

We get an optic normal (ON) figure by looking down Y, normal to the plane of the two optic axes (see Figures 5.60 and 5.61). Grains that yield an optic normal figure are those that have maximum retardation, which means maximum interference colors. The interference figure resembles a poorly resolved Bxa, but the isogyres leave the field of view with only a slight rotation of the stage. Biaxial optic normal figures appear similar to uniaxial flash figures.

5.6.2.4 Determining Optic Sign and *2V* of a Biaxial Mineral

Determining optic sign from a Bxa figure is equivalent to asking whether the Bxa view is parallel to the fast direction (biaxial negative crystals) or to the slow direction (biaxial positive crystals). We can often make the determination in much the same manner as for a uniaxial optic axis figure. However, for figures where the isogyres leave the field of view, this is not the recommended method because we can easily confuse Bxa and Bxo figures when *2V* is greater than 70° or 80°. An alternative way to learn optic sign and *2V* is to find a grain that yields a centered optic axis figure. Finding such grains is often not difficult because they show very low-order interference colors, or may appear isotropic under crossed polars. Below, we discuss both methods.

5.6.2.5 Determining Sign and *2V* from a Bxa Figure



5.73 Determining optic sign and *2V* from a Bxa interference figure

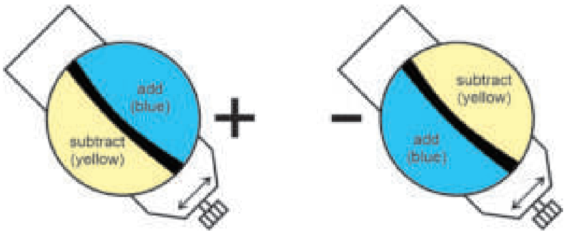
To measure optic sign and *2V* using a Bxa figure, we rotate the stage so the isogyres are in the southwest and northeast quadrants (Figure 5.73). The Y direction in the crystal is now oriented northwest-southeast. The points corresponding to the optic axes (the melatopes) are the points on the isogyres closest to each other, and either X or Z is vertical depending on optic sign.

To determine optic sign, we must know which direction (X or Z) is vertical, corresponding to Bxa. If the slow direction (Z) corresponds to Bxa, the crystal is positive. If the fast direction (X) is Bxa, the crystal is negative. To make the determination, we insert the full-wave accessory plate (with slow-oriented direction southwest-northeast) and note any changes in interference colors on the concave sides of the isogyres. If the interference colors add on the concave sides of the isogyres (and subtract on the convex sides), the mineral is positive (Figure 5.73).

In positive minerals with low to moderate retardation, the colors in the center of the figure will be yellow (subtraction), and those on the concave side of the isogyres will be blue (addition). In a negative mineral, the color changes will be the opposite. For minerals with high retardation, it may be difficult to decide whether a full-wave accessory plate adds or subtracts retardation because isochromes of many repeating colors circle the melatopes. A quartz wedge simplifies determination. As we insert the wedge, color rings move toward the melatopes if there is addition of retardation, or the rings move away from the melatopes if there is subtraction. If the interference colors move toward the optic axes from the concave side of the isogyres, and away on the convex side, the mineral is positive. We see the opposite effect for a negative mineral.

We can estimate *2V* from a well-centered Bxa figure by noting the maximum of separation of the isogyres during stage rotation. For standard lenses, if the isogyres just leave the field of view when they are at maximum separation, *2V* is 60° to 65°. If the isogyres barely separate, 2V is less than about 10°.

5.6.2.6 Determining Sign and *2V* from an Optic Axis Figure



5.74 Determining optic sign and *2V* from a biaxial optic axis figure

Determining the optic sign from an optic axis figure can often be simpler than looking for a Bxa. To find an OA figure, we look for a grain displaying zero or very low retardation. Once we have an interference figure, we rotate the stage and we should see one centered or nearly centered isogyre (Figures 5.70). (If, instead, we see two isogyres that stay in the field of view when we rotate the stage, we are looking at a Bxa for a mineral with low *2V*.) We rotate the stage so the isogyre (or the most nearly centered if there are two isogyres) is concave to the northeast (Figure 5.74). Note that isogyres rotate in the opposite sense from the stage.

We then insert the full-wave accessory plate. If the retardation increases on the concave side of the isogyre (and decreases on the convex side), the mineral is positive (Figures 5.74). In minerals with low to moderate retardation, we need only to look for yellow and blue. Blue indicates an increase and yellow a decrease in retardation. The increase or decrease of retardation will be opposite if the mineral is negative.

We estimate *2V* by noting the curvature of the isogyre. If *2V* is less than 10° to 15°, the isogyre will seem to make a 90° bend. If *2V* is 90°, it will be straight. For other values, it will have curvature between 90° and 0° (Figure 5.70).

5.7 Identifying Minerals and Mineral Properties in Thin Section

Learning to identify minerals in thin section takes practice. But, if we have a hand specimen or know what kind of rock we are looking at, the most likely possibilities are limited – and identification is simplified. And some common minerals have key properties that make identification straightforward. So, just like identifying hand specimens based on physical properties, it is not always necessary to check or measure every optical property to figure out what a mineral is. To see photos of the most common minerals in thin section with a discussion of key properties that aid identification, go to our website Optical Mineralogy. For many more, and higher quality photographs of minerals in thin section, go to Frank Mazdab’s rockPTX.com website.

With the above said, a standard approach works well. This approach involves looking at multiple grains of each mineral and changing back and forth between plane polarized (PP) and crossed polarized (XP) light. Sometimes we need an interference figure. But for routine mineral identification, obtaining an interference figure is often unnecessary and identification can be quite rapid. The flow chart in Box 5-4 below summarizes the key steps and questions to ask as you go along. If you do all that is described and you still cannot identify a mineral, you have been very unlucky.

● Box 5-4 Identifying Minerals and Measuring Mineral Properties with a Polarizing Microscope

1. Look at the whole thin section (and at a hand specimen if available):
   - What kind of rock is it?
   - How many different major minerals does it contain?
   - What are the associated minerals?
2. Examine several grains of the same mineral under PP light:
   - Is the mineral opaque or nonopaque?
   - What color is the mineral? Rotate the stage.
   - Is it pleochroic?
   - What is the color variation?
   - What is the crystal shape and habit?
   - What cleavage does it display, if any?
   - What is its apparent relief?
3. Now cross the polars to examine several grains of the same mineral under XP light:
   - Rotate the stage. Is the mineral isotropic or anisotropic?
4. If anisotropic:
   - Rotate the stage. What is the range of interference colors?
   - Estimate the maximum birefringence by looking at grains with the highest order of interference colors.
   - For minerals with a long dimension of principal cleavage: What is the maximum extinction angle?
   - Is the mineral length fast or length slow ?
   - Is the mineral twinned? If so, what kinds of twins?
5. If necessary, obtain an interference figure. You may have to try several different grains to get one that is useful:
   - Is the mineral uniaxial or biaxial?
   - What is its optic sign?
6. If biaxial:
   - Estimate *2V*.

●Figure Credits

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5.2 Microscope lenses and a thin section, “Introduction to Petrology” by Johnson, E.A., Liu, J. C., and Peale, M., https://viva.pressbooks.pub/petrology
5.3 Fractured grains of garnet, lobotka.net
5.5 Ore from Butte, Montana, Eastman (2017)
5.8 Wavelengths and colors of visible light, caltechletter.org
5.10 Light refraction, ucar.edu
5.13 Light dispersion, Cepheiden, Wikimedia Commons
5.14 Diamond dispersion, thoughtco.com
5.18 Looking at fish, shadesdaddy.com
5.25 Angular scale on a microscope, Johnson et al. (ibid)
5.26 Microscope turret, Johnson et al. (ibid)
5.27 Microscope eyepieces, Johnson et al. (ibid)
5.28 Quartz wedge and accessory plates, Johnson et al. (ibid)
5.35 Garnet and halite, lobotka.net.
5.36 Grains in refraction oil, sun.ac.za
5.39 Becke lines, gemsandmineralacademy.files.wordpress
5.45 Double refraction, sciencesource.com
5.49 Raith–Sørensen chart, Sorensen (2013)
5.50 Michel-Lévy chart, Sorensen (2013)
5.56 Plagioclase in rhyolite, alexstrekeisen.it
5.57 Quartz in thin section, pinterest.com
5.65 Uniaxial optic axis figure, jm-derochette.be
Video 2: Becke lines, Brent Owens
Video 7: Interference colors, Johnson et al. (ibid)
Video 8: Twinning and zoning, unknown origin
Video 9: Calcite interference figure, AmiGEO
Video 10: Benitoite interference figure, Frank Mazdab
Video 11: Biaxial interference figures, Johnson et al. (ibid)
Video 12: Optic axis figure – bertrandite, Frank Mazdab
Video 13: Bxa figure – titanite, Frank Mazdab
Video 14: Bxa figure – phlogopite, Frank Mazdab

6 Igneous Rocks and Silicate Minerals

6.1 Xenoliths in basalt from San Carlos, Arizona. The brown xenolith contains olive-green olivine and brown orthopyroxene. The green xenolith contains light green olivine, (minor) emerald-green clinopyroxene, and darker orthopyroxene.

6 Igneous Rocks and Silicate Minerals

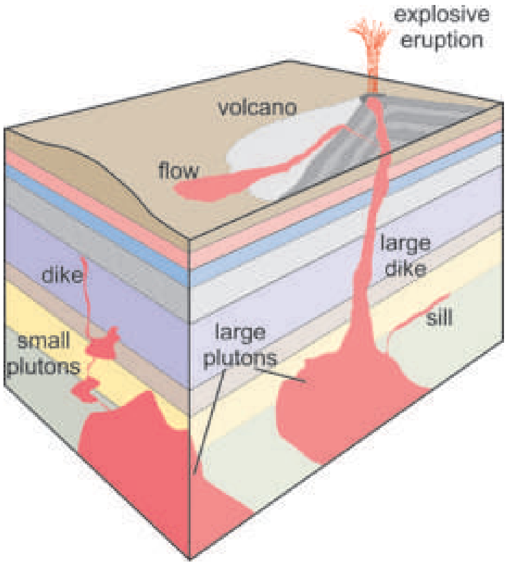
KEY CONCEPTS

- Igneous minerals crystallize from a magma to form igneous rocks.
- Magmas have variable compositions giving rise to many different kinds of rocks containing different minerals.
- Cooling rate affects crystal size and rock texture.

- Minerals crystallize in an orderly and predicable way during magma cooling.
- Silicates are the most important minerals in igneous rocks.
- We classify silicates based on the arrangement and ordering of SiO4 tetrahedra within them.
- Different silicate minerals have distinctive properties, atomic arrangements, and origins.

6.1 Magmas and Igneous Rocks

Igneous rocks and minerals form from *magma*, molten rock that originates beneath Earth's surface. Magma often collects in large *magma chambers* at depth in Earth, but magma is also mobile and can flow through fissures and sometimes reach the surface. Mid-ocean ridges and subduction zones contain most magmas at or near Earth's surface. Continental rifts and hot spots, places where anomalous heat rises from depth, account for the rest.



6.2 Different occurrences of igneous rocks and minerals

Magmas are complex liquids that vary greatly in composition and properties. They have temperatures as great as 1,400 °C and often originate in regions 50 to 200 km deep in Earth. They may be entirely liquid or partially crystalline, containing some crystals of high-temperature minerals such as leucite, olivine, or pyroxene. Because magma has a lower density than the solid upper mantle and crust of Earth, buoyancy moves it upward. The race between upward movement and cooling ultimately determines whether magma becomes an *intrusive* or *extrusive* igneous rock.

Magma solidifies as an intrusive rock if it crystallizes before it reaches the surface. Intrusive rocks form *plutons* (a general term given to any intrusive igneous rock body), so geologists sometimes use the terms *intrusive* and *plutonic* interchangeably. Figure 6.2 shows some examples of the most common plutonic rock bodies: plutons, dikes, and sills.

6.3 Shiprock and one of the dikes radiating from it in New Mexico

This spectacular photo shows a dike revealed by erosion of surrounding sediments. Shiprock, a peak in northwestern New Mexico, is in the background. The tall jagged peak is what remains of the internal plumbing of a volcano that was once present. The dike was created by the same magma that powered the volcano.

Magmas that form intrusive rock bodies are normally surrounded by very warm rocks, so they cool (and crystallize) slowly, perhaps only 1 to several degrees in 1,000 years. In contrast, magmas that reach the surface cool quickly. They may produce lava flows or erupt explosively into the air, ejecting *pyroclastic material* (ash and other debris of variable size). The result is sometimes just unconsolidated volcanic debris. Typically, though, eruptions produce *extrusive* rocks (generally called *volcanic rocks* although a volcano may not be involved).

Cooling rate directly affects grain size of an igneous rock. The common plutonic rock *granite* contains crystals of quartz and potassium feldspar that are easily seen with the naked eye. In the photo of granite below (Figure 6.4), the quartz is gray and the feldspar is salmon colored. A common volcanic rock, rhyolite (Figure 6.5) has the same minerals, but we need a microscope to see the crystals. The rhyolite in Figure 6.5 is pink because it contains small crystals of pink potassium feldspar. It also contains larger crystals of quartz that appear as dark specks in the rock. Crystals in granites have a long time to form and may grow large. In contrast, volcanic rocks, such as rhyolite, crystallize rapidly because extrusion exposes the lava to water or to the cool atmosphere at the surface of Earth, and crystals are small.


6.4 Granite


6.5 Rhyolite


6.6 Porphyry

Sometimes extrusive igneous rocks cool so quickly that no crystals form. This is especially likely to happen if lava meets water. The result is a rock composed of volcanic glass called *obsidian*. Examples of obsidian appeared in Figures 1.21

(Chapter 1) and Figure 4.5 (Chapter 4). In other cases, different minerals may grow to distinctly different sizes. The result may be a *porphyry*, a rock in which coarse crystals called *phenocrysts* are floating in a sea of fine-grained crystals called *groundmass*. The porphyry shown if Figure 6.6 includes large phenocrysts of both gray quartz (a bit hard to see) and slightly pinkish blocky K-feldspar. The phenocrysts are surrounded by dark fine grained groundmass.

Quickly cooled plutonic rocks may be very fine grained and difficult to tell from volcanic rocks. Some petrologists, therefore, prefer to classify and name igneous rocks based on their grain size rather than their genesis (origin). They divide rocks into those containing very fine grains (*aphanitic*), rocks containing very coarse grains (*phaneritic*), and rocks containing combinations of large and small crystals (*porphyritic*).

6.1.1 Where Do Igneous Rocks Occur?

Silica (SiO_2) Content of Some Common Igneous Rocks

	45-55 wt%	**55-65 wt%**	**>65 wt%**
volcanic rock	basalt	andesite	rhyolite
plutonic rock	gabbro	diorite	granite

All igneous rocks are made of the same major elements, but elemental ratios vary. The most significant variations are the amounts of silica (SiO_2) present (see table). Most igneous rocks contain between 45 and 65 wt% silica. They range from lower-silica basalt and gabbro to higher-silica rhyolite and granite. Other elemental concentrations vary systematically, too. For example, basalt and gabbro contain more iron and magnesium than andesite and diorite, and andesite and diorite contain more iron and magnesium than rhyolite and granite. Other elemental variations are less profound or regular.

6.7 Pillow basalt from just north of the Golden Gate Bridge, San Francisco. The largest pillow is about a half meter across

Extrusive igneous rocks are found worldwide, and individual varieties are not restricted to a single tectonic setting. Basalt is the most abundant igneous rock in Earth’s crust. The oceans cover two-thirds of Earth, and basalt forms at mid-ocean ridges to become the main component of the uppermost oceanic crust. Ocean basalt typically is found in 1/2-km-thick layers that may or may not be covered by sediments. These basalts sometimes form as pillow basalts, like the basalt seen in this photo (Figure 6.7). The pillow structure develops as the basalt is extruded into cold ocean water. Lesser amounts of basalt are found at subduction zones where, in association with andesites, rhyolites, and related rocks, basalts may be part of composite volcanos.

6.8 Cliffs of Columbia River Flood Basalt, Washington

In continental interiors, hot spots and rifts can produce large volumes of basalt flows, in some places creating huge flood basalt provinces such as the Columbia River Flood Basalts of Idaho, Washington, and Oregon. Lava flows may be thick; the basalt cliff in the photo here is about 150 m tall. Because all basalts have similar compositions, they generally contain the same minerals, most importantly plagioclase and pyroxene. Often they contain small or large amounts of volcanic glass as well.

6.9 Fifes Peaks, Cascade Mountains, Washington

Large volumes of andesite, the most common volcanic rock after basalt, are found with dacite and rhyolite in island arcs and at continental margin subduction zones. The photo in Figure 6.9 shows subduction-related andesite at Fifes Peaks in western Washington. Less commonly, andesite is associated with continental rifts or hot spots. Even more rarely, andesite is found at mid-ocean ridges. Andesite is always rich in plagioclase, and may contain biotite, pyroxene, or hornblende. Quartz and olivine are rare. Rhyolite, always containing quartz and K-feldspar, occurs in the same settings as basalt and andesite but is only common in continental areas. Rhyolites are especially abundant at hot spots such as the Yellowstone Hotspot in northwest Wyoming. They are also associated with continental rifts such as the Rio Grande Rift in southern Colorado and New Mexico, and at subduction zones.

Plutonic igneous rocks, too, occur in many diverse settings. Granites, granodiorites, and related rocks collectively called *granitoids*, are found worldwide and are major components of the continental crust. They are especially common in Precambrian shields and younger mountain belts, where they form intrusions of all sizes, from small dikes and plutons to large batholiths.

6.10 El Capitan in Yosemite Valley National Park

6.11 Photo of Mt. Whitney (the highest point in the 48 states) and surrounding peaks near Lone Pine, California. The exposed rock is part of the Sierra Nevada Batholith.

Batholiths (masses of intrusive rock composed of multiple plutons) form the cores of many mountain ranges. The Sierra Nevada Batholith in California and Nevada, for example, is a mostly granitic mass that crops out, or is just beneath the surface, in a 650 km long region that is 100 to 125 km wide. The photo in Figure 6.10 shows a cross section of the batholith exposed in the vertical face of El Capitan in Yosemite Valley. Look closely at the photo and you can see that there are several different colored rock types. Most are white or salmon colored granite; the darker patches are diorite. Overall, the mineralogy of the Sierra Nevada Batholith is mostly quartz, plagioclase, and potassium feldspar with lesser amounts of biotite and hornblende. Although typically found in shields and mountain belts, batholiths and other granitic rocks are also associated with rifts, spreading centers, and hot spots.

6.12 Gabbro of the Duluth Complex

Plutonic rocks span a wide range of compositions. Those that contain less silica than granite, including for example gabbro (equivalent in composition to the most common volcanic rock, basalt), also form plutons of all sizes. They do not, however, form large batholiths. Large volumes of gabbro make up the lower part of oceanic crust. Lesser amounts are found in layered intrusions or associated with continental hot spots and rifts. The Duluth Complex, west and north of Lake Superior, is one of the largest known gabbroic occurrences. The complex is a 16-km thick sill, composed mostly of gabbro with lesser amounts of anorthosite and granitic rocks. The gabbro seen in Figure 6.12 consists of light-colored plagioclase and darker pyroxene.

6.2 Compositions of Igneous Rocks

6.2.1 Mafic and Silicic Magmas

The table below gives chemical analyses for seven different plutonic rocks that formed from seven magmas of different compositions. These compositions include several examples each of very silica-rich and very silica-poor rocks, and cover the range for typical magmas. The most significant variations are the amount of silica (SiO_2), and the relative amounts of alkali oxides (Na_2O+K_2O) compared with CaO. Although compositions cover a wide spectrum, most magmas contain 40 to 75 wt % SiO_2. This is because silicon and oxygen are dominant elements in the crust and mantle where magmas originate. Alkali oxide content varies from 2.70 to 14.21 %. Some rare and unusual magma types produce igneous rocks rich in nonsilicate minerals including carbonates or phosphates, but we will not consider them here.

Compositions of Some Magmas (wt% of oxides)

oxide	**Silicic magmas** (Relatively SiO_2-rich magmas)			**Mafic magmas** (Relatively SiO_2-poor magmas)				
	higher — Na_2O+K_2O — *lower*			*higher* — Na_2O+K_2O — *lower*				
	alkali granite	**granite**	**tonalite**	**alkali syenite**	**syenite**	**diorite**	**gabbro**	**peridotite**
SiO_2	73.86	72.08	66.15	55.48	59.41	51.86	50.78	43.54
TiO_2	0.20	0.37	0.62	0.66	0.83	1.50	1.13	0.81
Al_2O_3	13.75	13.86	15.56	21.34	17.12	16.40	15.68	3.99
Fe_2O_3	0.78	0.86	1.36	2.42	2.19	2.73	2.26	2.51
FeO	1.13	1.67	3.42	2.00	2.83	6.97	7.41	9.84
MnO	0.05	0.06	0.08	0.19	0.08	0.18	0.18	0.21
MgO	0.26	0.52	1.94	0.57	2.02	6.12	8.35	34.02
CaO	0.72	1.33	4.65	1.98	4.06	8.40	10.85	3.46
Na_2O	3.51	3.08	3.90	8.86	3.92	3.36	2.14	0.56
K_2O	5.13	5.46	1.42	5.35	6.53	1.33	0.56	0.25
H_2O	0.47	0.53	0.69	0.96	0.63	0.80	0.48	0.76
P_2O_5	0.14	0.18	0.21	0.19	0.38	0.35	0.18	0.05

Magmas richest in SiO_2, such as alkali granite, granite, and tonalite are generally deficient in MgO. We term such magmas *silicic* (Si-rich) or *felsic* (contraction of *feldspar* and *silica*). Light-colored minerals dominate felsic rocks, so many geologists use the term felsic to refer to any light-colored igneous rock, even if the chemical composition is unknown. At the other end of the spectrum, magmas with <50 wt % SiO_2 are usually rich in MgO and contain more FeO and Fe_2O_3 than silicic magmas. These include diorite, gabbro, and peridotite. We call them *mafic* (contraction of the words *magnesium* and *ferric*) and, for peridotite, *ultramafic*. They are usually dark in color. The term *intermediate* describes rocks with compositions between mafic and silicic (but no intermediate rock analyses are in the table above).

6.13 Nepheline syenite from Brazil

Besides distinctions between mafic, intermediate, and silicic rocks, petrologists often classify igneous rocks based on their alkali (K_2O + Na_2O) and CaO contents. *Alkalic rocks* are those with high (K_2O + Na_2O):CaO ratios. The table above reveals that alkalic rocks can be either silicic or mafic compositions. Overall, though, the most common alkalic rocks are silicic. We grouped alkali syenite and syenite with the other mafic magmas because alkali syenite and syenite are silica-poor compared with silicic magmas, but their most significant distinctions are their high alkali oxide contents compared with CaO content. The photo seen here (Figure 6.13) shows a syenite from Brazil. The main minerals are gray potassium feldspar and lighter colored nepheline. The black mineral is hornblende.

Rocks melt in many places within Earth, and magma compositions reflect the sources. Mid-ocean ridge and ocean hot-spot magmas are mostly mafic; subduction zone magmas are generally silicic to intermediate. Continental rifts produce a variety of magma types. Rocks of different compositions have different melting temperatures because some elements combine to promote melting.

Silicon and oxygen, in particular, promote melting because they form very stable molten polymers (long chains of Si and O) that persist even when melted. Silicic minerals, and SiO_2-rich rocks, therefore, melt at lower temperatures than mafic minerals and SiO_2-poor rocks.

6.2.2 Volatiles

6.14 Vesicular olivine basalt from Hawaii

Magmas may also contain gases, liquids, or vapors, collectively called *volatiles.* H_2O and CO_2 are the most common volatiles, but volatile compounds of sulfur, chlorine, and several other elements may also be present. Sometimes, these compounds separate from a melt to form bubbles, most commonly in cooling lava, creating empty *vesicles* as the magma solidifies. Figure 6.14 shows a basalt from Hawaii with vesicles (remnants of gas bubbles) up to several millimeters across. Often, vesicles like these become filled with secondary zeolites or other minerals over time. This rock contains green crystals of olivine, but most of it is dark colored volcanic glass. The specimen also contains a piece of black and white gabbro that was plucked from the lower crust as the magma rose to the surface.

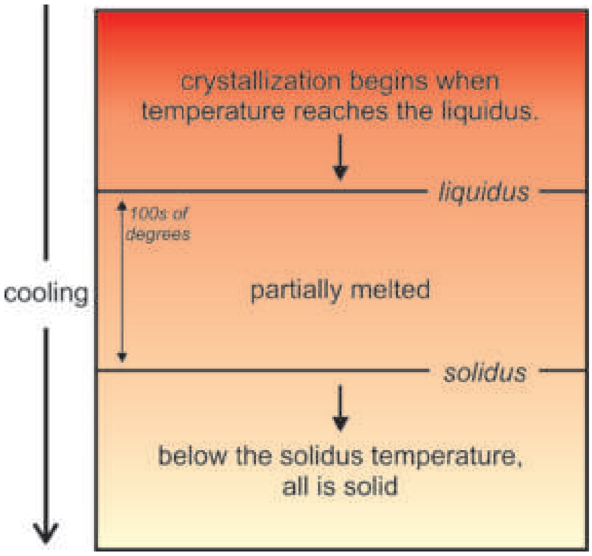
6.15 Mt. Saint Helens, May 1980

Water is especially important during eruptions because just a small amount of water can produce large amounts of steam and violent eruptions. This is especially true for silicic magmas. The explosive May 18, 1980 eruption of Mt. Saint Helens in Washington is an example. A series of earthquakes and small eruptions began at Mt. Saint Helens in March, 1980. A bulge developed on the mountain’s north side and grew for two months as magma moved upward. On May 18, an earthquake caused the north slope to slide away and gas-powered semi-molten magma exploded out of the volcano’s side. The eruption produced a column of ash that rose 24 km into the sky. Ash was deposited in a dozen states and two Canadian provinces. Nearly 60 people were killed by what some people call “the most disastrous volcanic eruption in U.S. history.” The photo in Figure 6.15 shows one of many smaller steam eruptions that preceded the main event.

6.3 Crystallization of Magmas

6.3.1 Equilibrium Between Crystals and Melt

Every mineral has a characteristic melting temperature. This can be expected to lead to an orderly and predictable sequence of minerals crystallizing as magma cools and solidifies. It does, sort of. Complications arise because some minerals do not crystallize at a single temperature, but instead form from other minerals while reacting with magma. This is called *incongruent melting*. Further complications arise because minerals together may melt (and crystallize) at lower temperatures than if they if they were alone. This is called *eutectic melting*. For example, at 1 atm pressure, diopside melts at about 1391 Ĉ and anorthite melts at 1553 Ĉ. A rock composed of diopside and anorthite, however, will melt at 1278 Ĉ.



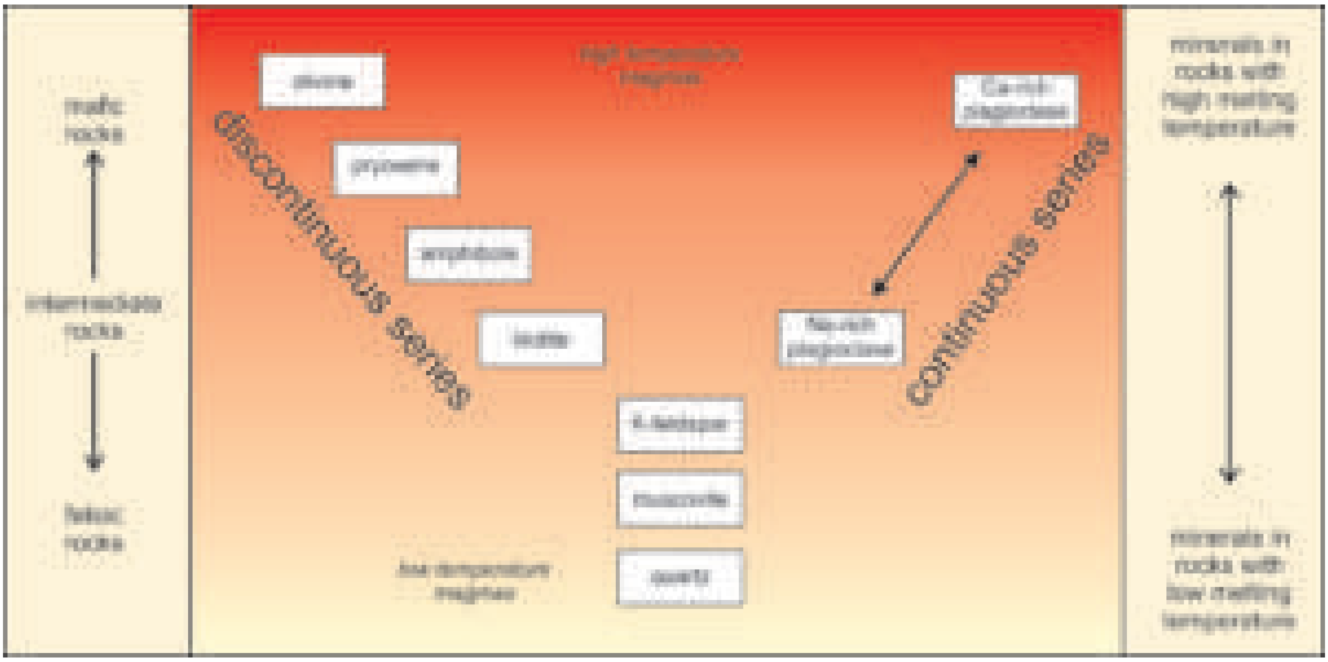
6.16 Rocks melt over a range of temperature

Crystallization of a cooling magma is a step-wise process with some minerals forming before others. So, crystallization occurs over a range of temperature. As seen in Figure 6.16, the first mineral crystals form at a temperature called the *liquidus*. Crystallization continues until the magma reaches the *solidus* temperature. Above the liquidus, all is melted. Below the solidus, all is solid. Between the two temperatures a rock is *partially melted*. The differences between liquidus and solidus temperatures can be 100s of degrees and is different for different composition magmas.

Different magmas produce different minerals, and different minerals crystallize at different temperatures. Consequently, composition is the key factor that determines the temperature at which crystallization begins. Temperatures measured in flowing lavas generally range from 900 to 1,100 °C, with higher temperatures corresponding to basaltic (mafic) lavas and lower temperatures to andesitic or rhyolitic (intermediate to silicic) lavas. For mafic rocks, the first minerals to crystallize are typically olivine, pyroxene, or plagioclase. For silicic rocks, the first crystals may be alkali feldspars or micas. Eventually, a magma completely solidifies, and the last drop of melt crystallizes at the solidus temperature. For some magmas, the solidus is well above 1,000 °C, but for granites and other silicic magmas it may be as low as 700 °C.

6.3.2 Bowen’s Reaction Series

N. L. Bowen pioneered in the study of magma crystallization, for which he received the Roebling Medal from the Mineralogical Society of America in 1950. By studying naturally occurring igneous rocks and conducting laboratory experiments, he derived an idealized model for equilibrium crystallization in a magmatic system. We call the model *Bowen’s reaction series*; it is depicted below. Although Bowen’s series is a generalization that does not apply in detail to all magma types, it is an excellent model to describe the process of crystallization. Some petrologists have developed more precise models for magmas of specific compositions.



6.17 Bowen's Reaction Series

Bowen's reaction series shows the (hypothetical) order in which minerals crystallize from cooling magma. It contains nine mineral names arranged in a Y-shape. We call the left-hand side of the Y the *discontinuous side* because abrupt changes occur as different minerals crystallize in sequence. We call the right-hand side the *continuous side* because plagioclase is continually present during crystallization, starting as Ca-rich plagioclase at high temperature and changing to Na-rich plagioclase as cooling progresses. The minerals at the bottom of Bowen's series crystallize at the lowest temperatures. Although not evident from this diagram, just like plagioclase, minerals on the discontinuous side of the series change composition as cooling proceeds. At higher temperatures, for example, olivine usually has a greater magnesium to iron ratio (Mg:Fe) than at lower temperatures.

Mineral crystallization temperatures depend on mineral composition. So, Bowen's series reflects general trends in mineral chemistry. Minerals at the top of the series (olivine, pyroxene, and calcium-rich plagioclase) are mafic (relatively silica poor). Those at the bottom are silicic (relatively silica rich). Silica content is the most significant factor controlling melting and crystallization temperatures. The mafic minerals at the top of the discontinuous series also are deficient in aluminum and alkalis and rich in iron and magnesium, compared with minerals at the bottom.

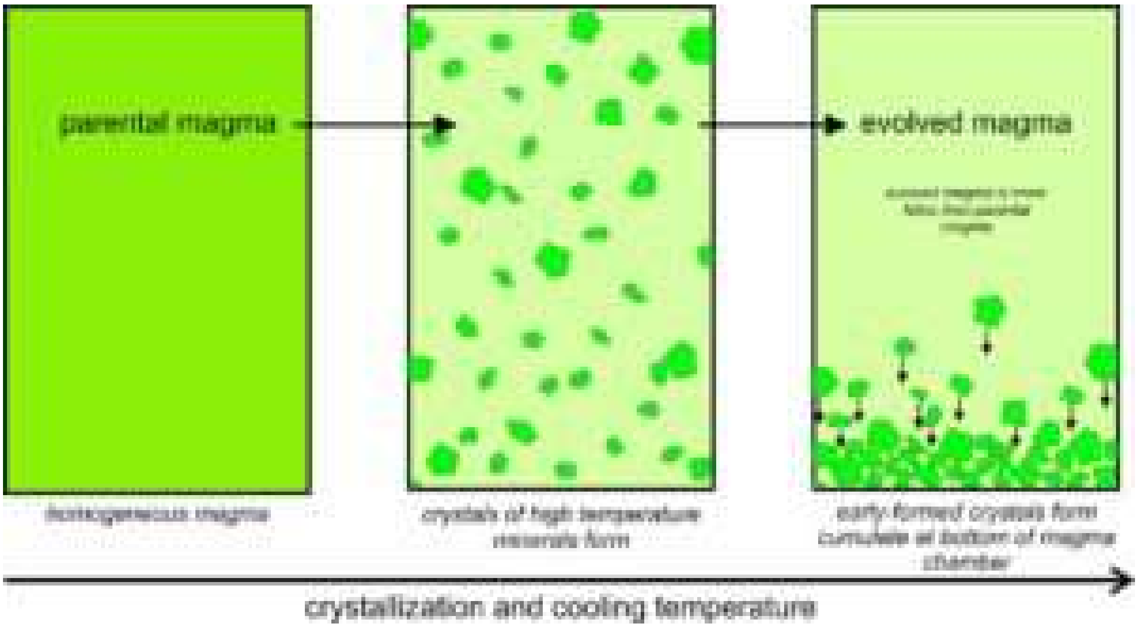
Bowen’s Reaction Series is not meant to imply that all magmas start out crystallizing olivine and end up crystallizing quartz. Consider, for example, a hypothetical magma that is 100% SiO_2. It cannot crystallize any minerals in Bowen’s reaction series except quartz because it does not contain the necessary elements. It will skip all the other minerals and just form quartz.

On the other hand, if a melt were 100% Mg_2SiO_4, it would crystallize forsterite (olivine of composition Mg_2SiO_4) and be completely solidified. These two extreme examples do not exist in nature, but compositions of natural magmas do control the extent to which crystallization follows Bowen’s reaction series and which minerals crystallize first (and last). And, although all magmas crystallize different minerals at different temperatures, none follow the complete series.

Bowen’s Reaction Series is a convenient way to remember the minerals that are common in different kinds of rocks. Mafic magmas, which crystallize at high temperature, produce rocks containing minerals at the top of the series. Silicic magmas, which crystallize at lower temperatures, produce rocks that contain minerals at the bottom of the series. So mafic rocks such as basalt or gabbro commonly contain olivine, pyroxene and Ca-rich plagioclase. Felsic rocks such as rhyolite or granite are generally rich in K-feldspar and quartz. And, intermediate composition rocks may contain pyroxene, amphibole, or biotite with plagioclase.

6.3.3 Disequilibrium

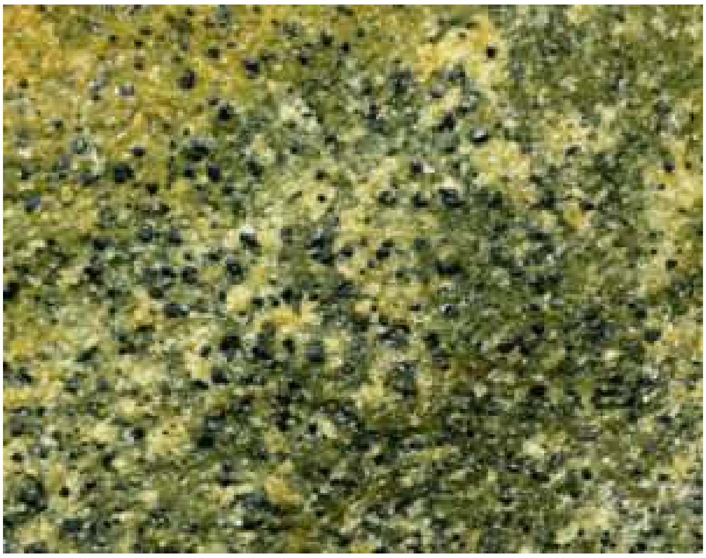
If magma and minerals remain in equilibrium, different minerals crystallize at different temperatures – sometimes more than one at a time, and mineral compositions change as temperature decreases. Continuous reactions take place as elements move from magma into growing crystals. These relationships are orderly and predictable for a magma of any given composition. But, they are highly dependent on composition. Granite and gabbro, for example, do not crystallize the same minerals, nor do they crystallize at the same temperatures.



6.18 Formation of a cumulate during partial crystallization

However, mineral crystals and magmas do not always remain in equilibrium during crystallization. Several things may cause disequilibrium. For example, as depicted in Figure 6.18, the first crystals that form may become separated from the rest of the magma if they settle to form a layer called a *cumulate* at the bottom of the magma chamber. The crystals, then, will not stay in equilibrium with the magma above them. As this happens, an original *parental magma* changes composition and becomes an *evolved magma*. Many minerals, including feldspars, pyroxenes, and oxides, can be found in thick, nearly single-mineral cumulates. And, even if a thick cumulate layer does not develop, the composition of the upper part of the magma chamber may not be the same as the lower part. When a melt gets separated from early formed crystals, we call the process *partial crystallization*, or *fractional crystallization*.

6.19 Chromite cumulates in the Bushveld Complex, South Africa



6.20 Olivine and chromite cumulate in the Stillwater Complex, Montana

The photos above in figures 6.19 and 6.20 show examples of cumulates. The photo on the left (Figure 6.19) shows dark layers of chromite (chrome-iron oxide) that settled to the bottom of a magma chamber in the Bushveld Complex of South Africa. The light material around the chromite layers is mostly the plagioclase. The Bushveld region is one of the world’s foremost mining regions, in part because the natural concentration of chromite makes it easy for the ore to be mined and produced for industrial consumption. Figure 6.20 shows a cumulate from the Stillwater Complex (Montana) that contains both olivine (green) and chromite (black). Like the Bushveld, the Stillwater Complex sees significant mining activity.

● Box 6-1 Layered Mafic Intrusions

Mafic and ultramafic layered intrusions, often called *layered mafic complexes*, are rare but are found worldwide – generally in old continental interiors. The largest, the Bushveld Complex of South Africa, is more than 66,000 km^2. Smaller layered intrusions, such as the Skaergaard Complex (Greenland), may be only 100 km^2 or less.

These complexes contain mafic rocks with compositional layering caused by fractional crystallization. They have cumulate layers piled on top of each other. Early formed crystals settled to the bottom of the magma chamber because they were denser than the melt. As the magma cooled and other minerals crystallized, they too settled. Consequently a layered sequence developed with ultramafic (high-temperature) minerals at the bottom and successively more silicic (lower-temperature) minerals on top. New pulses of magma added more layers. Besides silicates, chromite and other oxide minerals accumulate in mafic complexes. Rarely, plagioclase forms a cumulate layer at the top of a magma chamber when it floats on denser magma.

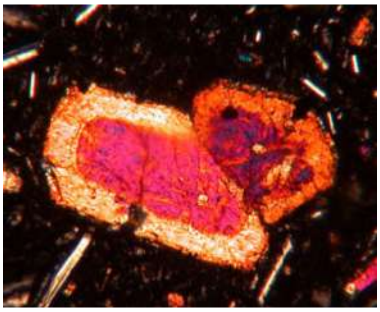
6.21 A 10 cm wide sample of ore from the Stillwater Complex

Because of their high metal content and natural separation into concentrated layers, mafic complexes often host rich ore deposits. They are especially important for production of chrome and platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, platinum). The Bushveld complex is, perhaps, the most valuable ore deposit in the world, producing significant amounts of platinum group metals, as well as chromium, iron, tin, titanium, and vanadium.

In the United States, Montana’s Stillwater Complex accounts for most of the platinum group metals mined in the western hemisphere. The photo seen in Figure 6.21 shows some of the richest ore at Stillwater. The metallic minerals are pyrrhotite and chalcopyrite that contain significant amounts of platinum, palladium, osmium, and other generally rare elements.

6.22 Zoned tourmaline from Pakistan

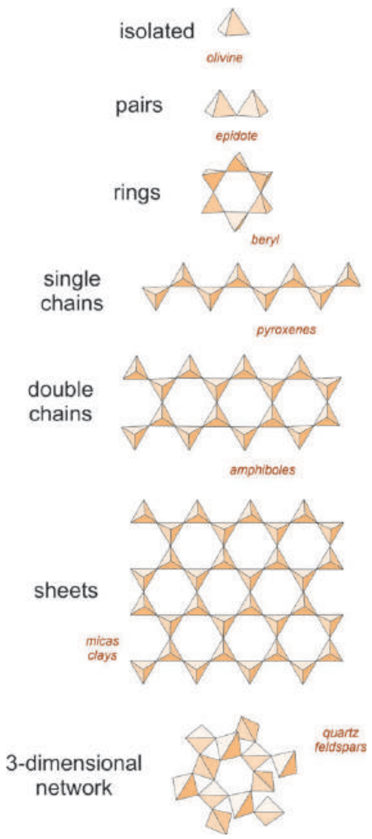
Besides separation of crystals and melt, disequilibrium occurs for other reasons. Sometimes large mineral grains do not remain in equilibrium with a surrounding magma. For example, because diffusion of elements through solid crystals is slow, different parts of large crystals may not have time to maintain equilibrium compositions. In principle, mineral crystals should be homogeneous, but in zoned crystals, such as the tourmaline crystals seen in this photo (Figure 6.22), only part of the crystal remains in equilibrium with the melt as crystallization takes place. Consequently, different zones have different compositions (and sometimes different colors).



6.23 Zoned clinopyroxene seen in thin section

Marked chemical zonation often occurs if a magma begins to cool at one depth and then rapidly moves upward to cooler temperatures. The result is often a porphyritic rock with large zoned phenocrysts. The zones may be visible with the naked eye, for example the tourmaline in Figure 6.22, if color or textural variations mirror the compositional variations. Other examples of visibly zoned minerals include the tourmaline in Figure 4.13 (Chapter 4), and the fluorite in Figure 4.37 (Chapter 4). If the zoning is not visible to the naked eye, it may be visible when a crystal is viewed in thin section with a petrographic microscope . The thin section photo seen here (Figure 6.23) shows zoned clinopyroxene. The colors are artifacts and are not real mineral colors. Zoning can also be detected using a scanning electron microscope. See, for example, the electron microscope images of zoned plagioclase in Figure 4.38 (Chapter 4).

6.4 Silicate Minerals



6.24 Different ways that silicon

tetrahedra can polymerize

Silicate minerals dominate igneous rocks because silicon and oxygen are the most common elements in magmas. So, in the following discussion we systematically consider the important silicate minerals and groups.

Recall from Chapter 1 that the fundamental building block in silicate minerals is an $(SiO_4)^{4-}$ tetrahedron with oxygen at the corners and silicon in the center. Individual tetrahedra bond to other tetrahedra or to cations to make a wide variety of atomic arrangements. The top drawing in this chart (Figure 6.24) shows a single isolated tetrahedron.

Sometimes aluminum substitutes for silicon, so silicate minerals may contain both (SiO_4) and (AlO_4) tetrahedra. A key property of both silicon and aluminum tetrahedra is that they can share the oxygen anions (O^{2-}) at their corners. When they do this, they form polymers that are various kinds of rings, chains, sheets, or three-dimensional arrangements. Figure 6.24 shows some of the possibilities. (For a slightly different view, see Figure 1.33 in Chapter 1).

In some minerals, $(SiO_4)^{4-}$ tetrahedra are not polymerized. They do not share oxygen atoms, and instead are joined together by bonds to other cations. These minerals, called *isolated tetrahedra silicates*, or *island silicates*, include most importantly minerals of the olivine group.

In a few minerals, especially minerals of the epidote group, tetrahedra join to form pairs. These are the *paired tetrahedral silicates*, sometimes called *sorosilicates* or *butterfly silicates*. In the pyroxenes and other *single chain silicates*, tetrahedra link to create zigzag chains. The amphibole minerals are *double chain silicates*. Micas and clays are *sheet silicates*. In sheet silicates, tetrahedra share three of their four oxygen with other tetrahedra, creating sheets and minerals with layered atomic arrangements.

Finally, the feldspars and quartz are examples of *network silicates*, sometimes called *framework silicates*, in which every oxygen is shared between two tetrahedra, creating a three-dimensional network. The drawing in Figure 6.24 does a poor job of showing this arrangement but the key characteristics are that all oxygen atoms are shared between two tetrahedra and the overall structure is about the same in all directions. The most important framework silicates are quartz and other SiO_2 minerals, and the feldspars. In the feldspars, and a related group of minerals called *feldspathoids*, alkali and alkaline earth elements – mostly Na, K, or Ca – occupy large sites between tetrahedra.

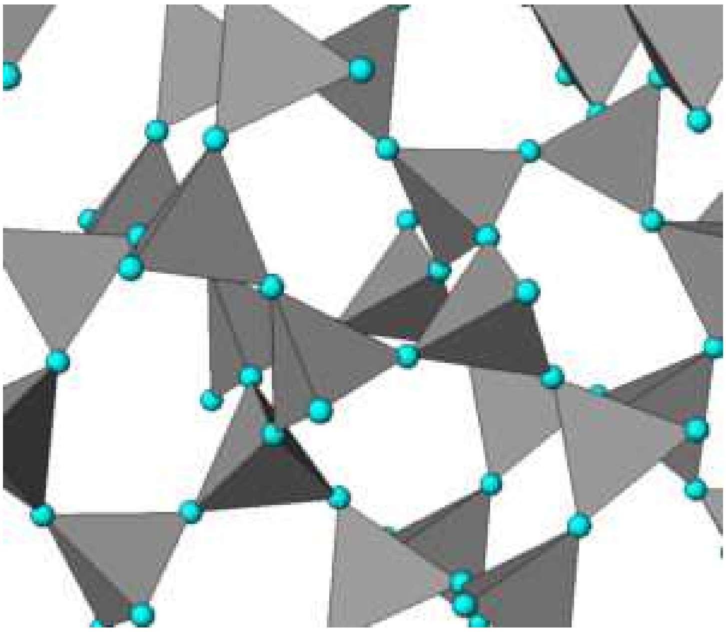
We will start our review of silicate minerals by looking at the SiO_2 polymorphs, the feldspars, and the feldspathoids, and then work our way upwards in the figure above, towards minerals with less polymerization.

6.4.1 SiO_2 Polymorphs

Silica Minerals

SiO_2

α-quartz, *β*-quartz,
stishovite, coesite,
tridymite, cristobalite



6.25 The atomic arrangement in cristobalite

Quartz, like many other minerals, is polymorphic. Mineralogists and chemists have identified more than 10 different silica (SiO_2) polymorphs, but some do not occur as minerals. We briefly looked at the most common of these polymorphs in Chapter 4. All the silica minerals (except stishovite) are framework silicates; the differences between the minerals are the angular relationships between the tetrahedra that comprise them. Figure 6.25 shows the atomic arrangement in cristobalite, one of the high-temperature polymorphs. The blue spheres are oxygen atoms and silicon atoms are at the centers of every gray tetrahedron. For some spectacular scanning electron microscope images of several silica polymorphs, see Figure 12.35 in Chapter 12.

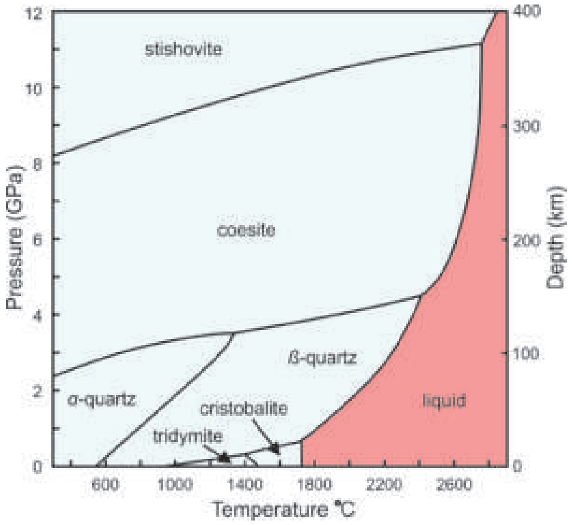
6.26 Common quartz

6.27 A cluster of euhedral quartz crystals from La Libertad, Peru

Common quartz, more properly called *low quartz* (because it has lower symmetry than high quartz), is the only polymorph stable under normal Earth surface conditions, but it has many different appearances. The anhedral specimen seen in Figure 6.26 has a very common look. But euhedral crystals, such as those shown in Figure 6.27, are also common. Some of the different quartz varieties have specific names, such as *milky quartz*, *rose quartz*, *Herkimer diamond*, *amethyst*, and *citrine*. Photos of these were in previous chapters, including:

- Figures 1.8 (Chapter 1) shows a cluster of clear quartz crystals
- Figure 3.4 (Chapter 3) contains a photo of subhedral rose quartz
- Figure 3.32 (Chapter 3) shows a Herkimer diamond
- Figure 3.44 (Chapter 3) show purple amethyst and orange citrine
- Figure 3.61 (Chapter 3) is a photo of anhedral milky quartz
- Figure 4.17 (Chapter 4) shows amethyst in a geode

Silica Polymorph Stability



6.28 Stability fields for different silica polymorphs

For several decades, petrologists have understood that different silica polymorphs occur in different geological settings because they are stable under different pressure-temperature conditions. This phase diagram (Figure 6.28) shows the stability relationships of some SiO_2 polymorphs. The horizontal axis is temperature. The vertical scale on the left gives pressures in gigapascals (GPa), and the scale on the right shows the depths in Earth corresponding to those pressures.

Pressure-temperature (P-T) phase diagrams such as the one seen here show which mineral is stable for any combination of P-T. Solid lines divide pressure-temperature space into *stability fields* where different polymorphs are stable: stishovite, coesite, α-quartz, β-quartz, tridymite, and cristobalite. For example, at 1400 Ĉ and 6 GPa, coesite is the stable polymorph. Low quartz (α-quartz) is the stable phase at low temperature and pressure, including normal Earth surface conditions (which would plot way off to the left on the bottom of this diagram). Low quartz is therefore the most common polymorph. If all rocks maintained and stayed at equilibrium, we would have no samples of any other silica polymorphs to study. However, the other polymorphs sometimes persist and exist metastably at Earth’s surface. (Although given enough time, they usually change into low quartz.)

Stishovite and coesite are dense minerals, only stable at very high pressures — pressures not normally encountered on or in Earth's crust. They are usually associated with meteorite impact craters. Tridymite and cristobalite only exist in certain high temperature silicic volcanic rocks. They require temperatures greater than 900 °C to form. Although not shown in this diagram, just like quartz, tridymite and cristobalite have both high- and low-symmetry polymorphs.

The red field in the phase diagram above (Figure 6.28) shows conditions where silica melts. Melting temperature is greatest at high pressure, and is different for the different polymorphs. So, with cooling, molten SiO_2 will crystallize to form stishovite at high pressure, coesite at somewhat lower pressure, β-quartz at still lower pressure, and cristobalite at 0.0001 GPa (equivalent to atmospheric pressure at Earth's surface). Consider what happens when a volcano erupts and silica-rich magma cools. If stability is maintained, cristobalite will crystallize at about 1725 °C. With further cooling, it will turn into tridymite at about 1460 °C, then into β-quartz at about 950 °C, and become α-quartz at 573 °C. This happens most of the time but occasionally metastable polymorphs can be found in volcanic rocks.

Quartz in Rocks

Essential minerals are minerals that must be present for a rock to have the name that it does, and quartz is an essential mineral in silicic and intermediate igneous rocks, many sediments, and many metamorphic rocks. Quartz is not normally found in mafic igneous rocks because crystallization of mafic minerals such as olivine or pyroxene generally consumes all silica that is available, so there is none left over to form quartz.

6.29 Gray quartz with pink K-feldspar, white plagioclase, and black biotite

Granites contain essential quartz. In silicic plutonic rocks such as granite, quartz is always associated with K-feldspar, commonly in a mosaic pattern similar to what is seen in this photograph (Figure 6.29). The largest of the grains in this view are pinkish K-feldspar about 1 cm across. Quartz is glassy gray. White plagioclase and black biotite are also present.

6.30 Arkose from the Garden of the Gods, Colorado

Quartz is also an essential mineral in sandstone and some other sedimentary rocks. Quartz is the only mineral present in some sandstones or cherts. But, sandstone may also contain significant amounts of other minerals including feldspar or clay, and sometimes pebbles or rock fragments. Figure 6.30 shows an arkose, a feldspar-containing variety of sandstone, composed of gray quartz, pinkish-orange feldspar, and some obvious quartz pebbles up to 5 mm across.

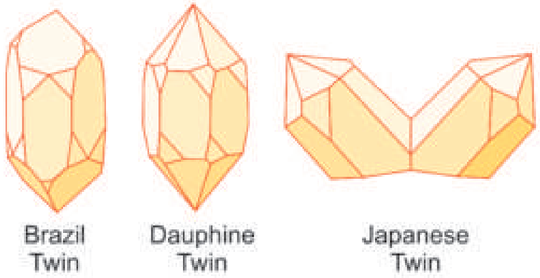
Quartz cannot exist in rocks containing corundum (Al_2O_3), because the two minerals would react to form an aluminosilicate mineral of some sort. It cannot exist in rocks containing feldspathoids (leucite, nepheline, or analcime) because quartz and feldspathoids react to give feldspars. For similar reasons, quartz is absent or minor in many alkali-rich igneous rocks and in rocks containing the oxide mineral spinel ($MgAl_2O_4$).

6.31 Quartz veins cutting through a weathered granite, Kings Canyon National Park, California

6.32 Amethyst (quartz) in a geode from Uruguay

Quartz may crystallize from silica-saturated water. The photograph on the left above (Figure 6.31) shows white quartz veins cutting through altered granite in Kings Canyon National Park, California. The quartz formed when hot hydrothermal water infiltrated the rock along fractures before the rock was uplifted to the surface and eventually weathered. Temperature need not be high, however, for quartz to precipitate. For example, the amethyst (purple quartz) in the geode shown in Figure 6.32 precipitated from water at low temperature. Figure 4.17 (Chapter 4) shows another example of quartz in a geode.

Quartz Twins



6.33 Different kinds of twinning of quartz

Most quartz crystals are twinned, but the twinning can be impossible to see or easily overlooked. The drawings seen here (Figue 6.33) show the three major ways that quartz twins. Brazil twins and Dauphine twins are penetration twins, and Japanese twins are contact twins. All three are generally growth twins but can also form in other ways. Some quartz crystals exhibit more than one kind of twinning.

Quartz twinning video

Brazil and Dauphine twins are distinguished by symmetry relationships between crystal faces of particular shapes, sometimes by identifying *striations* (fine lines on crystal faces that developed when the crystal formed), but sometimes are difficult to tell apart. Click on the crystal drawing (right) to see a 15 second video showing Dauphine twinning; the striations on the crystal faces are also apparent. The two large quartz crystals in Figure 6.27, earlier in this chapter, show an example of Japanese twinning.

6.4.2 Feldspars

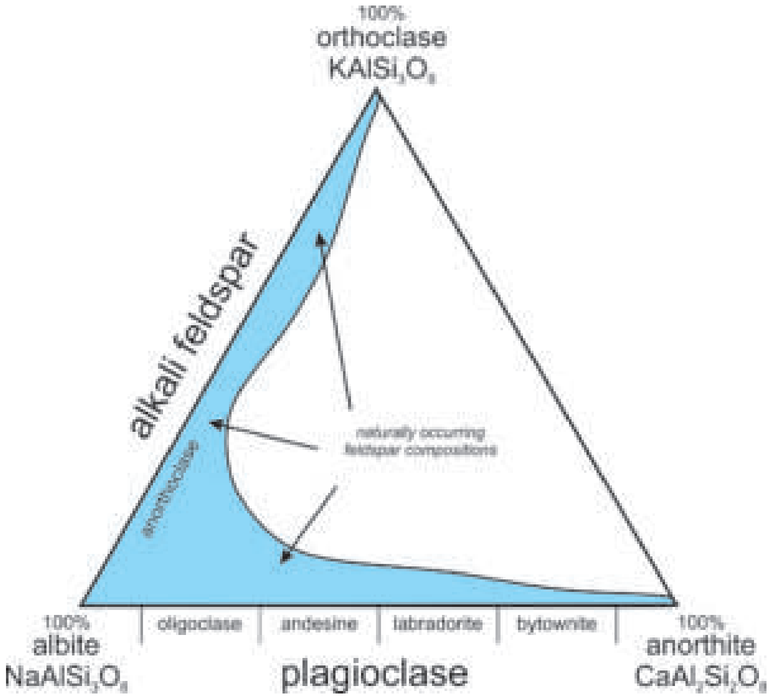
Feldspars

$(Ca,Na,K)(Si,Al)_4O_8$

Most important end members

anorthite	$CaAl_2Si_2O_8$
albite	$NaAlSi_3O_8$
orthoclase	$KAlSi_3O_8$

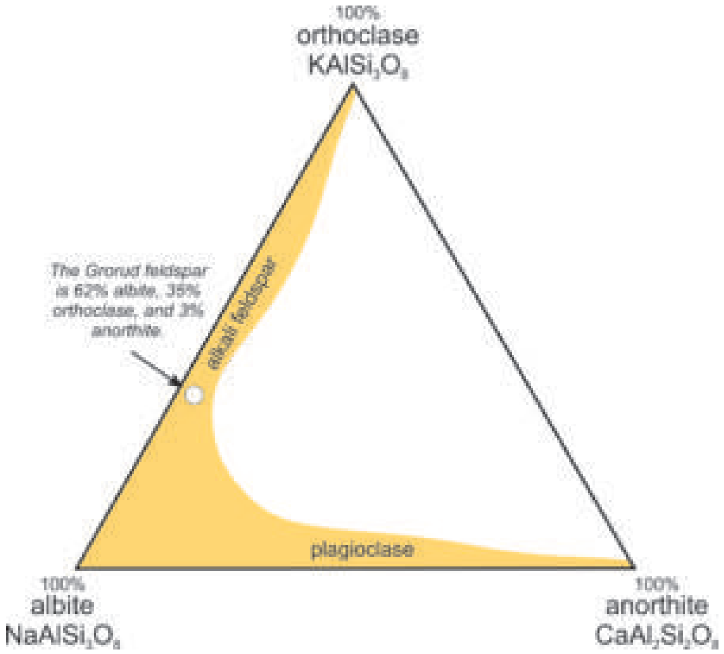
Feldspars are the most abundant minerals in Earth’s crust, in part because they contain six of the seven most abundant elements in the crust. They are widespread and are essential minerals in many igneous, metamorphic, and sedimentary rocks. Feldspars are solid-solution minerals and have the general formula $(Ca,Na,K)(Si,Al)_4O_8$. Rarely, they contain significant amounts of other elements such as Ba, Sr, B, or Fe. For most purposes, we consider them to be ternary solutions, which means we can describe their composition in terms of three end members and plot them on diagrams such as the one shown in Figure 6.34 and in Figure 2.22 (Chapter 2). The important feldspar end members are *albite* ($NaAlSi_3O_8$), *anorthite* ($CaAl_2Si_2O_8$), and *orthoclase* ($KAlSi_3O_8$).



6.34 Naturally occurring feldspars

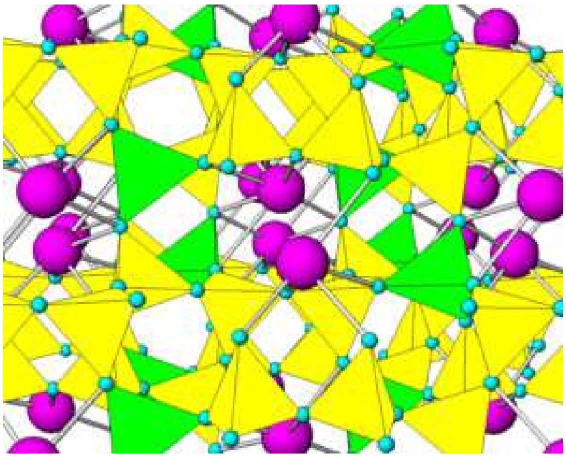
In Figure 6.34, the blue region shows the compositions of naturally occurring feldspars. Natural feldspars form two distinct series, the *alkali feldspar series* and *plagioclase*, both labeled on this triangular diagram. Alkali feldspar, mainly solutions of orthoclase and albite, sometimes contains up to 15 wt % anorthite. Plagioclase, often called *plagioclase feldspar*, is mostly a solid solution of albite and anorthite, although it may contain up to 10 wt % orthoclase. We call any feldspar with composition near $NaAlSi_3O_8$, *albite*, and one with composition near $CaAl_2Si_2O_8$, *anorthite*, even if other components are present. Intermediate plagioclase compositions are commonly given specific names (labeled in the figure): *oligoclase*, *andesine*, *labradorite*, and *bytownite*. Labradorite, for example, is plagioclase with composition between 70% anorthite-30% albite and 50% anorthite-50% albite. Labradorite may also contain a small amount of orthoclase. Compositions between plagioclase and alkali feldspar (that would plot in the white part of the triangle) are rare or do not exist.

Confusion sometimes arises because the names of some composition ranges are the same as the names of feldspar end members (albite, anorthite, orthoclase). Orthoclase, for example, is the name given to end member $KAlSi_3O_8$. It is also the name we give to any feldspar that is >90 $KAlSi_3O_8$. The alkali feldspars, with compositions between $NaAlSi_3O_8$ and $KAlSi_3O_8$ have not been divided into as many bins as plagioclase feldspars. The term *anorthoclase*, however, is often used to refer to alkali feldspars with intermediate compositions (10-36% $KAlSi_3O_8$ with the rest being mostly $NaAlSi_3O_8$).



6.35 The composition of the Grorud feldspar

The triangular diagram in Figure 6.35 is similar to the one in Chapter 2 (section 2.5.1); it shows the composition of a feldspar from Grorud, near Oslo, Norway. This feldspar is an example of anorthoclase. It has a composition of about $(Ca_{0.03}Na_{0.62}K_{0.35})(Al_{1.03}Si_{2.97})O_8$, so it contains 3 mol % anorthite ($CaAl_2Si_2O_8$), 62 mol % albite ($NaAlSi_3O_8$), and 35 mol % orthoclase ($KAlSi_3O_8$). For this feldspar, $X_{An} = 3$, $X_{Ab} = 62$, and $X_{Or} = 35$, where the symbol X stands for *mole fraction*. Often, we describe the compositions of feldspars by using abbreviations with subscripts. Thus, the Grorud feldspar has composition $An_3Ab_{62}Or_{35}$.



6.36 The arrangement of atoms in feldspar

Like quartz, feldspars are framework silicates. Unlike quartz, feldspars contain both SiO_4 and AlO_4 tetrahedra. As an example, Figure 6.36 shows the atomic arrangement in albite. The purple atoms are sodium, and the yellow and green tetrahedra are (SiO_4) and (AlO_4), respectively. In all feldspars, Na, K, or Ca occupy spaces between tetrahedra.

Feldspars in Igneous Rocks

Most igneous rocks contain feldspar of some sort, but the kind of feldspar varies with rock composition. In silicic igneous rocks, such as granite, plagioclase is absent or subordinate to K-rich alkali feldspar. If plagioclase is present, it is always albite-rich. Similarly, in mafic rocks, alkali feldspar is not normally present but plagioclase is common. Because mafic rocks contain much more Ca than Na, the plagioclase in them is generally anorthite-rich. Intermediate igneous rocks nearly always contain both feldspars.

6.37 Albite crystals from the Ziller Valley, Austria

6.38 Anorthite crystals from near Mt. Vesuvius, Italy

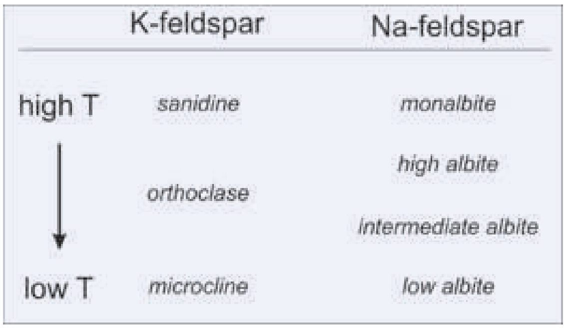
The two photos above show light colored albite crystals from a classic locality in Austria and anorthite crystals from near Naples, Italy. These are both examples of plagioclase.

Feldspars with compositions close to $KAlSi_3O_8$ are generally called *K-feldspar,* or *K-spar*. But, K-feldspar has three polymorphs with slightly different atomic arrangements: *orthoclase*, *microcline*, and *sanidine*. Photos of each are shown below in Figures 6.39, 6.40, and 6.41. In these photos the polymorphs have different colors, but color is not a good diagnostic property because the different polymorphs all come in many colors. Note the well developed penetration twins in the sanidine specimen.

6.39 Orthoclase from Minas Gerais, Brazil

6.40 Microcline from Araçuai, Brazil

6.41 Twinned sanidine from Monts-Dore massif, France



6.42 Different feldspar polymorphs are stable at different temperatures

The different K-feldspar polymorphs are stable under different conditions. Sanidine forms in high temperature rocks; orthoclase and microcline form in lower temperature rocks (Figure 6.42). Sanidine commonly crystallizes from silicic lava but may change into orthoclase and, perhaps, microcline if the lava cools relatively slowly. Just about all microcline forms by recrystallization of sanidine or orthoclase.

Like K-feldspar, Na-feldspar forms different polymorphs, with different atomic arrangements, depending on temperature (Figure 6.42). At high temperatures, just below albite's melting point, we call the feldspar *monalbite*. Three other polymorphs exist at lower temperatures, all generally called *albite*. Unlike the SiO_2 polymorphs, the differences in atomic structure between the feldspar polymorphs are not great and the boundaries on phase diagrams are poorly known. And, when high-temperature feldspars change into low-temperature ones because of cooling or reequilibration at Earth's surface, crystal shape may not change even though atoms move and bonds adjust. Distinguishing between the different Na-feldspar polymorphs can be difficult or impossible without X-ray analysis.

Twinning of Feldspars

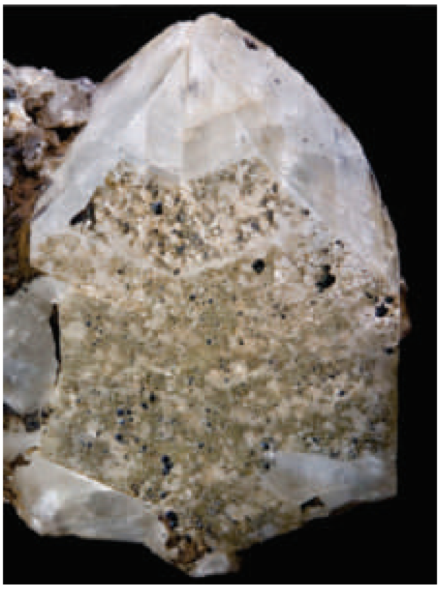
6.43 Example of polysynthetic twinning in feldspar

Figure 6.43 shows a plagioclase crystal with twin striations across its top. The striations derive from a type of polysynthetic twinning called *albite twinning*. The atomic arrangements in alternating domains are slightly different and are reflections of each other. See the drawing of albite twinning in Figure 4.43 (Chapter 4) and look at the photo in Figure 4.44 (Chapter 4) for another example of this kind of twinning.

Twinning occurs in all kinds of feldspars but is generally not visible with the naked eye. So, although a feldspar crystal appears homogeneous, it may be composed of two or more twin domains. We most easily see feldspar twinning when using a polarizing microscope to view a feldspar in a thin section. The different domains are visible because they have different optical properties.


6.44 Carlsbad twin


6.45 Baveno twin


6.46 Mannebach twin

Feldspars twin in several different ways that have different names, for example Carlsbad, Baveno, or Manebach twinning, shown in the three photos above (Figures 6.44, 6.45, and 6.46). The crystals seen in these figures are about 4 cm, 4 cm, and 7 cm tall, respectively. These three kinds of twins are simple twins involving only two twin domains.

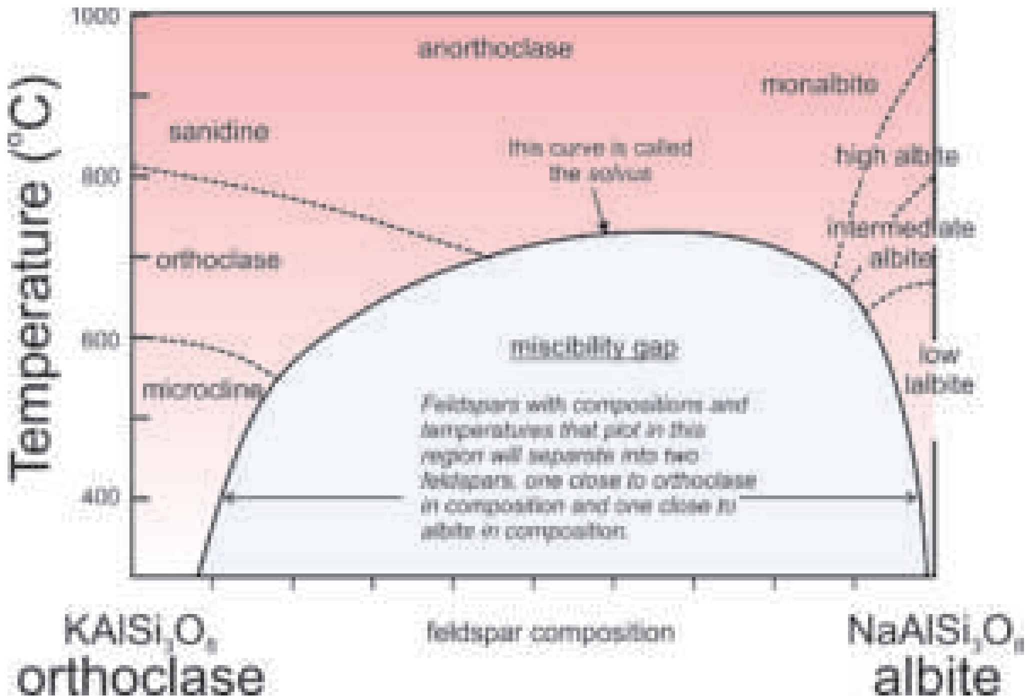
Carlsbad twins are penetration twins common in orthoclase, and sometimes in plagioclase. The photo above (left) shows Carlsbad twinning with two orthoclase crystals that appear to have grown through each other. Figures 4.41 (Chapter 4) and 4.42 (Chapter 4) also show Carlsbad twinning. *Baveno twins* are contact twins that occur most often in orthoclase and microcline. The photo above (center) shows a feldspar with a Baveno twin. A vertical composition plane separates the left and right sides of the crystal. Manebach twins are most common in orthoclase. The photo on the right, above, is a crystal with a *Manebach twin*. The reentrant angle (two small crystal faces forming a vee shape that points into the crystal) in its top shows where the near-vertical composition plane passes through the crystal. Both Baveno and Manebach twins are rarer than Carlsbad twins. When both are present, Carlsbad and Manebach twinning are diagnostic for orthoclase.

Polysynthetic twins, such as the twins in Figure 6.43 (above), are common in plagioclase and sometimes visible with the naked eye. *Albite twinning* is one kind; *pericline twinning* is another. The difference between the two is that domains in albite twins are related by reflection, and domains in pericline twins are related by rotation. Albite twinning is a diagnostic property for plagioclase. Figures 4.43 (Chapter 4)and 4.44 (Chapter 4) show additional examples of albite twinning. Sometimes albite twinning combines with Carlsbad twinning to produce complex crystals, but it is still generally recognizable.

6.47 Twinning in microcline

Microcline is the stable K-feldspar polymorph at normal Earth surface conditions. So, other K-feldspars may turn into microcline. Pericline twinning is produced during the polymorphic transformation of sanidine or orthoclase to microcline, and most microcline exhibits both pericline and albite twinning. The combined twinning produces typical *microcline twinning*, sometimes called *cross-hatched twinning* or *tartan twinning*, but we can only see this twinning with a polarizing microscope. Figure 6.47 shows cross-hatched twinning (albite perpendicular to pericline twinning) when viewed with a polarizing microscope. The colors are artifacts and are not the true colors of the domains. The field of view is 2 mm across, and the veins that cut across the field of view contain albite.

Solvus and Miscibility Gaps



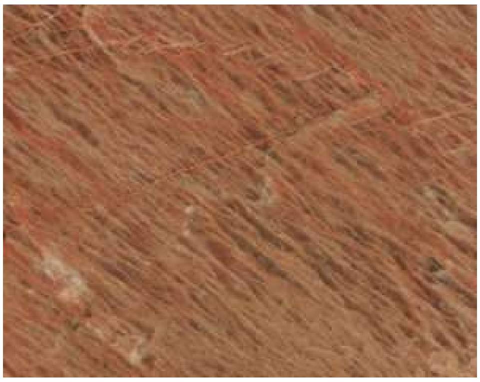
6.48 Phase diagram and solvus for K-Na feldspar at 1 atm pressure

Consider alkali feldspars that are solutions of $KAlSi_3O_8$ and $NaAlSi_3O_8$. At high temperature, as long as they are not so hot that they melt, these feldspars can have any composition between sanidine ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$), and may be anorthoclase (part way between the end members). However, as shown in this phase diagram (Figure 6.48), intermediate compositions (anorthoclase) are stable only at high temperatures. At lower temperatures, instead of having one intermediate feldspar, anorthoclase unmixes to produce two separate feldspars, one K-rich and the other Na-rich. This happens because a miscibility gap exists between albite and orthoclase. A *miscibility gap* is a composition range within which no single mineral is stable under a particular set of pressure-temperature conditions. It is the gray region shown in the phase diagram. The curve above and around the miscibility gap is called the *solvus*.

6.49 Fat separating from chicken broth with cooling

Miscibility gaps are common in mineral systems because some elements do not mix well under all conditions. Many mineral series show complete miscibility at high temperatures, meaning that all compositions are stable. At low temperatures, partial or complete *immiscibility* restricts possible compositions. We might make an analogy to a pot of homemade chicken soup that separates into two compositions (fat and chicken broth) with cooling (Figure 6.49).

We call the process of a single feldspar separating into two compositions *exsolution*, equivalent to *unmixing*. If an intermediate-composition alkali feldspar cools rapidly, it may not have time to exsolve. Thus, we have examples of anorthoclase to study. On the other hand, if cooling is slow, the feldspar will unmix. This may result in separate grains of K-feldspar (orthoclase or microcline) and Na-feldspar (albite) developing in a rock. More often, it results in alternating layers or irregular zones of orthoclase and albite within individual crystals. If the layers or zones are planar or nearly so (appearing long and thin in thin section), we call them *exsolution lamellae*. The lamellae are sometimes visible with the naked eye, but frequently require a microscope to detect. The figure below (Figure 6.50) shows the surface of a once homogeneous feldspar that has separated into two kinds of lamellae, one K-rich and one Na-rich.



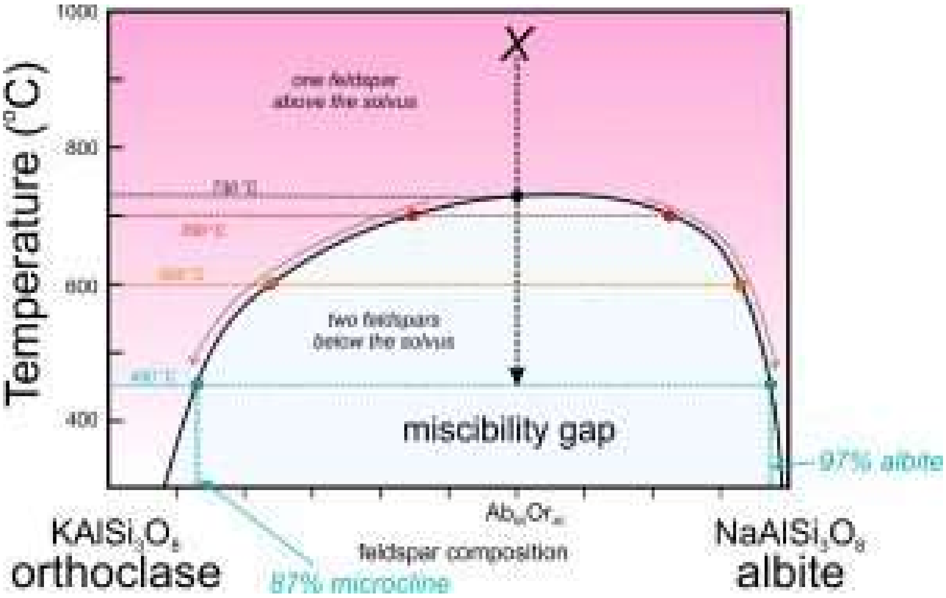
6.50 Perthite

If the original feldspar was K-rich, most of the layers will be K-rich feldspar. After it exsolves, it is technically called *perthite*. If the original feldspar was Na-rich, most of the layers will be Na-rich, and after exsolution, it is technically called *antiperthite*. For practical purposes, most mineralogists call any exsolved alkali feldspar *perthite*, because they need compositional information to distinguish perthite from antiperthite. The photo seen in Figure 6.50 shows perthite with salmon colored veinlets of K-feldspar and lighter colored veinlets of Na-feldspar. This is a polished slab of rock; the view is 4.5 cm across.

6.51 Labradorite from Ylämaa, Finland

Because they exsolve, alkali feldspars form what is called a *limited solid solution* at lower temperatures. Intermediate compositions between orthoclase and albite do not exist. In contrast, intermediate plagioclase between albite and anorthite is common. At high temperatures all compositions are stable and, with cooling, there is generally no significant exsolution. But, several small solvi exist at very low temperature which – if cooling is slow enough – can result in microscopic unmixing. The exsolution may give the feldspars an iridescence or a play of colors that helps to identify them. Labradorite, for example, is identified by its *labradorescence*, a bluish schiller, caused by exsolution. Figure 6.51 show several examples of labradorite; see also Figure 3.53 (Chapter 3). Because exsolution, if present in plagioclase, is on a very fine scale, mineral properties are relatively homogeneous. So, for most purposes, we can ignore the presence or absence of exsolution in plagioclase.

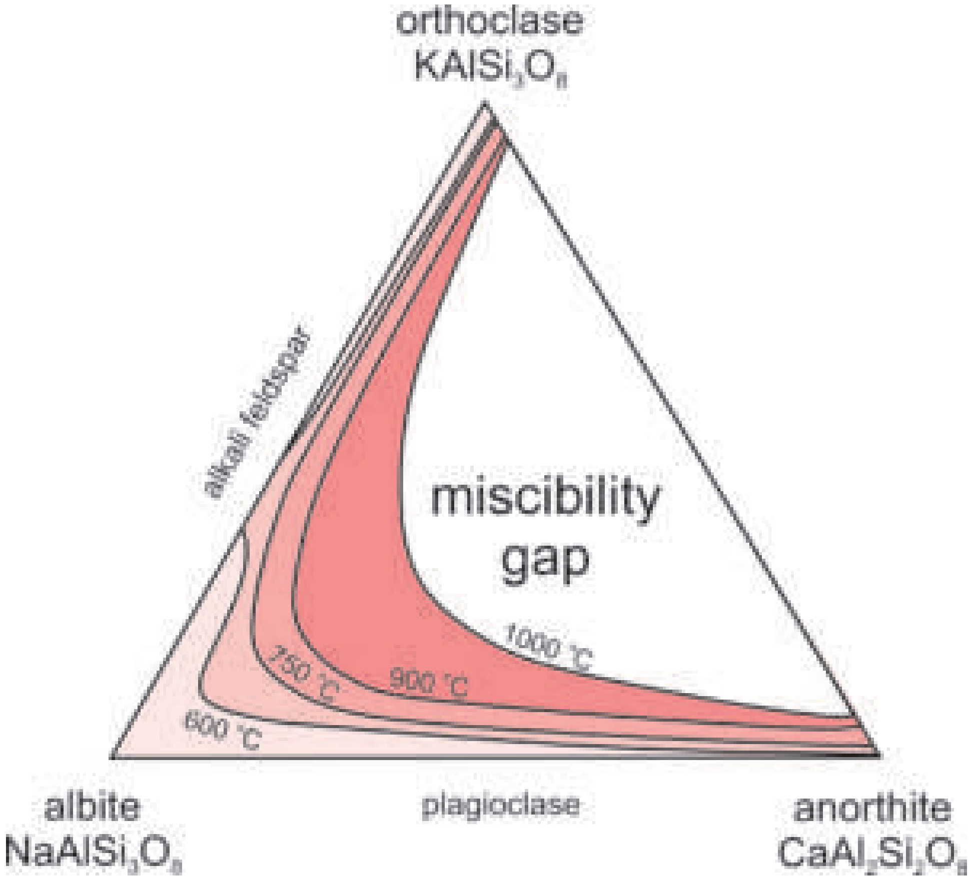
● Box 6-2 Miscibility Gaps



6.52 Alkali feldspar phase diagram

This figure (6.52) is a slight modification of the temperature-composition (T-X) phase diagram in Figure 6.48. Consider a feldspar of composition $Ab_{60}Or_{40}$ (marked with an X on the diagram). At high temperature, it will exist as one alkali feldspar (anorthoclase). As it cools to low temperature it separates into two feldspars beginning at about 730 °C. At 700 °C, for example, the compositions of the two feldspars are shown as red dots. At 600 °C, the two compositions are shown as orange dots. And at 450 °C, the compositions are shown by light blue dots. The compositions start at $Ab_{60}Or_{40}$ and then follow the solvus toward orthoclase and albite (gray arrows) as temperature decreases. At 450 °C, the composition of the albite-rich feldspar will be 97% $NaAlSi_3O_8$, while that of the orthoclase-rich feldspar will be about $Ab_{13}Or_{87}$. The K-feldspar polymorph stable at low temperature is microcline. So, if the feldspar cools completely, the final result will be a mix of microcline-rich feldspar and nearly pure albite, and because the overall composition is closer to albite than orthoclase, there will be more albite than microcline. The likely result will be anitperthite – a single feldspar crystal that contains exsolution lamellae of different compositions

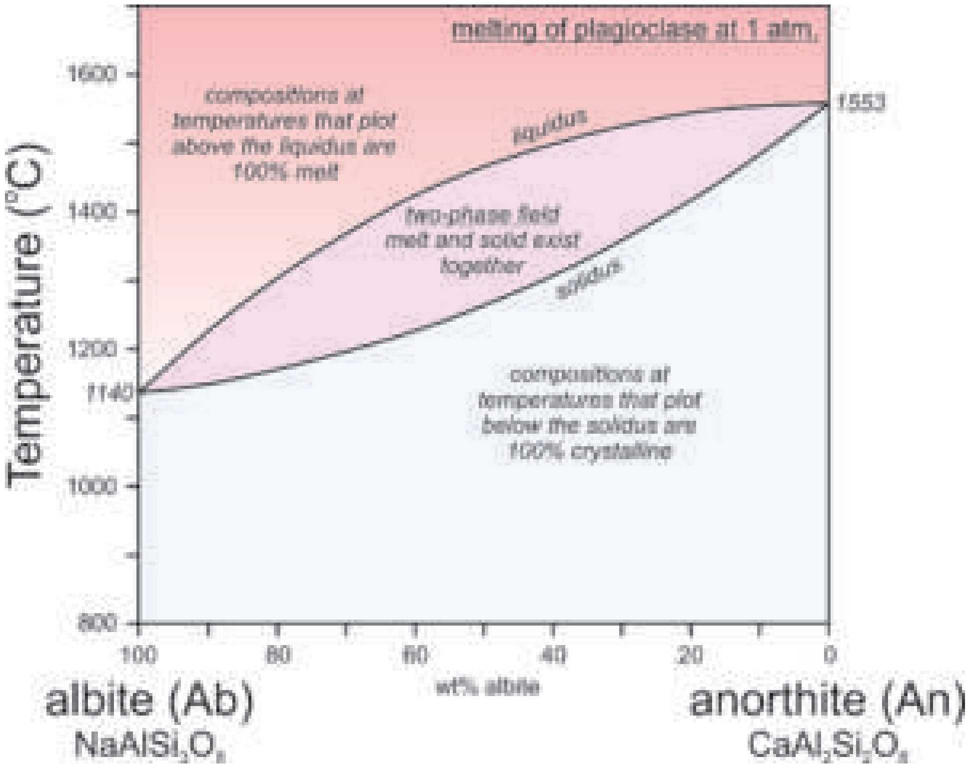
Exsolution and Ternary Feldspars



6.53 Feldspar ternary diagram with miscibility gaps at different temperatures

Above, we considered exsolution in alkali feldspars, K-Na feldspars. But, what about ternary feldspars, K-Na-Ca feldspars? As noted, both alkali feldspar and plagioclase exist in a wide range of igneous rocks. But, feldspars with compositions in the middle of the feldspar ternary (shown in white in Figure 6.53) are rarely found because they unmix to form coexisting alkali feldspar and plagioclase. There is a large miscibility gap in the ternary system. At 1000 °C all feldspar compositions, except those that plot in the white region, are stable. But, as temperature decreases the miscibility gap grows wider (show by the temperature contour lines), and if temperature gets as low as 600 °C, feldspar is limited to compositions shown in the lightest pink in this figure.

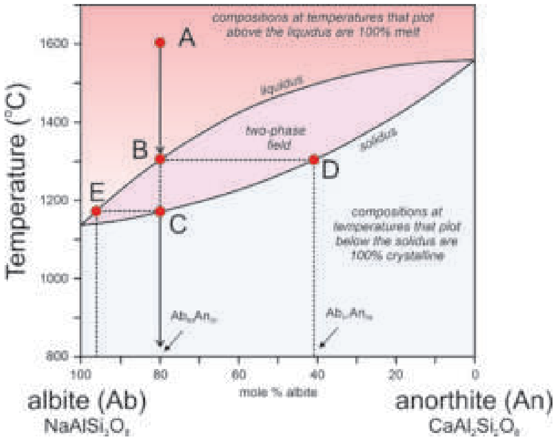
Feldspar Crystallization – Plagioclase



6.54 Plagioclase crystallization at 1 atm pressure

The crystallization temperatures of the two plagioclase end members are different. Albite crystallizes at 1140 °C and anorthite crystallizes at 1553 °C (Figure 6.54). For compositions between albite and anorthite, crystallization is complicated (see Box 6-3) because when an intermediate feldspar begins to crystallize, the first crystal produced is more calcium-rich than the original melt itself. In effect, the anorthite part of the feldspar crystallizes faster than the albite part. If an intermediate plagioclase is partially crystallized, the melt will become more albite-rich. The feldspar that crystallized will therefore have to be more anorthite-rich than the original melt. So, end-member albite and anorthite crystallize *congruently*. This means they crystallize at specific temperatures and the crystals are the same composition as the melt. But, intermediate composition feldspars crystallize *incongruently*. They crystallize over a range of temperature and the crystal produced is not the same composition as the melt until crystallization is complete. The temperature at which crystallization begins for a specific composition feldspar is shown by the *liquidus* curve in the diagram above. Crystallization starts and then continues until temperature reaches the *solidus*. At temperatures between the liquidus and solidus, in the *two-phase field*, crystals and melt exist together and are of different compositions.

● Box 6-3 The Plagioclase Phase Diagram and Fractional Crystallization



6.55 Plagioclase crystallization at 1 atm pressure

Figure 6.55 is modified from Figure 6.54, the T-X phase diagram describing plagioclase melting and crystallization at 1 atm pressure.

At the highest temperatures, above the liquidus, plagioclase of any composition will be melted. At the lowest temperatures, below the solidus, any plagioclase composition will be entirely crystalline. In between, in the two-phase field, solid crystals and melt will coexist but be of different compositions. This is best described by example.

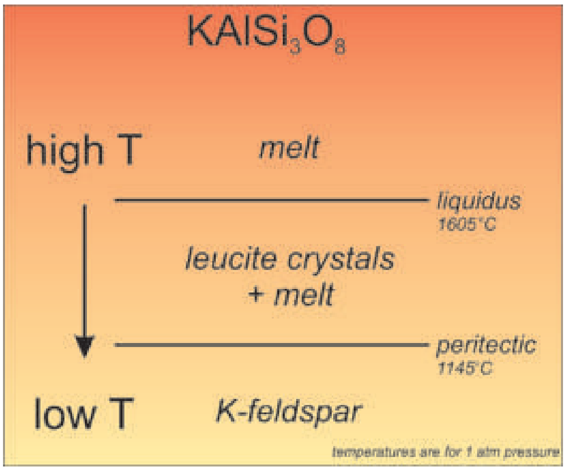
Point A represents an albite-rich feldspar melt at 1,600 °C. The melt has the same composition as plagioclase that is 80% albite and 20% anorthite ($Ab_{80}An_{20}$) but is completely molten. As the melt cools, at about 1,300 °C, the first crystals begin to form (point B). A horizontal line at 1,300 °C intersects the liquidus at the melt composition (Point B) and the solidus at the initial crystal composition (Point D). Thus, when crystallization begins, the liquid still has its original composition, but the crystals that start to form are considerably more anorthite-rich than the melt. They have composition $Ab_{41}An_{59}$.

As the melt continues cooling, crystals continue to form, but they change composition from D to C, following the solidus as temperature decreases. Previously crystallized plagioclase reacts with the melt, so crystal composition changes with cooling and all crystals are homogeneous and have the same composition. A horizontal line can be drawn at any temperature. The intersection of the line with the solidus indicates plagioclase composition and the intersection of the line with the liquidus indicates the composition of the remaining melt. Because the crystals are more anorthite-rich than the melt, the melt becomes more albite-rich as crystallization continues.

As crystallization goes to completion, plagioclase crystals change in composition from $Ab_{41}An_{59}$ (Point D) to $Ab_{80}An_{20}$ (the composition of the original melt). Simultaneously, melt composition changes from $Ab_{80}An_{20}$ to an extremely albite-rich composition ($Ab_{96}An_{04}$), indicated by Point E on the diagram. At about 1,165 °C, the last drop of melt will crystallize. And, if everything stayed in equilibrium, after complete crystallization, all plagioclase crystals would have the same composition, which must equal that of the original melt.

So, if the crystallization process always went to completion, plagioclase crystals would always end up the same composition as the original melt. However, several things can disrupt this equilibrium. Often crystallization occurs so fast that crystals do not have time to react with the melt as they form. In such cases, the first plagioclase to crystallize is preserved in the centers of large crystals. The crystals are compositionally zoned, the outer zones being more albite-rich. Another complication arises if crystals and melt get separated during the crystallization process. This may occur due to crystal settling, or because remaining melt “squirts off” after the melt is partially solidified. In such cases, crystal-melt equilibrium is not maintained. Both processes are kinds of *fractional crystallization* that can create melts of different compositions from their parent melts.

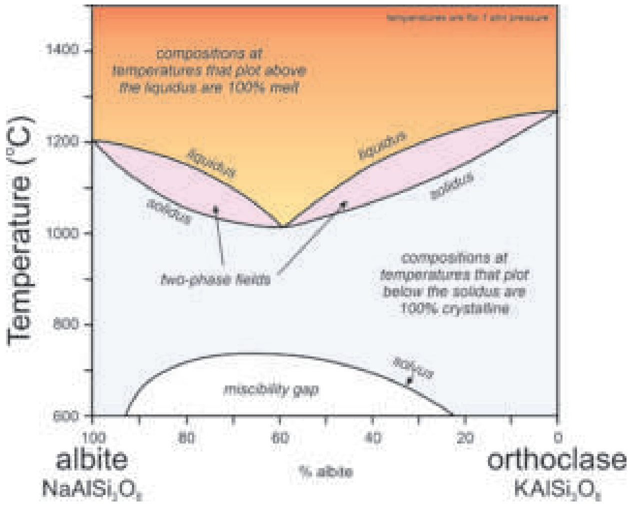
Feldspar Crystallization – K-feldspar



6.56 Incongruent crystallization of K-feldspar

K-rich feldspars can crystallize from a magma, but they exhibit an interesting kind of incongruent crystallization. Consider a melt with composition $KAlSi_3O_8$. If it cools, it will eventually reach the liquidus temperature and crystallization will begin. But, as shown here (Figure 6.56), the initial crystals formed will be leucite ($KAlSi_2O_6$) instead of K-feldspar ($KAlSi_3O_8$). So, as crystallization proceeds, the remaining melt will become more SiO_2-rich. Finally, when the temperature reaches what is called the *peritectic temperature*, the leucite crystals will react with the remaining melt to produce K-feldspar and all will be solid. The difference between liquidus and peritectic temperatures is about 400 °C depending on pressure. If everything stays in equilibrium, we can ignore the temporary presence of leucite crystals. But, sometimes liquid and crystal become separated and leucite may be left behind.

Feldspar Crystallization – Alkali Feldspars



6.57 Melting and crystallization of alkali feldspars

The discussion above is directed at crystallization of K-feldspar, but most alkali feldspars are solid solutions between orthoclase and albite. They are $(K,Na)AlSi_3O_8$ feldspars. This complicates crystallization relationships considerably. The phase diagram in Figure 6.57 ignores the incongruent crystallization that would complicate the left side at high temperatures. Assuming that leucite does not crystallize, or that we can ignore it, the alkali feldspar series involves a pair of two-phase fields, similar to the two-phase field on the plagioclase phase diagram (Figure 6.54). There is a temperature minimum (at about 1000 Ĉ) for a composition of about $Ab_{60}Or_{40}$ – this is the lowest temperature where melt can exist. All other compositions are completely crystallized at this temperature.

If melt and crystals stay in equilibrium, when the temperature drops below 1000 Ĉ, any composition alkali feldspar will be entirely crystalline and will have the same composition as the original melt. However, the solvus and miscibility gap at lower temperature mean that with more cooling, intermediate composition feldspars will exsolve. They will separate into an albite-rich feldspar and an orthoclase-rich feldspar. The likely result is that perthite will form. See Box 6-2 for further discussion.

6.4.3 Feldspathoids

Feldspathoids

Some important species

analcime	$NaAlSi_2O_6 \bullet H_2O$
leucite	$KAlSi_2O_6$
nepheline	$NaAlSiO_4$
sodalite	$Na_4(Al_3Si_3)O_{12}Cl$

The *feldspathoid* minerals are framework silicates similar to feldspars in many of their properties. They are, however, much less common. Feldspathoids are a family of about a dozen minerals; they are all Na-, K-, and Ca-aluminosilicates. The family is not like other mineral groups, whose members are related by similar atomic arrangements and chemistries. Instead these minerals are grouped together because of their relationship to feldspars. The blue box lists some examples of feldspathoids and their formulas.

6.56 Analcime from Martinique; image is 16 cm across

6.57 Leucite from Brazil

6.58 Nepheline

6.59 Sodalite with calcite from Afghanistan

The photos above in Figures 6.58 to 6.61 show the most common feldspathoids. They have compositions that are, for the most part, equivalent to silica-deficient feldspars. These minerals commonly crystallize from magmas that are relatively low in SiO_2 or that contain more Na, K, and Al than can fit into feldspars. These minerals have large openings in their atomic arrangements that allow the minerals to contain significant amounts of large anions and molecular anions, including chlorine, carbonate, and sulfate. They often occur with feldspars, and also with mafic minerals including amphiboles, olivine, and pyroxenes, but never with quartz. They are restricted to quartz-free rocks because they will react with quartz to produce feldspars by reactions such as:

$NaAlSi_2O_6 \bullet H_2O + SiO_2 = NaAlSi_3O_8 + H_2O$
analcime + quartz = albite + vapor

$KAlSi_2O_6 + SiO_2 = KAlSi_3O_8$
leucite + quartz = orthoclase

$NaAlSiO_4 + 2\ SiO_2 = NaAlSi_3O_8$
nepheline + 2 quartz = albite

Analcime, a zeolite, is often considered to belong to the feldspathoid family. Other important feldspathoids include leucite, nepheline, sodalite, and lazurite. Leucite is a rare mineral found in K-rich volcanic rocks. It is unknown in plutonic, metamorphic, or sedimentary rocks. Nepheline is a common mineral in syenite and other silica-poor volcanic or plutonic igneous rocks. Leucite and nepheline are usually associated with K-feldspar. Sodalite crystallizes from alkali-rich magmas and is also found in some metamorphosed carbonate rocks. Analcime also can crystallize from a magma, but it more commonly forms as a secondary mineral in vugs, cracks, or veins. Occasionally it is found as a secondary mineral in sandstones or tuffs. When it crystallizes from a magma, it is typically associated with olivine, leucite, and perhaps sodalite. When it is secondary, other low-temperature minerals, including zeolites or prehnite, often accompany it.

6.4.4 Micas

Micas

$(K,Na,Ca)(Al,Mg,Fe)_{2\text{-}3}(Si,Al)_4O_{10}(OH)_2$

general formula: $X\ Y_{2\text{-}3}Z_4O_{10}(OH)_2$

Most important end members

muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
annite	$KFe_3(AlSi_3O_{10})(OH)_2$
phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$

Others

margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$
paragonite	$NaAl_2(AlSi_3O_{10})(OH)_2$
lepidolite	$K(Li,Al)_2(AlSi_3O_{10})(OH)_2$

We just looked at framework silicates. In those minerals, all four oxygen in SiO_4 and AlO_4 tetrahedra are shared with another tetrahedron. This is what creates the 3-dimensional framework. In sheet silicates, tetrahedra only share three out of four of their oxygen with adjacent tetrahedra. The most important groups of minerals within the sheet silicate subclass are micas, chlorites, and clays. We will consider only the micas and, to a lesser extent, chlorites, in this chapter and defer discussion of clay minerals to the chapter on sedimentary rocks and minerals.

Micas have the general formula $XY_{2-3}Z_4O_{10}(OH)_2$. Some specific formulas are given in the blue box above. The X atoms are most often K and, less commonly Na or Ca, or rarer elements. If the X atom is K or Na, we call the mica a *common mica*, if it is Ca (*e.g.*, in margarite), we call the mica a *brittle mica*. Y atoms are generally Al, Mg, or Fe, and less often Mn, Cr, Ti, or Li. Z atoms are mostly Si, with lesser amounts of Al, and even lesser amounts of Fe or Ti. Additionally, some Cl or F may substitute for (OH). So, micas have highly variable chemistry. Structurally, micas are classified as *dioctahedral* if the number of Y atoms is 2, and *trioctahedral* if the number of Y atoms is 3. Intermediate micas, part way between dioctahedral and trioctahedral, do not exist. Of the micas listed in the box, muscovite, margarite, paragonite, and lepidolite are all dioctahedral; annite and phlogopite are trioctahedral. The photos below show examples common micas.

 6.61 Muscovite mass from Brazil. 6 cm wide.	 6.62 Biotite on pink calcite from Quebec. The specimen is 10cm tall.	 6.63 Flakes of brown phlogopite in calcite from Vietnam

6.64 Margarite with green chlorite from the classic locale at Chester, Massachusetts. The specimen is about 6cm tall.

6.65 Paragonite with blue kyanite and brown staurolite from Switzerland. The specimen is 10 cm tall.

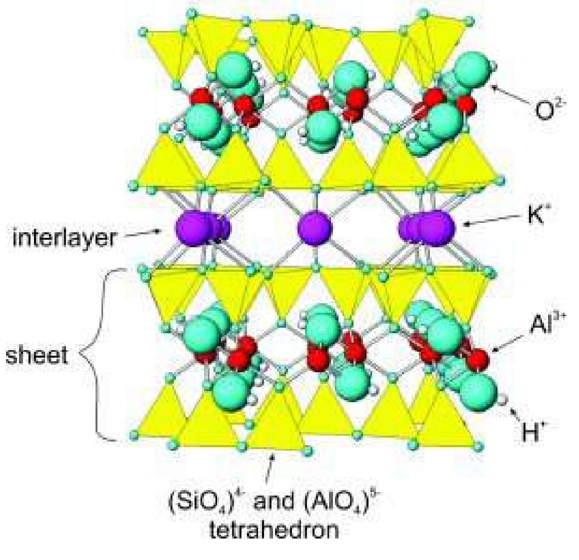
6.66 Lepidolite from Brazil, 6cm across.

By far, the most abundant micas are muscovite and biotite. *Biotite* is the name we use for micas that are mosty solid solutions of phlogopite and annite. Muscovite is more common than biotite, but both occur in a wide variety of igneous and metamorphic rocks. Muscovite (Figure 6.62, above) is dioctahedral and is usually close to the end-member composition $KAl_2(AlSi_3)O_{10}(OH)_2$. Without chemical analysis, it is sometimes hard to distinguish it from other silvery dioctahedral micas such as margarite (Figure 6.65), paragonite (Figure 6.66), and lepidolite (Figure 6.67). Biotite (Figure 6.63), $K(Fe,Mg)_3(AlSi_3)O_{10}(OH)_2$, is trioctahedral and may have any composition between the two end members annite and phlogopite (see formulas in the blue box above). Biotite sometimes incorporates a very small amount of muscovite as well.

Micas react to form clays and other minerals when exposed to prolonged weathering, and are therefore absent from most sedimentary rocks. Biotite, and especially muscovite, are relatively Al- and Si-rich compared with many other igneous minerals. Muscovite, therefore, is found in silicic igneous rocks such as granite, but rarely in rocks of intermediate or mafic composition. Biotite is found in rocks ranging from granitic to mafic composition. Phlogopite is occasionally found in ultramafic rocks.

The name *annite* refers only to the ideal iron-rich mica end member, but the name *phlogopite* is often used in a more general sense to describe any magnesium-rich biotite. Phlogopite is often brown, compared to the more common black color of biotite, so many geologists use the names muscovite, phlogopite, and biotite in a generic sense to refer to silvery, brownish, and black micas, respectively.

Besides Al-Fe-Mg substitutions, other substitutions, such as F^- substituting for OH^-, occur in micas, but they are generally minor. Lepidolite, an especially lithium-rich mica similar to muscovite, is an exception. It is a common large and euhedral mineral in pegmatites, and is often associated with the lithium-aluminum pyroxene, spodumene. The photo of lepidolite in Figure 6.67 has the typical lilac color of this mineral, but lepidolite may be yellow or other colors as well.



6.68 The atomic arrangement in muscovite

The drawing in Figure 6.68 shows the atomic arrangement in muscovite. The arrangement is just about the same in all micas, and other sheet silicates have atomic structures that are closely related to muscovite's. Micas contain sheets (layers) of $(Si,Al)O_4$ tetrahedra with alkalis and other metals between. Most micas, like muscovite, contain K^+ as an interlayer cation between the tetrahedral layers. Depending on the mica species, Fe^{2+} , Mg^{2+} , and Al^{3+} occupy positions between the apices of the tetrahedra. Within the tetrahedra themselves, Al^{3+} substitutes for some Si^{4+}.

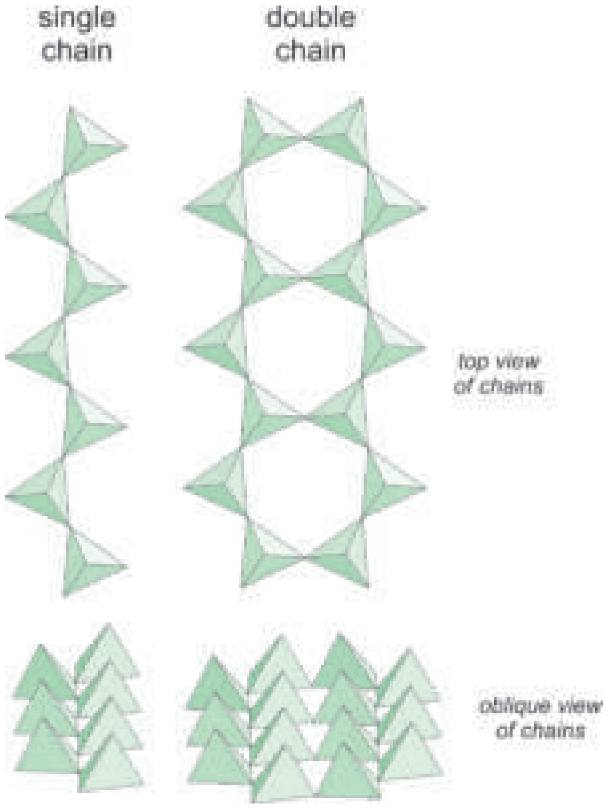
Bonding within a sheet (O^{2-} bonded to Si^{4+} and Al^{3+} in muscovite) is much stronger than bonding between sheets (K^+ bonded to O^{2-} in muscovite). Consequently, well-developed basal cleavage (planar and sheet-like) characterizes mica and most other sheet silicates. See the photos above in Figures 6.62 to 6.67 and also the biotite in Figure 3.59 (Chapter 3)

6.69 8 cm wide sample of clinochlore from near West Point, New York

The name *chlorite* is often used in a general way to refer to any greenish mica. But, strictly speaking, chlorite is a group of minerals consisting of a number of different species that are difficult to distinguish from each other. Chlorite compositions can be described by the simplified formula $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \bullet n(Mg,Fe)_3(OH)_6$. The photo in Figure 6.69 shows a rare bluish example of chlorite.

Chlorite’s atomic arrangement is similar to the arrangement in micas but the interlayer site contains $(Mg,Fe)(OH)_6$ instead of K. Clinochlore – $(Mg_5Al)(AlSi)_3O_{10}(OH)_8$ – is perhaps the most important chlorite end member. Chlorite group minerals are stable over a wide range of conditions, generally occurring in low to medium-grade metamorphic rocks. They are also common as alteration products in igneous rocks, where they form from biotite, pyroxene, amphibole, and other mafic minerals.

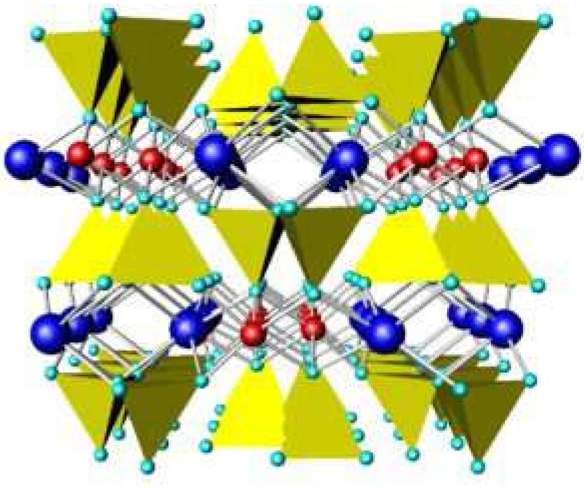
6.4.5 Chain Silicates



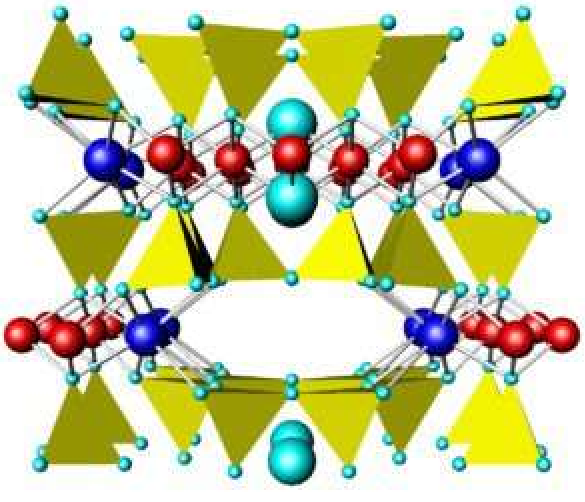
6.70 Single and double chain silicates

In micas, and other sheet silicates, silicon tetrahedra are polymerized to form sheets. In chain silicates, the tetrahedra polymerize to form chains. This is done in two ways, shown in Figure 6.70. *Single chain silicates* have tetrahedra that zig-zag back and forth. *Double chain silicates* also involve tetrahedra that zig-zag back and forth, but the chains come in pairs, and an oxygen anion, called a *bridging oxygen,* links chains together. A few relatively obscure minerals have chains that are wider and more complex than double chains – the are part way to being sheet silicates. Pyroxenes and amphiboles are the two most important groups of minerals in the chain silicate subclass. In fact, they are almost the only minerals in the subclass.

All chain silicates contain single or double chains of tetrahedra linked by cations. Pyroxenes, and their cousins *pyroxenoids*, are both single chain silicates and have closely related atomic arrangements. Amphiboles, such as tremolite or hornblende, are double chain silicates. Because two oxygen are shared with other tetrahedra, pyroxenes have formulas that contain (SiO_3) or (Si_2O_6). Less obvious, but equally valid, is that amphibole formulas contain (Si_8O_{22}). In both pyroxenes and amphiboles, however, Al may substitute for significant amounts of Si.



6.69 The atomic arrangement in diopside



6.70 The atomic arrangement in tremolite

Figures 6.71 and 6.72 above compare the atomic arrangements in diopside and tremolite. Diopside is a Ca-Mg pyroxene (single chain), and tremolite is a Ca-Mg amphibole (double chain). In both figures, the view is down the chain direction; the yellow tetrahedra are the (SiO_4) units that form the chains. In pyroxenes, the linking cations (blue and red in these figures) occupy two distinct kinds of sites between the chains; in amphiboles, they occupy three kinds of sites between the chains. In both pyroxenes and amphiboles, two interchain sites (blue) are significantly larger than the others. In diopside and tremolite, the large sites contain Ca and the smaller sites contain Mg. The large light blue spheres in the tremolite structure are hydroxyl (OH) groups. Compare these figures with the one above (Figure 6.70) to get a different perspective.

Pyroxenes are anhydrous minerals having simple formulas compared with amphiboles, all of which are hydrous. Still, the similarity between the structures of pyroxenes and amphiboles results in some similarity in physical properties. For example, unless cleavage is visible, it can be difficult to distinguish dark-colored pyroxenes from dark-colored amphiboles.

6.4.6 Pyroxenes

Pyroxenes

$(Ca,Na,Mg,Fe)(Mg,Fe,Al)(Si,Al)_2O_6$

<u>Most important end members</u>

wollastonite	$Ca_2Si_2O_6$
ferrosilite	$Fe_2Si_2O_6$
enstatite	$Mg_2Si_2O_6$
diopside	$CaMgSi_2O_6$
hedenbergite	$CaFeSi_2O_6$

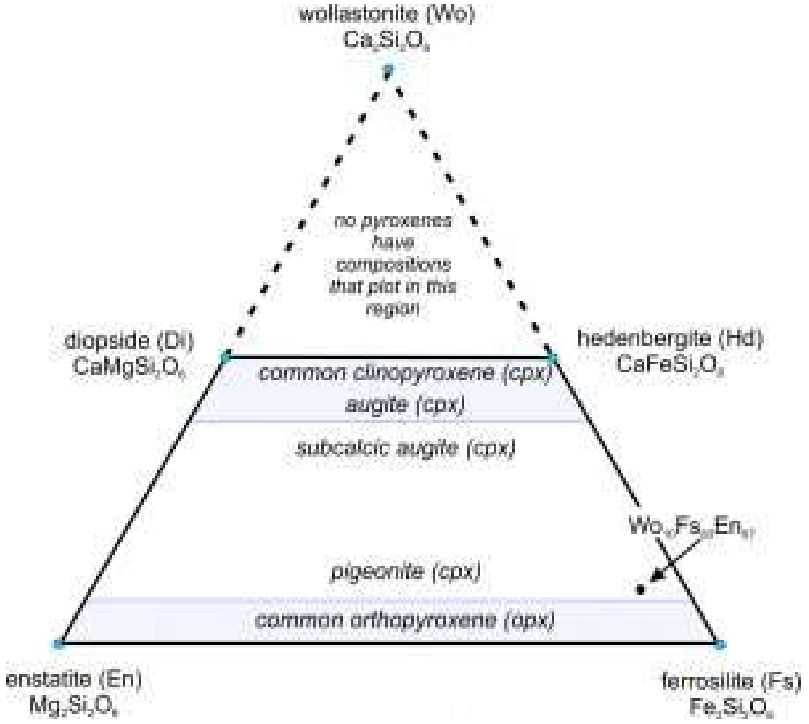
Pyroxenes contain many different elements, but all pyroxenes have the general formula shown in the blue box. The most common pyroxenes are close to $Ca(Mg,Fe)Si_2O_6$ or $(Mg,Fe)_2Si_2O_6$ in composition. So, we can describe the chemistries of most pyroxenes in terms of the five end members listed in the box. The formulas for wollastonite, ferrosilite and enstatite have been written with six oxygen, but they could be written with three. We generally use six to keep formulas consistent with other pyroxenes such as diopside and hedenbergite and also because Ca, Fe, and Mg occupy two distinctly different atomic sites in pyroxenes. Distinguishing the different pyroxene species can be challenging. In the absence of a chemical analysis, black colored pyroxenes are often called *augite*.

6.74 Yellow spodumene from near Sand Diego, California

6.73 Jadeite from California

Some pyroxenes contain minor to appreciable amounts of Na and Al. Na may substitute for Ca, Mg, or Fe. Al can substitute for Ca, Mg, or Fe, and also for Si. An end-member pyroxene, *jadeite*, has the formula $NaAlSi_2O_6$. It is found in high-pressure metamorphic rocks and is one of two types of jade that are sometimes prized as gemstones. (The other is an amphibole). Other Na-bearing pyroxenes such as *acmite* ($NaFeSi_2O_6$) are found in some igneous rocks. The photo in Figure 6.73 shows a sample of massive green jadeite from central California. It is about 5 cm across.

Li, Cr, and Ti also are sometimes in pyroxene, but are normally minor elements. However, *spodumene* ($LiAlSi_2O_6$), is a major mineral in some pegmatites. The photo seen here (Figure 6.74) shows a yellow spodumene crystal about 2 cm tall. Like jadeite, spodumene, especially the lilac-colored variety called *kunzite*, can be a valuable gemstone.



6.75 The pyroxene quadrilateral

The ternary diagram in Figure 6.75 is a wollastonite-ferrosilite-enstatite triangle with the important pyroxene end members labeled (enstatite, ferrosilite, diopside, hedenbergite, and wollastonite). The mineral *wollastonite*, although used as an end member to describe pyroxene compositions, is not a pyroxene. It has a slightly different atomic arrangement and belongs to the pyroxenoid group. (In pyroxenoids, the tetrahedral chains do not zig-zag back and forth as regularly as is shown in Figure 6.70.)

As with the feldspars, we use abbreviations to describe pyroxene compositions. For example, a pyroxene of composition $Wo_{10}Fs_{83}En_{07}$ is 10% $CaSiO_3$, 83% $FeSiO_3$, and 7% $MgSiO_3$. It has the formula $(Ca_{0.10}Fe_{0.83}Mg_{0.07})SiO_3$, equivalent to $(Ca_{0.20}Fe_{1.66}Mg_{0.14})Si_2O_6$. This composition is plotted as a dot near the ferrosilite corner of the triangle in Figure 6.75.

We call the lines between end members on ternary diagrams *joins*. The four-sided polyhedron bounded on the top by the diopside-hedenbergite join, and on the bottom by the enstatite-ferrosilite join, is the *pyroxene quadrilateral*. It encompasses the compositions of all natural Ca-Mg-Fe pyroxenes.

Natural pyroxenes fall into two main series, distinguished by slightly different atomic arrangements and different crystal shapes: the *orthopyroxene series* (Opx) and the *clinopyroxene series* (Cpx). Orthopyroxenes, predominantly solid solutions of the end members ferrosilite and enstatite, have the general formula $(Mg,Fe)_2Si_2O_6$. The photo on the left below (Figure 6.76) shows green enstatite crystals (orthopyroxene) in a volcanic rock from near Crater Lake National Park, Oregon. Natural orthopyroxenes often contain small amounts of $CaSiO_3$. So, their compositions do not plot on the bottom of the quadrilateral, but slightly above.

6.76 2 mm long green crystals of enstatite from Summit Rock, Oregon

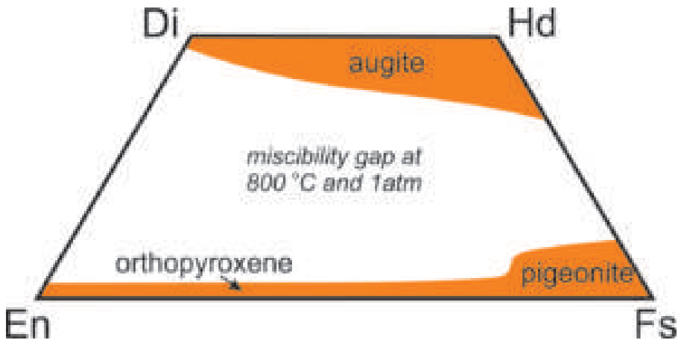
6.77 Green diopside with white calcite in a marble from the Adirondack Mountains, New York

The photo on the right above (Figure 6.77) shows an example of clinopyroxene, green diopside crystals in a metamorphosed limestone. Most clinopyroxene, is predominantly a solution of diopside and hedenbergite, and so has the general formula $Ca(Mg,Fe)Si_2O_6$. But natural pyroxenes may be somewhat deficient in $CaSiO_3$. This give them a composition that does not plot on the diopside-hedenbergite join but, instead, plots within the pyroxene quadrilateral. A less common kind of clinopyroxene, *pigeonite*, has composition close to orthopyroxene. No pyroxenes have compositions more calcic than diopside or hedenbergite because Ca is limited to only the larger two of the four sites between the tetrahedral chains in pyroxenes.

6.78 Black augite crystals from Muhabura Volcano, Rwanda

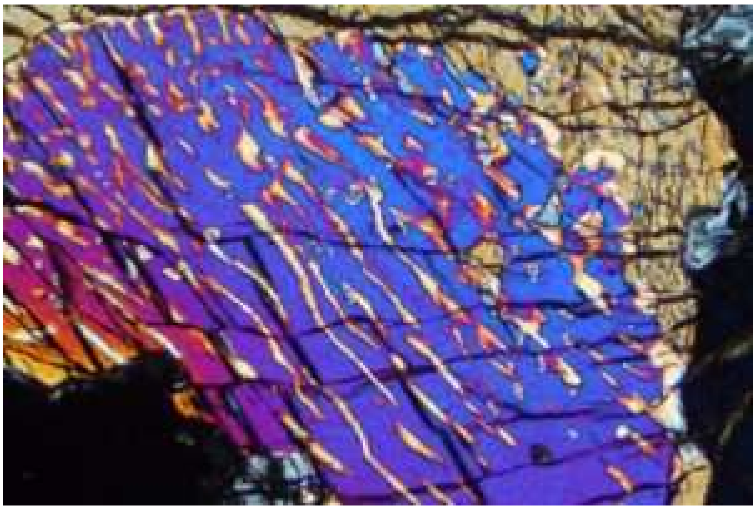
We call pyroxenes with compositions that plot within the quadrilateral *augite*, *subcalcic augite*, or *pigeonite* (see Figure 6.75) depending on their composition. Augite and subcalcic augite are clinopyroxenes with Ca : (Mg + Fe) ratios less than 1. Pigeonites, first found at Pigeon Point, Minnesota, are very high-temperature pyroxenes that only form in quickly cooled volcanic rocks. Figure 6.78 shows an example of large black augite crystals.

Because orthopyroxenes and clinopyroxenes have slightly different atomic arrangements there is a complex solvus between them. At high temperatures, intermediate composition pyroxenes – those that plot within the quadrilateral can be stable. At low temperatures most of the pyroxene quadrilateral is taken up by a large miscibility gap, so intermediate composition pyroxenes are unstable.



6.79 The large miscibility gap in the pyroxene quadrilateral at 800 ℃, 1 atm

Figure 6.79 shows the gap (in white) at 800 ℃. Because of this gap, homogeneous pyroxenes with intermediate compositions are only found in some rare high-temperature rocks. At lower temperatures they tend to “unmix.” Analogous to the feldspars, a homogeneous high-temperature pyroxene of intermediate composition may become unstable and separate into two pyroxenes at low temperature. This sometimes leads to exsolution and textures similar to perthitic feldspars.

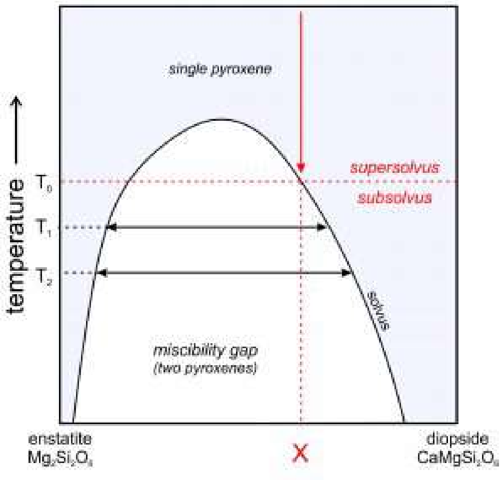


6.80 Microscope view of exsolution in a pyroxene grain. Field of view is 2mm across

The photo in Figure 6.80, taken through the lens of a petrographic microscope, shows exsolution in pyroxene. The colors are artifacts and not the true color of the minerals. An original pyroxene (subcalcic augite) unmixed upon cooling, producing exsolution lamellae (the stripes) and the texture we see here. The blue-red lamellae are clinopyroxene and the light colored lamellae are orthopyroxene. The compositions of both lamellae depend on the temperature at which exsolution occurred (Box 6-4). So, the compositions of exsolved pyroxene (and feldspar) lamellae are sometimes used as geothermometers to learn the temperature at which a rock equilibrated.

● Box 6-4 Diopside-Enstatite Solvus and Geothermometry

The miscibility gap between orthopyroxene (Opx) and clinopyroxene (Cpx) is sometimes used to calculate the temperature at which igneous or metamorphic rocks formed. Petrologists call such mineral systems *geothermometers*. Geothermometers are based on a fundamental consequence of thermodynamics: at high temperatures, solid-solution minerals may have intermediate compositions, but at low temperatures many solid solutions unmix so that compositions are relatively close to end members. Figure 6.80 (above) shows an example of a single pyroxene grain that has unmixed to become two pyroxenes.



6.81 The miscibility gap and solvus for Mg-Ca pyroxenes

Figure 6.81 is a schematic showing the Opx-Cpx gap between enstatite and diopside. The gap narrows at high temperature and does not extend to the very high temperatures where magmas crystallize and pyroxenes first form. Consequently, pyroxenes of any composition can crystallize from a magma. But, with cooling, many pyroxenes will unmix, producing compositions closer to end member enstatite and diopside than the original pyroxene.

A pyroxene of composition X will be stable at temperatures above T_0, but if it crystallizes or equilibrates at lower temperature, it will unmix to form two pyroxenes. So, as temperature decreases from supersolvus to subsolvus (at T_0), unmixing will produce separate grains of Opx and Cpx in the same rock, or it may produce single grains of pyroxene containing blebs (small inclusions with exsolved compositions in a larger host) or exsolution lamellae of different compositions. As temperature decreases from T_0 to T_1 to T_2, the coexisting pyroxenes will become closer to end member enstatite and diopside. By analyzing the compositions of coexisting Opx and Cpx, petrologists can estimate the temperature of equilibration.

Pyroxenes are not the only minerals that can be used as geothermometers. Feldspars, carbonates, and others can serve the same purpose. Geothermometry is not, however, always simple or straightforward. Many things besides temperature affect the compositions of coexisting minerals. Among others, petrologists must be concerned with the effects of pressure, of minor elements in minerals, and of disequilibrium.

6.4.7 Amphiboles

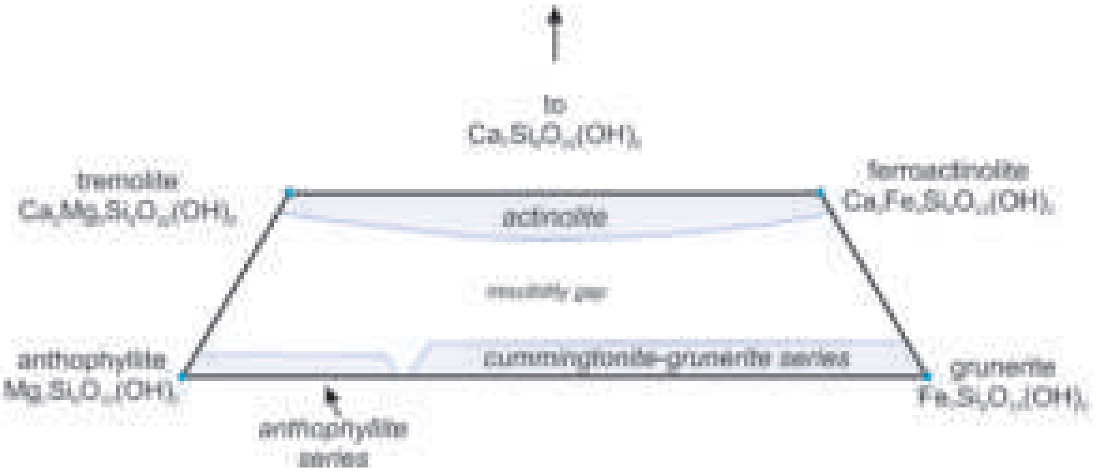
Amphiboles

$(K,Na)_{0\text{-}1}(Ca,Na,Mg)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$

Most important end members

tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
ferroactinolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$
anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
cummingtonite	$Mg_7Si_8O_{22}(OH)_2$
grunerite	$Fe_7Si_8O_{22}(OH)_2$
glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$

Amphiboles and pyroxenes are closely related minerals that commonly coexist. Both are chain silicates, but the atomic arrangement in amphiboles is more complex than in pyroxenes. Like pyroxenes, amphibole chemistry is highly variable and yields many different end member formulas. Just a few are listed in the blue box. Also, like the pyroxenes, amphiboles fall into two main series: the *orthoamphibole series* and the *clinoamphibole series*. Note that, in the box we have listed $Mg_7Si_8O_{22}(OH)_2$ two times. Anthophyllite is an orthoamphibole and *cummingtonite* is a clinoamphibole; the two are polymorphs. The lengthy generic formula at the top of the blue box describes *hornblende*, the most common kind of amphibole. The formula is complicated, but really does not reflect all possible compositional variations. Besides the elements listed, Mn and Ti are major components in some amphiboles, and F or Cl can replace (OH) in others. Note that hornblende contains variable amounts of K or Na (indicated by the subscript “0-1″) that are missing from all the other amphiboles listed in the box.



6.82 The amphibole quadrilateral

Figure 6.82 shows an amphibole quadrilateral, similar to the pyroxene quadrilateral we saw before. The quadrilateral contains a large miscibility gap between the calcic amphiboles and the calcium-poor amphiboles, analogous to the one between clinopyroxene and orthopyroxene. The quadrilateral includes the compositions of all Ca-Mg-Fe amphiboles. Along the base of the diagram, the figure is complicated because Ca-free amphiboles form two distinct series, having different atomic arrangements: the *anthophyllite series* and the *cummingtonite-grunerite series*.

6.83 Needles of anthophyllite from eastern Finland

We call the most Mg-rich amphiboles *anthophyllite* or, if they contain appreciable amounts of iron, *ferroanthophyllite*. Figure 6.83 shows a group of anthophyllite needles in a 4 cm wide specimen. The cummingtonite- grunerite series contains other intermediate and Fe-rich amphiboles that are poor in calcium. We give aluminous anthophyllite (not shown in the amphibole quadrilateral) the name *gedrite*.


6.84 Typical green blades of actinolite


6.85 4 cm wide sample of bladed tremolite


6.86 Hornblende. The largest piece is about 4 cm wide.

Calcic amphiboles can have any composition between an Mg end member (tremolite) and an Fe end member (ferroactinolite). We call compositions between *actinolite*. The left and center photos above, Figures 6.84 and Figure 6.85, show typical actinolite and tremolite. Actinolite is generally green, and tremolite is white or light colored. The bladed crystals form because of the chain nature of atomic arrangements.


6.87 Amphibolite from Huelva, southwestern Spain. Euro coin for scale

The amphibole quadrilateral depicts variations in Ca, Mg, and Fe content well, but many amphiboles, especially hornblendes, contain K, Na, Al, Ti, and other elements in significant amounts. Additionally, hornblende, the most common amphibole, is a complex mineral that contains many possible elements. It does not have the same number of atoms in its formula as quadrilateral amphiboles. Although many amphibole varieties have specific names, without chemical analyses, telling different amphiboles apart is difficult. So, the name *hornblende* is commonly used to refer to any black amphibole. The photo in Figure 6.86 shows three pieces of massive hornblende. This photo (Figure 6.87) shows an outcrop of metamorphic rock called *amphibolite*. All the dark mineral grains are hornblende.

Many amphibole end members have analogs in the pyroxene group; we compare some of the more important end members in the tables below.

Pyroxene End Members or Series	
enstatite	$Mg_2Si_2O_6$
ferrosilite	$Fe_2Si_2O_6$
Mg-Fe Opx	$(Mg,Fe)_2Si_2O_6$
diopside	$CaMgSi_2O_6$
hedenbergite	$CaFeSi_2O_6$
Mg-Fe Cpx	$Ca(Mg,Fe)Si_2O_6$
jadeite	$NaAlSi_2O_6$
acmite	$NaFeSi_2O_6$
augite	complex chemistry

Amphibole End Members or Series	
Mg-anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
Fe-anthophyllite	$Fe_7Si_8O_{22}(OH)_2$
anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
ferroactinolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$
actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
glaucocphane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$
riebeckite	$Na_2Fe_3Al_2Si_8O_{22}(OH)_2$
hornblende	complex chemistry

Amphiboles are important and essential minerals in many kinds of igneous rocks. For example, hornblende is widespread. It is common in granitic rocks but is even more common in rocks of intermediate to mafic composition. Amphiboles also exist in many metamorphic rocks, including marbles and metamorphosed mafic igneous rocks. They are especially common in high-temperature amphibolites like the one seen above in Figure 6.87. Amphibolites always contain amphibole and plagioclase, and generally other minerals including biotite, epidote, or garnet.

6.88 Glaucophane (blue) with minor omphacite (a pyroxene)

Figure 6.88 shows *glaucophane*, a blue sodic amphibole, that has the general formula $Na_2Al_2Si_8O_{22}(OH)_2$. Its presence is often associated with rocks formed in subduction zones under high pressures and moderate temperatures. Other Ca-free amphiboles (anthophyllite, gedrite, cummingtonite, and grunerite) are found in metamorphic rocks and occasionally in extrusive igneous rocks. Tremolite is common in high-temperature marbles. As with some other silicates found in marbles, identifying it may be difficult because of its inconspicuous white color. See Figure 6.85, above.

6.4.8 Ring Silicates and Paired Tetrahedral Silicates

Ring Silicates and Paired Tetrahedral Silicates	
The most common ring silicates	
beryl	$Be_3Al_2Si_6O_{18}$
tourmaline	$(Na,Ca)(Fe,Mg,Al,Li)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$
cordierite	$(Mg,Fe)_2Al_3(Si_5AlO_{18})$
The most common paired tetrahedral silicates	

epidote	$Ca_2(Al_2,Fe)(SiO_4)(Si_2O_7)O(OH)$
zoisite	$Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$
lawsonite	$CaAl_2Si_2O_7$

Ring silicates, generally containing rings of six silicon tetrahedra (see Figure 6.24), are relatively rare. Beryl, tourmaline and cordierite are the only common examples. A few obscure and uncommon minerals have rings of three tetrahedra.

Beryl, tourmaline, and cordierite are sometimes beautiful gemstones. But, the more common varieties are often rather drab. Figures 6.89 and 6.90 show examples of common beryl and tourmaline. Because these mineral have atoms arranged in hexagonal rings, their crystals often exhibit hexagonal symmetry, as can be seen in Figure 6.89. Figure 6.108, later in this chapter, shows an example of gemmy tourmaline. It is similar to one we saw in Figure 4.13 (Chapter 4). Figures 4.1 and 4.30 (Chapter 4) show examples of aquamarine and emerald, both gemmy varieties of beryl.

6.89 Beryl

6.90 Tourmaline

Paired tetrahedral silicates contain linked pairs of silicon tetrahedra that create an Si_2O_7 group (see Figure 6.24 earlier in this chapter). Epidote, zoisite, and lawsonite are the most common examples. But, epidote and zoisite contain paired tetrahedra and tetrahedra in other configurations as well. The photos, in Figures 6.91, 6.92, and 6.93 show beautiful examples of these minerals. More common specimens are not so pretty.

6.91 Epidote from Prince of Wales Island, Alaska. The specimen is 5.2 cm across.

6.92 Zoisite from Tanzania. The crystal is 7.2 cm tall.

6.93 Lawsonite from just north of the Golden Gate Bridge, San Francisco. The largest crystals are about 5 mm across.

Beryl and tourmaline contain beryllium and boron, respectively – these elements are generally quite rare. But, they concentrate in some pegmatites, and that is where most beryl and tourmaline are found. Cordierite and zoisite are both common metamorphic minerals. Lawsonite is a rare high pressure metamorphic mineral associated with metamorphism in subduction zones. The chemistry of tourmaline is highly variable, but the other minerals are generally close to the end member compositions listed in the blue box above.

6.4.9 Olivine Group Minerals

Olivine Group Minerals

$(Mg,Fe,Ca,Mn)SiO_4$

Olivine end members

forsterite	Mg_2SiO_4
fayalite	Fe_2SiO_4
tephroite	Mn_2SiO_4
calcio-olivine	Ca_2SiO_4

Other olivine group minerals

larnite	Ca_2SiO_4
monticellite	$CaMgSiO_4$

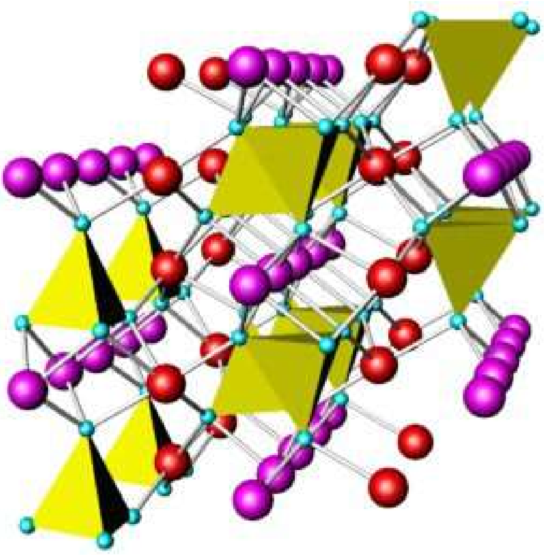
Related minerals

zircon	$ZrSiO_4$
topaz	$Al_2SiO_4(F,OH)_2$

Olivine group minerals, belonging to the isolated tetrahedra silicate subclass, all have similar atomic arrangements. By far, the most important mineral of this group is called *olivine*. In contrast with some of the other silicates previously discussed, olivine chemistry is quite simple. Its general formula is $(Mg,Fe,Ca,Mn)_2SiO_4$ but often we omit Mn and Ca because they are normally minor components. The most important end members are listed in the blue box.

Besides olivine, other minerals of the group include *larnite*, a polymorph of calcio-olivine, and *monticellite*. Both are rare. *Zircon* and *topaz*, have different atomic arrangements than the olivine minerals and so are not members of the group. They are, however, other important isolated tetrahedra silicates and so are listed here.

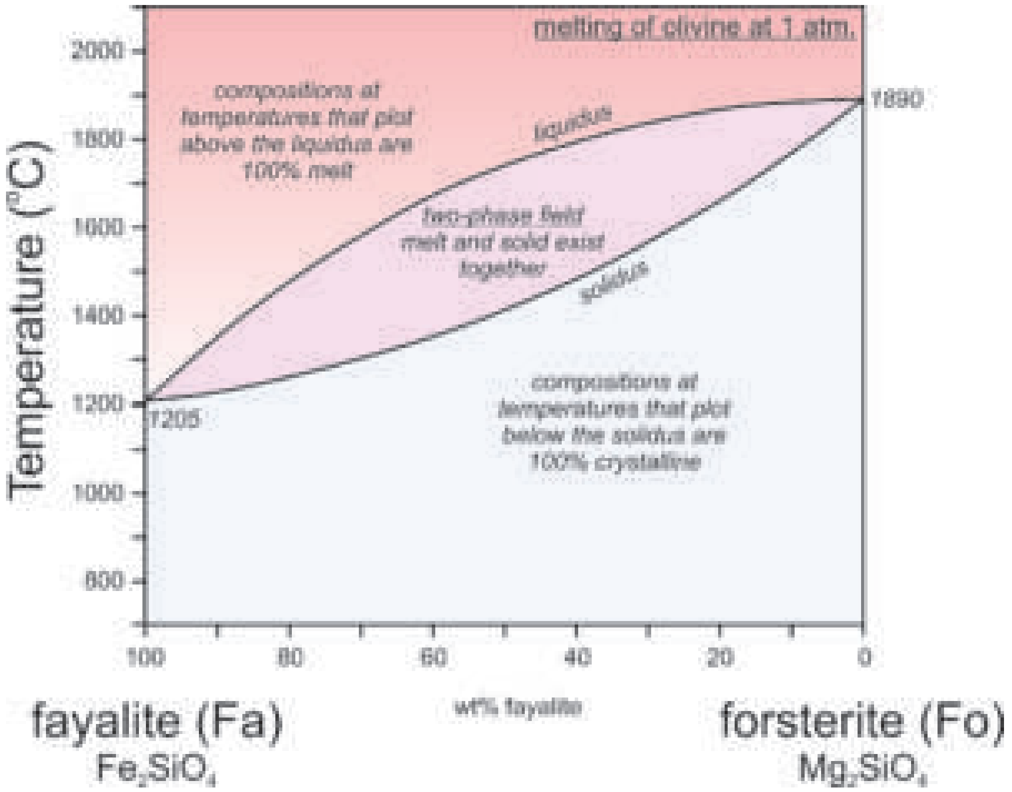
Natural olivines are generally solid solutions of fayalite and forsterite with only minor tephroite and calcio-olivine. We usually use abbreviations and subscripts to indicate olivine compositions. $Fo_{88}Fa_{09}Te_{02}La_{01}$, for example, refers to an olivine of composition $(Mg_{0.88}Fe_{0.09}Mn_{0.02}Ca_{0.01})_2SiO_4$.



6.94 The atomic arrangement

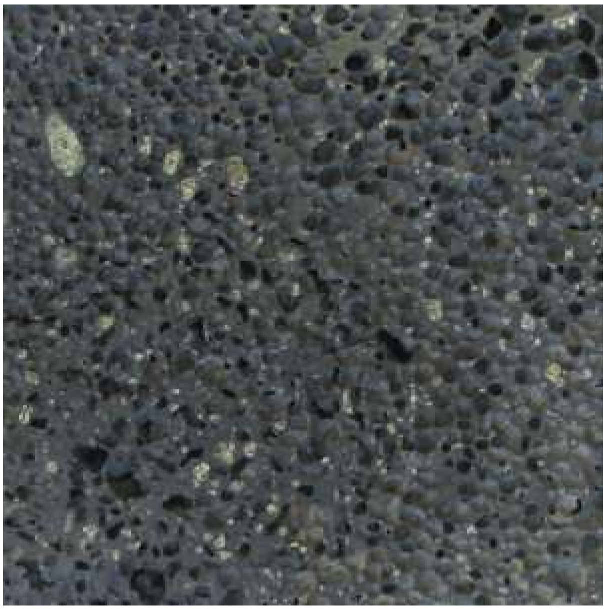
in olivine

In olivine group minerals, SiO_4 tetrahedra do not share oxygen but, instead, are linked via bonds to other cations. Figure 6.94 shows an example. The red and purple spheres are mostly Fe and Mg in common olivine. In monticellite, the red spheres are Ca and the purple spheres are Mg. Because the silicon tetrahedra are isolated, bond strength is about the same in all directions. Consequently, olivine has no direction of good cleavage.



6.95 Olivine crystallization at 1 atm pressure

Olivine is primarily an igneous mineral, crystallizing from high-temperature magmas. Its two most important end members, forsterite and fayalite, melt at different temperatures, and olivine’s crystallization behavior is similar to that of plagioclase. Figure 6.95 is a phase diagram that describes crystallization of forsterite-fayalite olivines, and the two-phase field between the liquidus and solidus. Compare this with Figure 6.54 (plagioclase phase diagram); they are nearly identical. Partial crystallization of olivine-rich melts leads to crystals that are more Mg-rich than the parent melt, and partial melting of olivine crystals leads to melts that are more Fe-rich than the parent crystals. If the melt and crystals become separated, the Fe-rich melt will move upwards and carry iron from depth toward Earth's surface. Magnesium will be left behind. This is one reason why Earth's crust is more Fe-rich than the mantle.



6.89 Green olivine phenocrysts and vesicles in basalt from the Canary Islands. Field of view is about 10 cm.

6.97 Mantle xenolith containing green olivine and dark brown pyroxene. 9 cm across

Olivine occurs predominantly in mafic and ultramafic igneous rocks. Its very mafic composition restricts its occurrence, and other mafic minerals containing the same elements with additional silicon are more abundant. In some basalts Mg-rich olivine forms large green phenocrysts in a fine-grained plagioclase-pyroxene groundmass; Figure 6.96 shows an example from the Canary Islands.

Mg-rich olivine is never found in felsic rocks, but Fe-rich olivine is occasionally found in some granites. Olivine occurs in some metamorphic rocks, including marble and metamorphosed igneous rocks. Olivine also is found in *mantle xenoliths* –

samples of the mantle that have been carried to the surface by magmas. The photo in Figure 6.97 is dark basalt that contains a mostly green xenolith. The green colored crystals in the xenolith are olivine. Dark brown orthopyroxene is also present, but in lesser amounts.

6.4.10 Summary: Silicate Minerals and Igneous Rocks

The table below lists the silicate minerals just considered. Quartz, at the very top of the table, has an Si:O ratio of 1:2. The ratio decreases downward in the table, and olivine, at the bottom of the list, has an Si:O ratio of 1:4. This reflects the fact that quartz is a felsic mineral and olivine is a mafic mineral. Things are a bit more complicated for minerals other than quartz and olivine because some Al commonly substitutes for some Si. But the ratio of Si plus the substituting Al (collectively called T) to oxygen increases from 1:2 at the top of the chart to 1:4 at the bottom. The key parts of the mineral formulae that show this are highlighted in blue in the table.

Silicate Minerals

silicate subclass	important examples	compositions	key part of formula
framework silicates	quartz & polymorphs feldspar group feldspathoid family	[illegible] [illegible] [illegible]	[illegible] [illegible] T:O = 1:2
sheet silicates	mica group chlorite group clay minerals	[illegible] complex sheet silicates complex sheet silicates	[illegible] T:O = 4:10
double chain silicates	amphibole group	[illegible]	[illegible] T:O = 8:22
single chain silicates	pyroxene group pyroxenoid group	[illegible] [illegible]	[illegible] T:O = 1:3
ring silicates	beryl tourmaline cordierite	[illegible] [illegible] [illegible]	[illegible] T:O = 1:3
paired tetrahedral silicates	epidote zoisite lawsonite	[illegible] [illegible] [illegible]	[illegible] T:O = 2:7
isolated tetrahedral silicate	olivine zircon topaz	[illegible] [illegible] [illegible]	[illegible] T:O = 1:4

The left hand column in this table lists the silicate subclass, and the right hand column shows the ratio Si:O, or (Si,Al):O in a formula. So, the ratio tells us whether a silicate mineral is a *framework, sheet, double chain*, etc. All double chain silicates, for example, contain $(Si,Al)_8O_{22}$ in their formulas. Paired tetrahedral silicates contain Si_2O_7 in their formulas. Note that a few minerals, including epidote and zoisite, belong to more than one silicate subclass. Their formulas contain both SiO_4 and Si_2O_7 and so they are partly paired tetrahedral silicates and partly isolated tetrahedral silicates.

Two caveats: Sometimes formulas are simplified by dividing by two or some other factor. For example, the pyroxene *enstatite* has formula $Mg_2Si_2O_6$ but can also be written $MgSiO_3$. It is the ratio (2:6 or 1:3) of Si:O tells us it is a single chain silicate. Also, sometimes subscripts are combined in formulas such as zoisite’s – it can be written $Ca_2Al_3Si_3O_{12}(OH)$, which gives no hint about the way tetrahedra are polymerized.

Accessory Minerals in Igneous Rocks

magnetite	Fe_3O_4
ilmenite	$FeTiO_3$
apatite	$Ca_5(PO_4)_3(OH,F,Cl)$
zircon	$ZrSiO_4$
titanite	$CaTiSiO_5$
pyrite	FeS_2
pyrrhotite	$Fe_{1-x}S$
allanite	$(Ca,Ce)_2(Al,Fe)_3Si_3O_{12}(OH)$
tourmaline	see formula in table above
sodalite	$Na_3Al_3Si_3O_{12}$•NaCl
fluorite	CaF_2

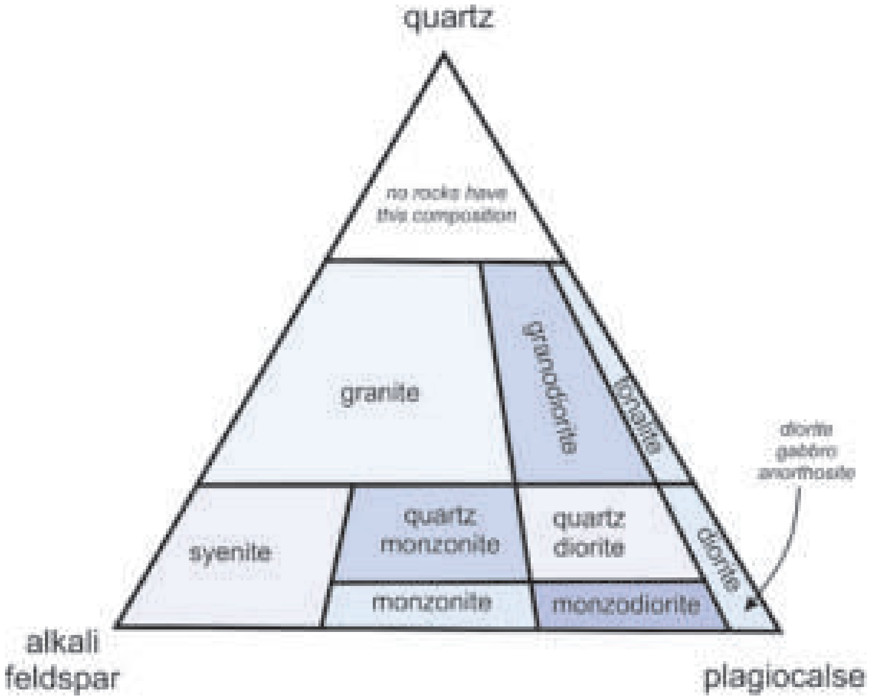
This chapter focused on silicates, but igneous rocks often contain other minerals. The most common are listed in the table seen here. Most exist as *accessory minerals* because they are composed of rare elements or of elements that easily fit into other minerals. Magnetite and ilmenite, for example, are generally minor because they comprise elements that also easily fit into other more abundant essential minerals. Rocks that contain fluorine (F), zirconium (Zr), or phosphorus (P) may contain fluorite, zircon, or apatite, but F, Zr, and P are very minor elements in all but the most unusual rocks. Although not abundant, zircon often contains uranium and lead, which we may analyze to learn radiometric ages of igneous rocks.

6.5 Naming Igneous Rocks

There are a number of different ways to divide igneous rocks into groups and to give them names. Assigning names can be complicated because igneous rocks vary greatly in mineralogy and texture, and because rock types grade from one to another.

If we invoke too many names, terminology becomes too complicated to be useful. If we invoke too few names, they are too broad to have much meaning. The task is somewhat simplified because, with rare exceptions, the major elements in all igneous rocks are the same. Additionally, certain minerals have affinities for each other because of their chemical compositions. Mafic igneous rocks, for example, generally contain pyroxene and Ca-plagioclase. Silicic igneous rocks contain predominantly quartz, alkali feldspar, and micas. Mafic rocks, therefore, have a characteristic dark color, while silicic rocks are white or pink. Despite these generalizations, however, igneous petrology is complex and the nomenclature is complicated.

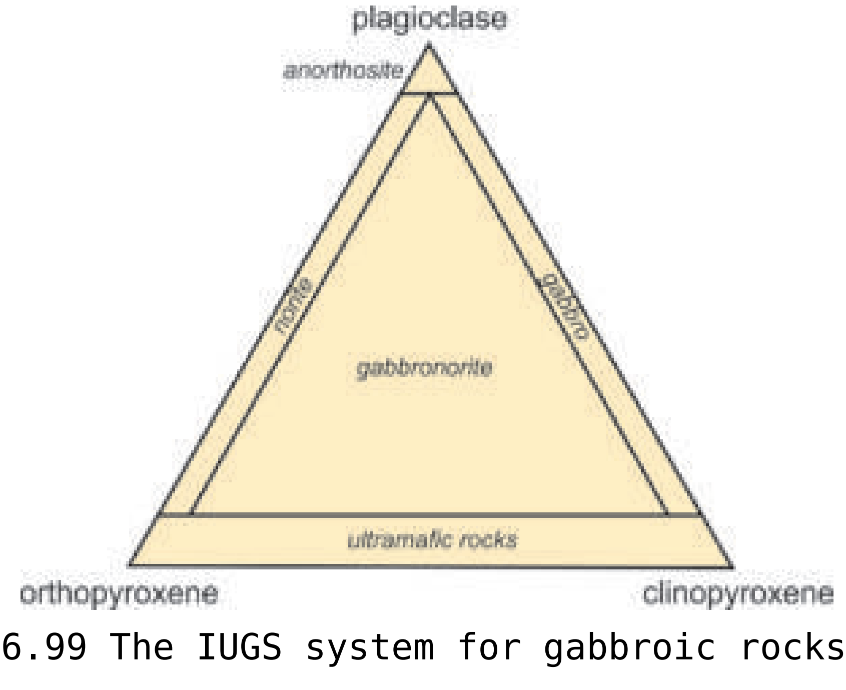
6.5.1 Simple Classification Scheme



6.98 The IUGS system for plutonic igneous rocks

Most igneous rocks contain feldspar or quartz. So, the most widely used and relatively straightforward classification scheme for igneous rocks is based on the relative amounts of quartz, plagioclase, and alkali feldspar that are present. It is the *International Union of Geological Sciences (IUGS)* system. Figure 6.98 shows a version for normal plutonic rocks. Other minerals may be present, but using this system, only the ratios of quartz, plagioclase, and alkali feldspar determine the rock name. As an example, we call a rock that contains nearly equal amounts of quartz and plagioclase, and that contains no or very little alkali feldspar, *tonalite*.

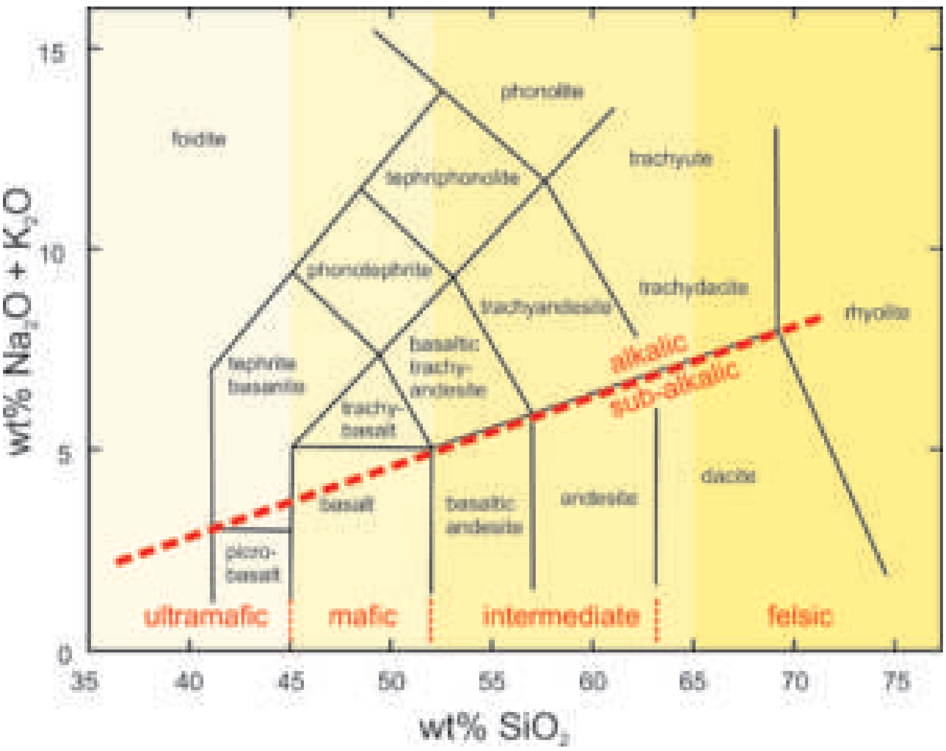
This IUGS system works well for many plutonic igneous rocks, and we can often identify quartz, plagioclase, and alkali feldspar in the field – so it is very convenient. It does not work well for rocks that do not contain significant amounts of quartz or feldspar, and it makes no distinction between rock types that contain similar amounts of quartz, alkali feldspar, and plagioclase but vary significantly with respect to other minerals. For example, gabbro, diorite, and anorthosite all contain plagioclase, with very minor alkali feldspar and quartz, if any. They plot in the bottom right corner of the triangle and consequently cannot be distinguished.



6.99 The IUGS system for gabbroic rocks

The main difference between gabbro and diorite is that gabbro, which is a mafic rock, contains calcium-rich plagioclase. Diorite, is more silicic than gabbro, and contains more sodic plagioclase. The standard IUGS system takes no account of feldspar composition, so this distinction is lost. Gabbro and anorthosite are closely related and compositions between are common. But, anorthosite is almost entirely plagioclase, and gabbro contains significant amounts of clinopyroxene in addition to plagioclase. The IUGS has developed a separate triangular diagram for gabbro and related rocks, it is shown here in Figure 6.99.

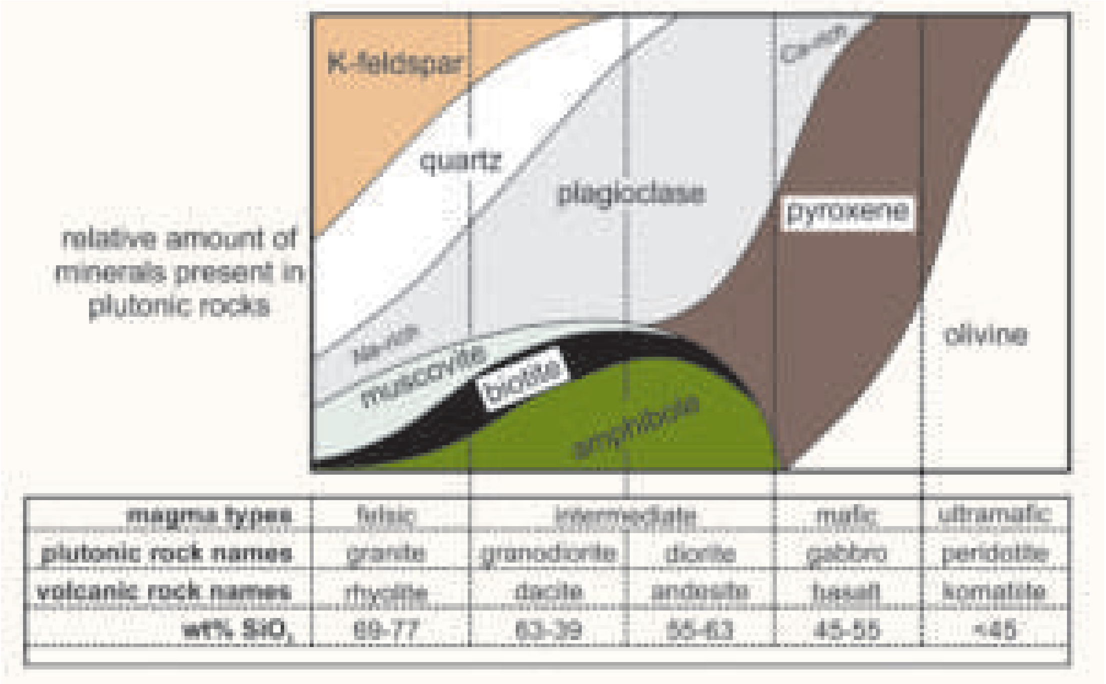
Magmas poor in SiO_2 but rich in alkalis will yield rocks containing nepheline or leucite (both members of the *feldspathoid group*) instead of feldspars. Similarly, ultramafic rocks, that often contain no quartz or feldspars are not represented on the standard IUGS diagram. So, the IUGS has developed different triangular diagrams for these kinds of rocks.



6.100 The total-alkali-silica (TAS) system for naming volcanic rocks

The diagram in Figure 6.98 is for plutonic rocks. The IUGS has a similar system for volcanic rocks, but volcanic rocks may be very fine grained, making mineral identification difficult or impossible, and they may contain significant amounts of volcanic glass in lieu of minerals. So, instead of naming volcanic rocks based on mineralogy, petrologists often assign names based on alkali and silica content. This is the *total-alkali-silica system* (TAS), shown in Figure 6.100. The diagonal red line divides rocks into those that we call *alkalic* (above the line) and *sub-alkalic* (below the line). The most common volcanic rocks are sub-alkalic, ranging in composition from basalt (mafic) to rhyolite (silicic).

6.6 Mineral Modes



6.101 Mineral modes of some common igneous rocks

K-feldspar, quartz, plagioclase, pyroxene, olivine, muscovite, biotite, and amphibole are the most common minerals in igneous rocks. Figure 6.101 depicts the typical amounts by volume – also called the mineral *modes* – of these eight minerals in some common plutonic rocks. Volcanic rock names are included in the table, but many volcanic rocks contain glass that replaces some or all of the minerals that could be present. The table below gives more explicit information about the minerals common to different kinds of rocks.

Figure 6.101, and table below, emphasize the affinities that some minerals have for others. Silicic to intermediate rocks always contain K-feldspar and quartz and are more likely to contain hydrous minerals such as muscovite or biotite. They may contain Na-rich plagioclase. The most common mafic rocks contain pyroxenes and Ca-rich plagioclase. They may contain olivine, and almost never contain quartz or K-feldspar. Olivine, nepheline, and feldspathoid minerals can never coexist with quartz, because they would react to form other silica-rich minerals. Thus, certain minerals can be associated with each other in nature, while others cannot. The minerals present are primarily controlled by the composition of the magma, which in turn reflects the process and source that generated it. So, different igneous rocks, formed in different environments, have characteristic mineral assemblages.

	Common Minerals in Igneous Rocks			
magma type	plutonic rock	volcanic rock	major minerals	other possible minerals
silicic	granite	rhyolite	K-feldspar, lesser plagioclase, quartz	biotite, hornblende,
	granodiorite	dacite	plagioclase, K-feldspar, quartz, hornblende	biotite,
	tonalite	quartz andesite	plagioclase, quartz	K-feldspar, biotite, hornblende
mafic	syenite	trachyte	K-feldspar, lesser to no plagioclase and quartz	biotite, hornblende
	monzonite	latite	K-feldspar, plagioclase, lesser to no quartz	biotite, hornblende clinopyroxene
	diorite	andesite	plagioclase, hornblende	biotite, K-feldspar
	gabbro	basalt	plagioclase, clinopyroxene	orthopyroxene, olivine
ultramafic	peridotite	komatiite	olivine, clinopyroxene, orthopyroxene	plagioclase, spinel, hornblende, phlogopite

6.7 Common Types of Igneous Rock

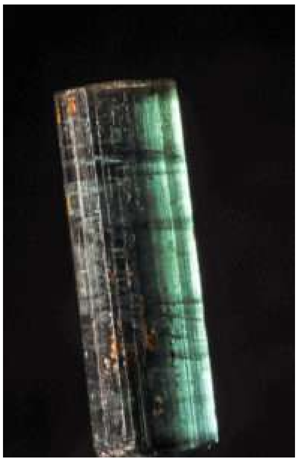
6.7.1 Silicic Igneous Rocks (>20% Quartz)

Silicic igneous rocks (see the table above) include the plutonic rocks *granite*, *granodiorite*, and *tonalite*, and their volcanic equivalents (*rhyolite, dacite, quartz andesite*). The plate below contains examples of each. All contain > 20% quartz and we name them based on the amounts of K-feldspar and plagioclase they present. Biotite, hornblende, and muscovite also may be present as minor minerals. Some granitic rocks contain no plagioclase, and some tonalitic rocks contain no K-feldspar, but feldspars of some sort are always there. Plagioclase in granitic rocks may be nearly pure albite (the Na end-member), but in other silicic igneous rocks plagioclase is more Ca-rich. In extrusive rocks, K-feldspar may be sanidine instead of orthoclase or microcline, and cristobalite or tridymite may replace quartz. Silicic volcanic rocks often contain glass instead of some of the minerals.

plutonic rocks	 6.102 Granite	 6.103 Granodiorite from Victoria, Austalia	 6.104 Tonalite from Germany
volcanic rocks	 6.105 Rhyolite	 6.106 Dacite from Lassen Volcanic National Park	 6.107 Quartz andesite with hornblende phenocrysts
	K-feldspar rich	both feldspars	plagioclase rich

Because they contain large amounts of quartz and feldspars, granitic and granodioritic rocks have light colors. Granite (Figure 6.102) and rhyolite (Figure 6.105) may have a pinkish color due to oxidized Fe in K-feldspar. These rocks also commonly contain biotite or hornblende. Granodiorite (Figure 6.103) and dacite (Figure 6.106) usually have a grayish color. These rocks contain quartz, plagioclase, and K-feldspar. Often they have hornblende or biotite, too. (The granodiorite in Figure 6.103 contains lots of biotite.) Tonalite (Figure 6.104) and andesite (Figure 6.107) may be darker than the other four rocks because they contain lots of calcic plagioclase (which commonly has a darkish color) and often large amounts of biotite, hornblende, and, occasionally, pyroxene. Note the hornblende phenocrysts in the photo of andesite (Figure 6.107). Accessory minerals in all these rocks can be magnetite, ilmenite, rutile, pyrite, pyrrhotite, zircon, sphene, or apatite.

Identifying the different plutonic rocks is generally possible based on their macroscopic appearance, perhaps aided by a hand lens. But, telling the volcanic rocks apart is problematic without looking at thin sections using a petrographic microscope. Even then, it can be a challenge. In the field, when we do not have detailed chemical or mineralogical information, we often call pink volcanic rocks *rhyolite*, white ones *andesite*, and darker colored rocks *basalt*. Volcanic glass is very common, and if a lot of glass is present, naming a rock based on mineralogy is problematic.



6.108
Tourmaline from Paraiba, Brazil

Slowly cooling magmas do not crystallize all at once. After partial crystallization, the remnant melt may contain water and dissolved *incompatible elements* that did not enter any of the minerals already formed. When the remnant melt finally crystallizes, pegmatites containing minerals rich in incompatible elements such as potassium (K), rubidium (Rb), lithium (Li), beryllium (Be), boron (B), or rare earth elements (REEs) may result. Pegmatites often contain large euhedral crystals because the water acts as a flux and promotes crystal growth. Many spectacular and valuable mineral specimens come from pegmatites. Pegmatites are also the focus of much mining because of high concentrations of exotic elements they contain. The photo seen here (Figure 6.108) is a colorful tourmaline crystal from a pegmatite in Paraiba, Brazil. It is about 8 cm tall.

We saw other examples of pegmatite minerals in Chapter 4:
- Figure 4.12 – Riebeckite (an amphibole) with K-feldspar and quartz
- Figure 4.13 – Tourmaline similar to the one shown in Figure 6.108
- Figure 4.30 – Emerald (beryl) on quartz from Brazil

6.7.2 Mafic and Intermediate Igneous Rocks (0% to 20% Quartz)

Mafic rocks contain less that 5% quartz, if any. A dark color, due to an abundance of hornblende, clinopyroxene, or olivine, and sometimes Ca-rich plagioclase, characterizes these rocks. They include *syenite*, *monzonite*, and *gabbro*, and their volcanic equivalents *trachyte*, *latite*, and *basalt*. K-feldspar dominates syenitic rocks. Plagioclase is the only feldspar in most gabbros. Plagioclase composition varies from Na-rich in syenite to intermediate Ca-rich in gabbro. Hornblende, biotite, and pyroxene are common, but usually in small amounts.

Intermediate igneous rocks are those in which quartz accounts for 5% to 20% of the rock. They include *quartz syenite*, *quartz monzonite*, and *diorite*, and their volcanic equivalents *quartz trachyte*, *quartz latite*, and *andesite*. The minerals in these rocks are the same as listed in the previous paragraph for their more mafic cousins. As with silicic rocks, intermediate rocks with more plagioclase (diorite and some monzonite) tend to have more mafic minerals and thus a darker color.

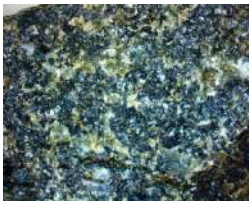
While all intermediate and mafic igneous rocks may contain hornblende and clinopyroxene, hornblende is more common in diorite and andesite, and clinopyroxene is more common in gabbros and basalts. Gabbros and basalts may also contain olivine. Magnetite, ilmenite, and apatite are common as accessory minerals in mafic and intermediate rocks.

The photos below (Figures 6.109 to 6.116) show some of the most common intermediate and mafic rocks. They include four plutonic rocks:
- syenite from Brazil that contains the feldspathoid, nepheline
- monzonite that contains subequal amounts of plagioclase and K-feldspar with hornblende

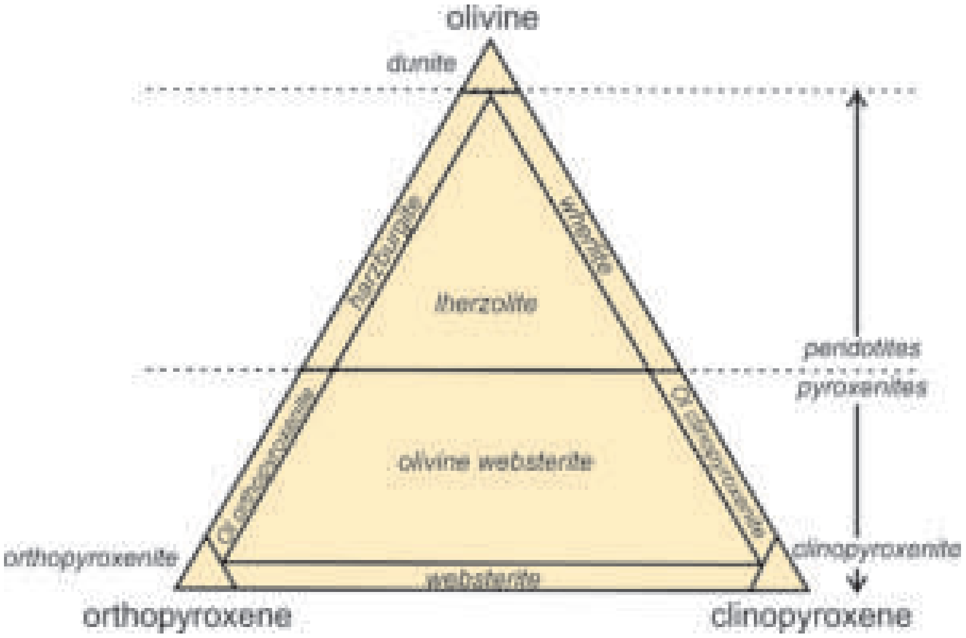
- diorite that contains almost entirely plagioclase and hornblende
- gabbro that contains green olivine, light colored plagioclase, and darker clinopyroxene

The bottom row in the table contains photos of the volcanic equivalents of the four plutonic rocks above them:

- trachyte from the Massif Central of France (mostly K-feldspar and biotite)
- latite of unknown origin with subequal amounts of plagioclase and K-feldspar
- andesite (containing dark colored xenoliths) from New Mexico
- a view of basalt outcrops in Washington

plutonic rocks	 6.109 Nepheline syenite in Rio de Janeiro	 6.110 Monzonite	 6.111 Diorite from Massachusetts	 6.112 Olivine gabbro
volcanic rocks	 6.113 Trachyte from Le Mont Dore, France	 6.114 Latite	 6.115 Rhyolite	 6.116 Outcrop with basalt columns in Mt. Rainier National Park
	K-feldspar rich	both feldspars		plagioclase rich

6.7.3 Ultramafic Igneous Rocks

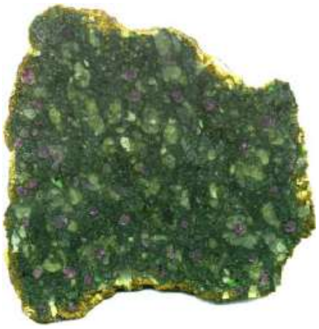


6.117 The IUGS system for normal ultramafic rocks

Ultramafic rocks are especially poor in SiO_2 and have high Mg:Fe ratios. Pyroxene (either orthopyroxene or clinopyroxene), olivine, and (less commonly) plagioclase are the dominant minerals in these rocks. The IUGS system, shown in Figure 6.117, names ultramafic rocks based on their relative amounts of olivine, orthopyroxene, and clinopyroxene. We call ultramafic rocks rich in olivine, *peridotite*. Those that are less than half olivine are *pyroxenites*. Other names, shown in the figure, divide peridotites and pyroxenites into smaller classes.

Many specimens of ultramafic rock are carried up from the mantle as *xenoliths* in magmas. The left and middle photos below (Figure 6.118 and 6.119) show examples. The photo on the left contains two different composition xenoliths. See the opening photo of this chapter for a larger view of this photo. The brown xenolith is mostly orthopyroxene and olivine. The green one contains light green olivine and darker green clinopyroxene, but they are hard to tell apart. The specimen also contains a few dark colored grains of orthopyroxene. Figure 6.119 shows a sample of garnet lherzolite that was carried to the surface in a South African kimberlite pipe. The garnets are red, olivine and orthopyroxene are green, and the less common emerald green grains are clinopyroxene. The photo on the right (Figure 6.120) shows a sample of pyroxenite, composed of large crystals of orthopyroxene and clinopyroxene. It is from the layered ultramafic Stillwater complex of Montana; two other photos of Stillwater rocks appeared earlier in this chapter (Figures 6.20 and 6.21).

6.118 Peridotite xenoliths in basalt from San Carlos, Arizona; 5.3 cm across.



6.119 Garnet lherzolite from South Africa; 9 cm across.

6.120 Pyroxenite from the Stillwater Complex, Montana; 7 cm across.

Ultramafic minerals are most stable at high temperature and they alter by reaction with water or carbon dioxide when exposed to normal Earth surface conditions. Consequently, finding fresh, unaltered ultramafic rock is difficult. Variable amounts of secondary serpentine, chlorite, talc, brucite, or calcite are nearly always present. We often find rocks called *serpentinites*, in which serpentine has replaced all or nearly all of the mafic minerals. Many ultramafic rocks – including those in kimberlite nodules – have been altered so much that we cannot determine their original mineralogy.

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6.1 Xenoliths in basalt from San Carlos, Arizona, James St. John, Wikimedia Commons
6.3 Shiprock and one of the dikes radiating from it in New Mexico, el ui, Wikimedia Commons
6.4 Granite, amazon.com
6.5 Rhyolite, Amcyrus2012, Wikimedia Commons
6.6 Porphyry, Mike Norton, Wikimedia Commons
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6.21 Ore from the Stillwater Complex
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6.23 Zoned clinopyroxene seen in thin section, www.ucl.ac.uk
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6.35 The composition of the Grorud feldspar
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6.43 Polysynthetic twinning in feldspar, imgur.com
6.44 Carlsbad twin, mineralauctions.com
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6.49 Fat separating from chicken broth with cooling, thepauperedchef.com
6.50 Perthite, Siim Sepp
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6.59 Leucite, Géry Parent, Wikimedia Commons
6.60 Nepheline, Andrew Silver, Wikimedia Commons
6.61 Sodalite, pyrite, and-calcite, Géry Parent, Wikimedia Commons
6.62 Muscovite and Albite, Robert M. Lavinsky, Wikimedia Commons
6.63 Biotite on calcite, Didier Descouens, Wikimedia Commons
6.64 Phlogopite with calcite, Géry Parent, Wikimedia Commons
6.65 Margarite, Robert M. Lavinsky, Wikimedia Commons
6.66 Kyanite, staurolite, and Paragonite, Robert M. Lavinsky, Wikimedia Commons
6.67 Lepidolite, Eurico Zimbres, Wikimedia Commons
6.69 Clinochlore from West Point, New York, Robert M. Lavinsky, Wikimedia Commons
6.73 Jadeite from California, greatmining.com
6.74 Yellow spodumene, Géry Parent, Wikimedia Commons
6.76 Enstatite crystals, Leon Hupperichs, Wikimedia Commons
6.78 Augite from Rwanda, Didier Descouens, Wikimedia Commons
6.80 Microscope view of exsolution in a pyroxene grain, www.alexstrekeisen.it
6.83 Anthophyllite from eastern Finland, Leon Hupperichs, Wikimedia Commons
6.84 Typical green blades of actinolite, plugin.us
6.85 Tremolite, Didier Descouens, Wikimedia Commons
6.86 Hornblende, James St. John, Wikimedia Commons
6.87 Amphibolite from Huelva, southwestern Spain, PepPEfe, Wikimedia Commons
6.88 Glaucophane with omphacite, James St. John, Wikimedia Commons
6.89 Beryl, Nkansah Rexford, Wikimedia Commons
6.90 Tourmaline, Jan Helebrant, Wikimedia Commons
6.91 Epidote from Prince of Wales Island, Didier Descouens, Wikimedia Commons
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6.97 Olivine nodule Zbynek Burival, Wikimedia Commons
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6.103 Granodiorite from Victoria, Australia, Solarence, Wikimedia Commons
6.104 Tonalite from Germany,Vberger, Wikimedia Commons
6.105 Rhyolite, Amcyrus2012, Wikimedia Commons
6.106 Dacite from Lassen Volcanic National Park, National Park Service
6.107 Quartz andesite with hornblende phenocrysts, cejones, pitt.edu
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6.109 Nepheline syenite in Rio de Janeiro, Amotoki, Wikimedia Commons
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6.113 Trachyte from Le Mont Dore, France, Francoise Foliot, Wikimedia Commons
6.114 Latite, www.alexstrekeisen.it
6.115 Rhyolite, Amcyrus2012, Wikimedia Commons
6.116 Basalt columns in Mt. Rainier National Park, Walter Siegmund, Wikimedia Commons
6.118 Peridotite xenoliths from San Carlos, James St. John, Wikimedia Commons
6.119 Garnet lherzolite from South Africa, James St. John, Wikimedia Commons
6.120 Pyroxenite from the Stillwater Complex, James St. John, Wikimedia Commons

7 Sedimentary Minerals and Sedimentary Rocks

7.1 Salt deposits on the shore of the Dead Sea, Jordan

7 Sedimentary Minerals and Sedimentary Rocks

KEY CONCEPTS

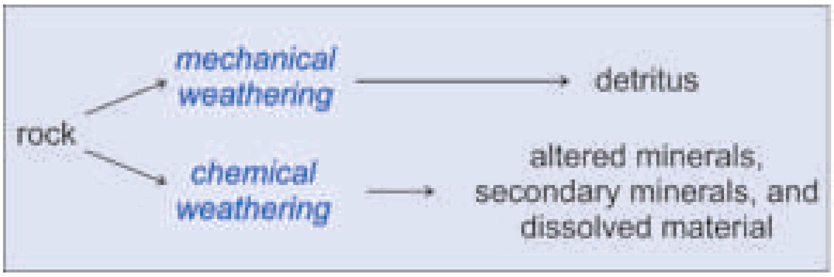
- Weathering involves the decomposition and breaking apart of rocks at Earth’s surface.
- Weathering produces solid clastic material and dissolved chemical material.
- Products of weathering may be transported and deposited

to produce clastic or chemical sediments.

- Sediments of all sorts may be lithified to become rocks.
- Clastic material typically comprises quartz and clays; less commonly other minerals.
- Minerals produced by chemical precipitation include clays, carbonates, sulfates, halides, zeolites, and chert.
- We name clastic sedimentary rocks based primarily on clast size.
- We name chemical sedimentary rocks based primarily on composition.

7.1 Weathering

Sediments are created by weathering. Weathering is the breaking apart and decomposition of rocks at the Earth's surface. It is caused by reactions with air, water, salt, and acid, by freezing and thawing, and by plants and animals. Weathering involves the decomposition of rock, and the breaking down of *primary minerals* in rock. The products include smaller pieces of rock, individual mineral grains, dissolved material that is carried away, and sometimes new *secondary minerals*.



7.2 Two kinds of weathering

Figure 7.2 shows the two parallel processes that may occur during weathering. An original source rock (igneous, metamorphic, or sedimentary) is exposed to forces that cause weathering. The weathering forces may be *mechanical* (water, wind, gravity, glaciers, waves, and frost) or *chemical* (dissolution by water, perhaps containing acids). Often the two kinds of weathering work together. And, these processes are selective. Some minerals dissolve or react and disappear faster than other minerals. Some rocks are harder and do not break apart as easily as other rocks. Over long times – geological times – chemical weathering has a much greater effect than mechanical weathering. Even apparently dry climates have enough water to promote chemical weathering on exposed surfaces, although the weathering rate may be slow.

Mechanical weathering breaks large or solid material into smaller pieces. The products produced vary greatly; we call them collectively *clasts* (from *klastos*, the Greek word meaning "broken"). *Clastic material*, also called *detritus* or *detrital material*, may be fine grains of individual minerals or it may be *lithic fragments* (rock fragments) composed of multiple minerals.

7.3 Talus on Electric Peak, Yellowstone National Park

The photo seen here (Figure 7.3) shows boulders on a *talus slope* that were produced by mechanical weathering (mostly freezing and thawing) in Yellowstone National Park. Freezing, thawing, and the action of ice created large blocky pieces of what was originally solid bedrock. Even apparently solid granites or other rocks can be broken apart this way. Talus slopes are examples of very coarse sediment. More commonly, mechanical weathering produces smaller rock fragments, or sand, or silt composed of individual mineral grains.


7.4 Weathered sandstone in Ohio

After chemical weathering, leftover rock may have a dissolved or eroded appearance, such as the sandstone seen in Figure 7.4. This sandstone has weathered to obtain a *honeycomb texture*, typical of sandstone in which the cementation of grains is not uniform. Weathering textures are not unique to sandstone. After chemical weathering, outcrops of many sorts often become rounded or pitted. The limestone outcrop shown in Figure 7.5, for example, shows signs of dissolution and chemical weathering. The surfaces are a dull chalky white and the corners are all rounded. Figure 4.24 (Chapter 4) shows another example of chemical weathering, a weathering rind on sandstone.


7.5 Weathered limestone outcrop in County Fermanagh, Northern Ireland

Minor chemical weathering can cause minerals to alter, perhaps to *oxidize* (rust). More intense weathering may cause some minerals to disappear. They may dissolve completely in water and be carried away in a *hydrolysate* (water containing dissolved ions). More often, minerals react to produce *secondary minerals* – minerals that were not present before weathering. Reactions that produce secondary minerals most commonly involve the reaction of water with previously existing minerals such as feldspars (common in many igneous rocks), to produce clays and dissolved elements. We call such reactions *hydrolysis reactions.* Secondary minerals may also form by *oxidations reactions* when primary minerals react with oxygen in air or water. For example, oxidation of iron-rich olivine or pyroxene commonly produces hematite (Fe_2O_3).

Mineral matter remaining after chemical weathering often includes original mineral grains that did not decompose. We sometimes call these minerals the *residual minerals*, or the *resistate*, because the minerals resisted weathering. Typical resistate minerals include quartz, clay, K-feldspar, garnet, zircon, rutile, or magnetite. After the more easily decomposed minerals break down and disappear, the resistate minerals remain to become sediment.

If we examine fresh (unweathered) outcrop in a road cut, rock often appears hard and shiny. Examination with a hand lens reveals that minerals have well-defined boundaries and generally sharp outlines. They may show good cleavage or crystal faces. Minerals may have their normal diagnostic colors: quartz is clear, feldspars are white or pink, muscovite is silvery and sparkly, magnetite appears metallic, and biotite and other mafic minerals appear black.

7.6 Weathered granite in a British quarry

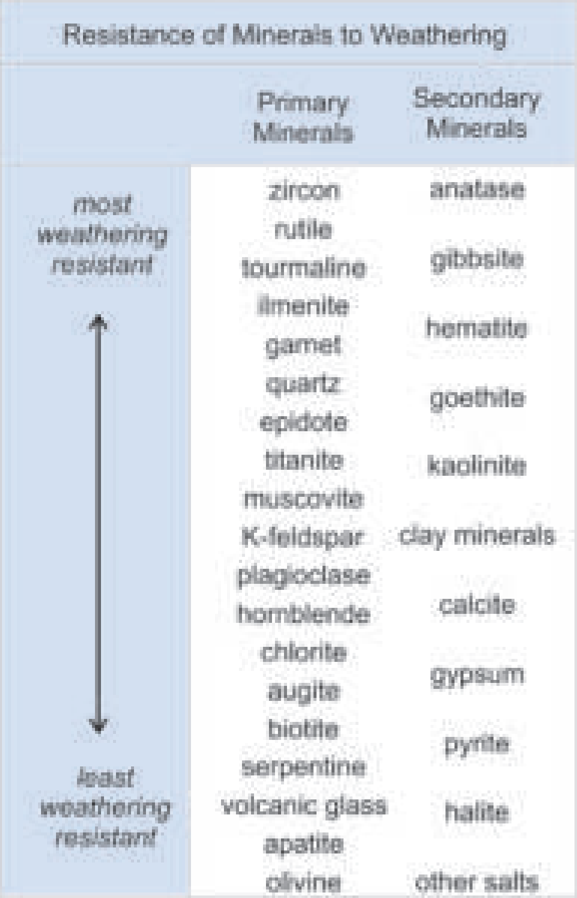
The picture is not the same if we examine outcrops exposed to weathering for a long time. After weathering, rock and most minerals have a dull or drab appearance. Grain boundaries and cleavages are obscured. Oxidation (rusting) and hydration may produce reddish, yellow, brown, or gray hues. Sometimes a layer of clay or other material coats all surfaces, obscuring diagnostic minerals. The photo shown here (Figure 7.6) shows granite that is being replaced by kaolinite (a clay) during weathering. The once solid crystalline granite is now a dull earthy mass.

Mafic silicates weather to create secondary clay minerals and iron oxides. Feldspars of all sorts weather to become clay minerals and dissolved material. Quartz is usually unchanged by weathering. Calcite weathers by dissolution producing dissolve ions. And aluminous minerals weather to gibbsite or other aluminum hydroxides. The table below lists weathering products for the most common minerals. Clays and limonite (a general term describing for a mix of hydrated Fe-oxides and hydroxides) dominate the list. Quartz and aluminous minerals may also be produced. While creating these secondary minerals, weathering also produces dissolved cations (especially alkalis and alkali earths) and anions, which may have a significant impact on water chemistry and quality.

Typical Chemical Weathering Products of Common Minerals		
mineral (composition)	**residual minerals**	**dissolved ions**
halite (Na chloride)		Na^+, Cl^-
gypsum (hydrated Ca sulfate)		Ca^{2+}, $(SO_4)^{2-}$
calcite (Ca carbonate)		Ca^{2+}, $(HCO_3)^-$
quartz (SiO_2)		$(SiO_4)^{4-}$
plagioclase (Ca-Na-Al silicate)	clay minerals	Ca^{2+}, Na^+, $(SiO_4)^{4-}$
alkali feldspar (K-Na-Al silicate)	clay minerals	K^+, Na^+, $(SiO_4)^{4-}$
olivine (Fe-Mg silicate)	limonite, hematite, clay	Mg^{2+}, $(SiO_4)^{4-}$
pyroxene (Ca-Fe-Mg silicate)	limonite, hematite, clay	Ca^{2+}, Mg^{2+}, $(SiO_4)^{4-}$
amphibole (Ca-Fe-Mg silicate)	limonite, hematite, clay	K^+, Mg^{2+}, $(SiO_4)^{4-}$
biotite (K-Fe-Mg-Al mica)	limonite, hematite, clay	K^+, Mg^{2+}, $(SiO_4)^{4-}$
muscovite (K-Al mica)	clay	K^+

Some minerals break down more easily than others. Geologists can compare weathering rates by looking at minerals in rock outcrops, and by studying the minerals present in sediments of different ages. Goldich (1938) made such observations, publishing what we call *Goldich's Weathering Series*. The series ranked the ease with which common igneous minerals break down. Goldich found that minerals that crystallize from a magma at high temperature – minerals relatively poor in silicon and oxygen – are generally less resistant to weathering than those that crystallize at low temperature.

Thus, the minerals at the top of Bowen’s reaction series weather most easily and those at the bottom are more resistant to weathering. Iron-magnesium silicates, such as olivine, pyroxene, or amphibole break down relatively easily. Calcic feldspars, and many minerals with high solubilities in water, are also quick to decompose. Quartz, some feldspars, and some nonsilicate minerals are relatively resistant to weathering because they contain more bonds, especially Si – O bonds, that do not break easily. It should not be surprising that minerals that characterize high-temperature igneous rocks, or those most often precipitated from water, are the first to decompose under Earth surface conditions where temperature is low and water is abundant.



Resistance of Minerals to Weathering

	Primary Minerals	Secondary Minerals
most weathering resistant	zircon	anatase
	rutile	
	tourmaline	gibbsite
	ilmenite	
	garnet	hematite
	quartz	goethite
	epidote	
	titanite	kaolinite
	muscovite	
	K-feldspar	clay minerals
	plagioclase	
	hornblende	calcite
	chlorite	
	augite	gypsum
	biotite	pyrite
	serpentine	
least weathering resistant	volcanic glass	halite
	apatite	
	olivine	other salts

Sedimentologists have made comprehensive lists of the relative ease with which minerals weather. Although there is some variation, the list shown here is typical (from Birkeland 1999). Like primary minerals, secondary minerals can break down and disappear, so this table compares weathering rates for both primary minerals and secondary minerals. Weathering resistance, however, does not necessarily mean that a particular mineral is abundant in weathered materials. Some of the minerals at the top of the list in the table are uncommon compared with others. Zircon, rutile, and tourmaline, for example, are very resistant to weathering but rarely are major components of sediments because they are only minor minerals in most parent rocks. Minerals at the bottom of the list are very unstable when exposed to the elements and, consequently, are absent from all but the youngest sediments.

After chemical weathering, dissolved material is carried away. Residual minerals and secondary minerals such as clay may remain where they form. For example, prolonged weathering of bedrock can lead to thick layers of reddish soil called *laterite* in tropical areas (see Box 7-1, below). Laterites vary but are always rich in oxide minerals and clays. Laterites are easily eroded. Over time, erosion by water, gravity, or wind can transport laterite debris, just like any other detrital material, away from its place of origin.

● Box 7-1 Laterites and Bauxites

7.7 Bauxite (red) above sandstone (white) at Pera Head, Weipa, Australia

Consider a tropical area with warm weather and abundant rainfall. Weathering and leaching will be extreme, and even clay minerals may decompose. Normally soluble elements, and even relatively insoluble silica, will be dissolved and removed. The remaining material, called a *residual deposit*, is often composed primarily of aluminum oxides and hydroxides, the least soluble of all common minerals. We term such deposits *laterites* (if unconsolidated) or *bauxites* (if lithified into rock). Figure 7.7 shows bauxite in Australia.

Bauxites and laterites are our most important source of aluminum. But, the mineralogy of a laterite depends on the composition of rocks weathered to produce it. Laterites can also be important sources of iron, manganese, cobalt, and nickel, all of which have low solubilities in water.

Most laterites are aluminous. The most important aluminum ore (bauxite), is a mixture of several minerals, including the polymorphs *boehmite* and *diaspore*, both $AlO(OH)$, and gibbsite, $Al(OH)_3$. Bauxite is mined in large amounts in Australia and Indonesia, and in smaller quantities in the Americas and in Europe. In some places, relatively young laterites produce ore, but in Australia economical laterite deposits are more than 65 million years old.

7.2 Siliciclastic Sediments

The Wentworth Scale for Grain Size	
classification	**particle size** **(diameter in mm)**
boulder	>256
cobble	64 to 256
pebble	4 to 64
gravel or granule	2 to 4
sand	1/16 to 2
silt	1/256 to 1/16
clay	<1/256

The term *siliciclastic* refers to sediments composed mostly of silicate minerals. The most common sedimentary rocks – including shale, sandstone, and conglomerate – form from siliciclastic sediments. Other, less common, kinds of sedimentary rocks consist of carbonates (in limestones), iron oxides and hydroxides (such as hematite or goethite), or other minerals. Geologists classify siliciclastic sediments based on grain size. The standard classification system is the *Wentworth Scale* (see table). Depending on size, grains may be boulders, cobbles, pebbles, gravel, sand, silt, or clay. The word *clay* sometimes causes confusion. Sedimentary petrologists use the term to refer to clastic grains smaller than 0.004 mm in longest dimension. In this text, however, we also use it to refer to minerals of the clay mineral group, no matter the grain size.

Clast sizes vary from fine clay and silt to huge boulders.

Small clasts are usually composed of a single mineral, generally quartz or clay. Larger clasts are commonly lithic fragments composed of multiple minerals. The photos below show some examples. Figure 7.8 is a view of mud along a river in Tasmania. The mud comprises fine grains of silt and clay. Figure 7.9 shows sand from Pfeiffer Beach, California. Quartz dominates most common sand, but the sand seen here contains mostly rosy garnet, and also epidote, zircon, magnetite, spinel, staurolite, and only minor quartz. Figure 7.10 shows centimeter scale pebbles on a beach in Greece. Most of the pebbles are lithic fragments (rock fragments) composed of more than one mineral. Figure 7.11 shows cobbles in a dry river bottom. These cobbles are all lithic fragments. The mineral grains in the Pfeiffer Beach sand are angular, but the clasts in the last two photos have been well rounded by abrasion caused by them being tumbled by flowing water.

7.8 Silt along the North Esk River, Tasmania

7.9 Sand at Pfeiffer Beach, California. Grains are about 1 mm across.

7.10 Pebbles on the beach, Lychnos, Greece. Grains are 1-3 cm across.

7.11 Cobbles, Hope River Valley, British Columbia. The piece of wood is about 15 cm long.

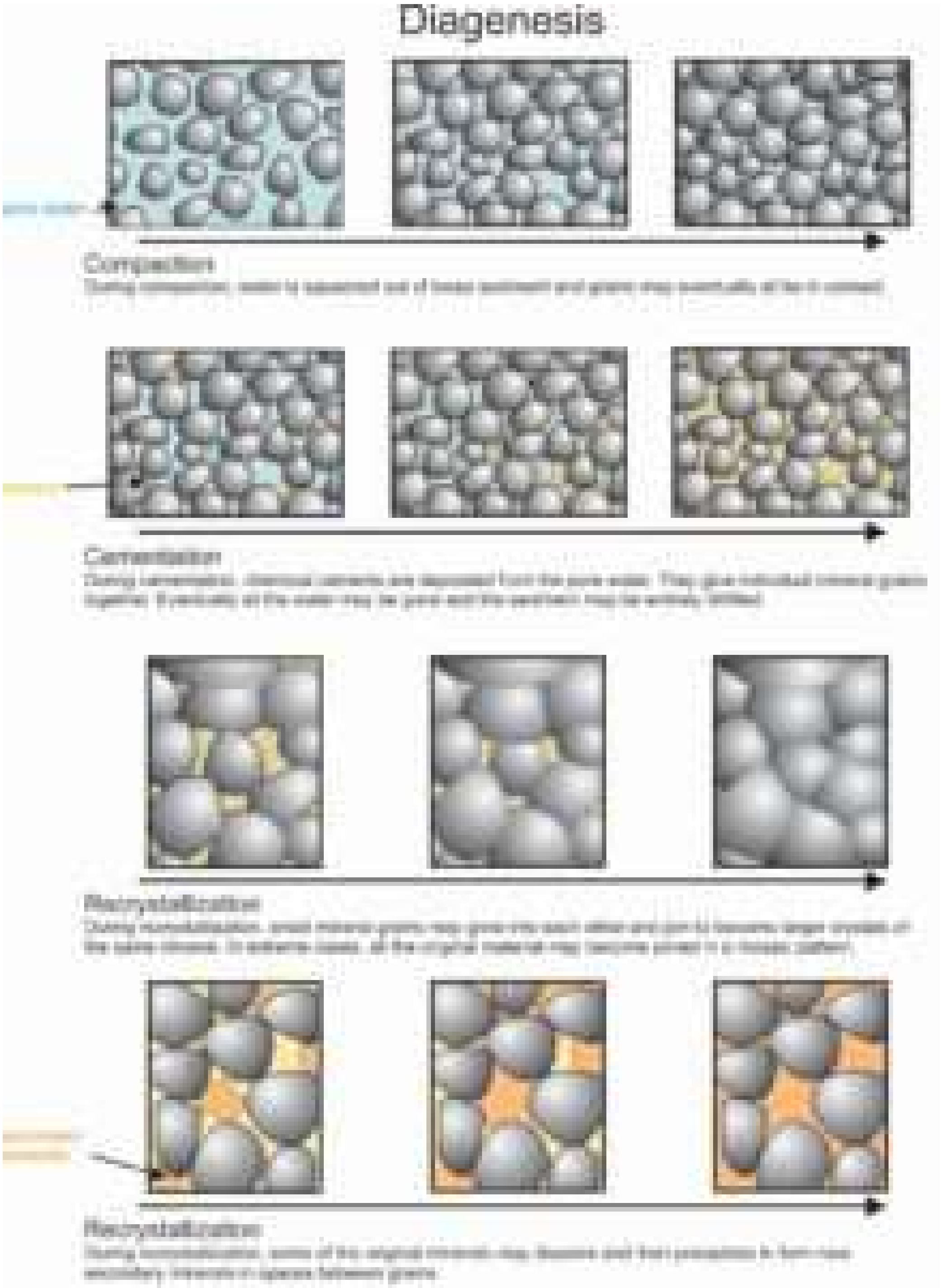
7.3 Transportation, Deposition, and Lithification

7.3.1 Clastic Sedimentation

7.12 Alluvium deposited by the Mendoza River, Argentina

Flowing water transports clastic material until it reaches a place where it collects, perhaps a river or lake bottom, or maybe a delta. Wind, gravity, and other agents can move clastic material as well. Eventually, sediments are deposited when the forces of gravity overcome those trying to move them. Large grains may not move far and are deposited first. As the energy of transportation decreases, smaller material is deposited. So, during transportation, sediments commonly become *sorted*, which means that sediment deposits often have relatively uniform grain size. Thus, for example, coarse material may be deposited near the headwaters of a stream, while only fine material makes it to a delta. Sorting is not ubiquitous; streambed gravel, for example, may contain a mix of silt, sand, and larger clasts, and glacial deposits often contain a jumble of material of many different sizes. The photo above (Figure 7.12) shows very poorly sorted *alluvium* (loose, unconsolidated nonmarine sediment deposited by rivers or streams) in Argentina.

After deposition, unconsolidated sediment may, over time, change into a *clastic sedimentary* rock by the process called *lithification* (from *lithos*, the Greek word meaning stone). Lithification involves compaction and cementation of clastic material. Common cementing agents include the minerals quartz, calcite, and hematite.



7.13 The processes of diagenesis

Before, during, and after lithification, sedimentary rocks undergo textural or chemical changes due to heating, compaction, or reaction with groundwaters. Biological agents, including small animals or bacteria, also can be important, as can chemical agents brought in by flowing water. We call these changes collectively *diagenesis*. Figure 7.13 depicts the major steps of diagenesis: compaction, *cementation*, and *recrystallization*.

Dissolution and removal of minerals (*leaching*) and the formation of clay or other minerals are both common during diagenesis. We call any new minerals that form, *authigenic minerals*. Zeolites, clays, feldspar, pyrite, and quartz can all be authigenic minerals. Although diagenesis creates many authigenic minerals, most are so fine grained that we cannot identify them without X-ray analysis.

Textural changes, including compaction and loss of pore space, are common and are part of diagenesis. *Recrystallization*, the changing of fine-grained rocks into coarser ones, is another form of diagenetic textural change. During recrystallization, as individual mineral grains grow together, secondary minerals may precipitate in open spaces, and more mineral cements may develop. Consequently, rocks become harder.

Diagenesis is equivalent to a low-temperature, low-pressure form of *metamorphism*, and the processes of sedimentation, lithification, diagenesis, and low-grade metamorphism form a continuum. Lithification changes unconsolidated sediment into a rock. Cementation by quartz, calcite, or hematite may be part of the lithification process. It also may be considered a diagenetic process. Similarly, the formation of many low-temperature minerals such as *zeolites*, a normal part of diagenesis, overlaps with the beginnings of metamorphism. Metamorphic petrologists often define the onset of metamorphism by the first occurrence of metamorphic minerals. This definition can be hard to apply because many diagenetic minerals are also metamorphic minerals. Furthermore, *laumontite*, often considered to be formed at the lowest temperature of all metamorphic minerals, is a zeolite that is hard to distinguish from minerals that form diagenetically.

7.3.2 Chemical Sedimentation

7.14 Travertine terraces at Hot Springs State Park, Thermopolis, Wyoming

Chemical weathering yields dissolved material that water transports until precipitation of chemical sediment occurs. Several things may cause precipitation; the most common causes are evaporation, changes in temperature or acidity (*pH*), and biological activity. Hot springs deposit a form of calcite called *travertine*, for example, when cooling water becomes oversaturated with $CaCO_3$. This photo (Figure 7.14) shows thick *travertine terraces* deposited by hot springs in Wyoming.

In freshwater streams or lakes, a *pH* change due to biological activity may cause precipitation of another form of calcite called *marl*. In marine settings, many reef-building organisms have shells or skeletons made of organic calcite. Calcite and other chemical sedimentary minerals, then, precipitate in many ways. In contrast with clastic sediments, chemical sediments usually lithify at the same time they precipitate.

7.15 Salt deposits at Devil’s Golf Course, Death Valley National Park, California

Natural waters contain dissolved minerals, and all minerals are soluble in water to some extent. Halides, many sulfates, and other salts have very high solubilities. Carbonate minerals, including calcite and dolomite, have moderate solubilities. Silicate minerals have relatively low solubilities. If water evaporates, it may become oversaturated in particular minerals and deposit chemical sediments, such as the salt deposits in the photo seen here (Figure 7.15). Precipitation will continue, decreasing concentrations of dissolved material, until the solution and sediments achieve equilibrium. Because of their high solubility, large amounts of evaporation may be necessary before salts such as halite, precipitate. In contrast, carbonate minerals (calcite and dolomite) and silica often precipitate early during evaporation. Silica (SiO_2), in the form of *chert*, is the only silicate mineral that commonly forms a chemical sedimentary rock.

Gypsum ($CaSO_4•2H_2O$), anhydrite ($CaSO_4$), halite (NaCl), and sylvite (KCl) consist of common elements and have high (gypsum and anhydite) to very high solubilities (halite and sylvite). So, their chemical components are common as dissolved species. As water evaporates, perhaps in a closed inland basin or an isolated sea, these minerals may precipitate to form thick beds of *evaporite minerals*. Besides these four minerals, many other (less common) minerals occur in evaporites, too. Evaporites are found in many parts of the world. Geologists estimate that thick evaporite beds, at some depth, underlie 35% of the United States.

7.16 The Trona Pinnacles in Searles Lake in the Mojave Desert, California

Figure 7.16 shows the *Trona Pinnacles* in Searles Lake, a southern California playa lake. Some of these pinnacles rise more than 40 m above the lakebed. These pinnacles consist of *trona* (a hydrated sodium carbonate) that precipitated from briny water. Like all playas, this lake is dry most of the time. But, past flooding and subsequent evaporation produced thick layers of evaporite minerals. More than 25 different minerals are found in the Searles Lake bottom. The list includes sodium and potassium carbonates, sulfates, borates, and halides. Borax (hydrated sodium borate), trona, and several other minerals are profitably mined from Searles Lake sediments today.

Most evaporite minerals are rare at Earth's surface because they are so soluble that they dissolve away in all but the most arid climates. Gypsum is the most common evaporite in outcrops because it is less soluble than others, and because it forms from any anhydrite exposed at or near Earth's surface. In the subsurface, massive gypsum and halite beds are common, as are the *salt domes* found in Texas and other Gulf Coast areas of the United States. Although generally dominated by just a few minerals, many other minerals may be present. In all, petrologists have reported nearly 100 minerals from evaporites. Less than a dozen are common.

7.17 Salt deposits on the shore of Utah's Great Salt Lake

Evaporites may be *marine* deposits associated with evaporation of ocean water. They may also be *non-marine*, associated with freshwater lakes or other continental waters. For water to become oversaturated, a water body must be somewhat isolated and the evaporation rate must be faster than any water flowing in. This is most common in an arid environment. For example, at various times in the past, the Mediterranean Sea has been cut off from an ocean. Evaporation led to thick salt deposits that lie beneath the Mediterranean today. And, today, evaporite minerals are collecting along the shores of the Dead Sea between Jordan and Israel (see Figure 7.1, the opening figure in this chapter), on the shores Utah's Great Salt Lake (Figure 7.17), and around many other isolated water bodies.

Some of the Most Common Evaporite Minerals		
mineral group	**mineral name**	**chemical**

chlorides	halite sylvite bischofite kainite carnallite	$NaCl$ KCl $MgCl_2\bullet 6H_2O$ $KMg(SO_4)Cl\bullet 3H_2O$ $KMgCl_3\bullet 6H_2O$
sulfates	anhydrite gypsum barite thenardite mirabilite kieserite langbeinite polyhalite kainite epsomite	$CaSO_4$ $CaSO_4\bullet 2H_2O$ $BaSO_4$ Na_2SO_4 $Na_2SO_4\bullet 10H_2O$ $MgSO_4\bullet H_2O$ $K_2Mg_2(SO_4)_3$ $K_2Ca_2Mg(SO_4)_4\bullet 2H_2O$ $KMg(SO_4)Cl\bullet 3H_2O$ $MgSO_4\bullet 7H_2O$
carbonates	dolomite calcite magnesite trona	$CaMg(CO_3)_2$ $CaCO_3$ $MgCO_3$ $Na_3(HCO_3)(CO_3)\bullet 2H_2O$
borate	borax	$Na_2B_4O_7\bullet 10H_2O$

As ocean water evaporates, minerals precipitate in predictable order from those that are least soluble to those that are most soluble. Calcite is first, followed by gypsum, anhydrite, and then halite. Many other minerals may precipitate in lesser amounts. Continental water contains different dissolved solids than marine water, so continental evaporites contain different minerals than marine evaporites. Water chemistry is also quite variable, so many different minerals are possible.

Continental evaporite deposits may contain halite, gypsum, and anhydrite but also typically have borax, trona, and many other non-marine salts. The table lists some minerals reported from evaporite deposits in North America. It is a long list.

7.4 Sedimentary Minerals

7.4.1 Common Minerals

The previous chapter discussed silicate minerals common in igneous rocks. In principle, they could all be detrital grains in sediments and sedimentary rocks. In practice, most break down so quickly that they cannot be weathered or transported very much before completely decomposing. Quartz is the most resistant to weathering. It is also a common component of many igneous and metamorphic rocks found at the Earth’s surface. Many minerals weather to produce clays. It is no surprise, therefore, that quartz and clays are the main silicate minerals in most clastic rocks. Feldspars and sometimes muscovite may also be present but are usually subordinate to quartz. They are absent from rocks formed from sediments transported long distances or weathered for long times. Mafic silicate minerals are exceptionally rare in sediments or sedimentary rocks. Besides quartz and clays, other silicates, including zeolites, may occasionally be present. Important nonsilicate minerals in clastic rocks include carbonates, sulfates, oxides, halide minerals and occasionally pyrite.

7.4.2 Clay Minerals

Clay Minerals	
illite group	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2 \bullet nH_2O$
smectite group	
montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \bullet nH_2O$
nontronite	$Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2 \bullet nH_2O$
beidellite	$Na_{0.5}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2 \bullet n(H_2O)$
saponite	$Ca_{0.25}(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \bullet n(H_2O$

kaolinite group	
dickite	$Al_2Si_2O_5(OH)_4$
halloysite	$Al_2Si_2O_5(OH)_4$
nacrite	$Al_2Si_2O_5(OH)_4$
related minerals	
vermiculite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \bullet 4H_2O$
talc	$Mg_3Si_4O_{10}(OH)_2$
pyrophyllite	$Al_2Si_4O_{10}(OH)_2$

The clay minerals include many different species; all are sheet silicates. The sheets comprise tetrahedral layers containing mainly Si and Al, and octahedral layers containig mainly Al, Mg, and Fe. They generally contain less potassium than micas. Some clays are hydrous, some having as much as 15 to 20 weight percent (wt %) H_2O. Their layered structure and the weak bonding between layers give them a characteristic slippery feel when wet.

The major differences between the different clay species are the compositions and stacking order of atomic layers. The formulas in the box here are only approximate because clays often contain many elemental substitutions.

Clay minerals account for nearly half the volume of sedimentary rocks. They are usually very fine grained, often less than 1 µm (10^{-6} m) in size, have complex chemistries, and are structurally variable. This makes identification of individual clay species difficult. X-ray analysis is often necessary to tell them apart. In contrast with quartz and feldspar, clays do not form in igneous and metamorphic environments.

Clays are common in shales and other sedimentary rocks. The clay species present depends on the sediment sources. Although usually fine grained, clays can form thick beds or layers. They also develop as coatings on other minerals undergoing weathering. These generalizations are true of all clay minerals, but there is a great deal of variety. In part, the variation is due to the low temperatures at which these minerals form. At high temperatures, minerals and mineral structures tend to be simple and ordered. At low temperatures, structures are often more complex or disordered, and many different mineral varieties may form.

The three most important kinds of clays are *illite, montmorillonite*, and the clays of the *kaolinite group*. Figures 7.18, 7.19, and 7.20 show examples of each, but these minerals have many different appearances. Kaolinites, also called *kandites*, vary less in composition and structure than other clays, although several kaolinite polymorphs (*dickite, halloysite, nacrite*) are known. Kaolinite is the principal clay used to make ceramic ware because it remains white when fired in a kiln. Illite is quite similar to muscovite in some ways, but contains more Si and less K.


7.18 Kaolinite


7.19 Illite


7.20 Montmorillonite

Montmorillonite, which belongs to the *smectite* group, can take up extra water or other fluids between layers of atoms. In the process the clay expands. So, we sometimes call montmorillonite and other clays of the smectite group *expandable* or *swelling clays*. Because they absorb liquids so well, gas station operators use them to clean up spilled oil, and homeowners use them as kitty litter. They are the major components of earthy material called *bentonite*, sometimes prized for its water-absorbing and cation-exchange properties. *Vermiculite*, another clay of the smectite group, is often used to lighten up potting soil. Montmorillonite dominates modern clay-rich sediments and sedimentary rocks; illite dominates most sedimentary rocks that are older than about 100 million years. Geologists ascribe this development to ongoing diagenesis, to variations in tectonic activity resulting in changes in sediment sources, and to changes in biological activity.

● Box 7-2 Clays Used in Industry, Arts, and Ceramics

Many different clays have industrial uses. Clays are widely used to make bricks, tile, paper, rubber, water pipes, and china. They are even used today by some restaurants to thicken milkshakes. Early peoples made bowls and other artifacts by shaping clay and allowing it to dry in the sun. Porcelain and china makers commonly use kaolinite. If baked to temperatures above 500 °C, kaolinite will dehydrate to metakaolinite ($Al_2Si_2O_7$), a non-mineral that is relatively hard. Such temperatures can be obtained over open fires, and much early pottery consists of metakaolinite. Although metakaolinite is porous, it will not soften when wetted, in contrast to sun-baked clays.

7.21 Porcelain Ming vase

Porcelain refers to a special type of high-grade white ceramic. The Ming vase, seen in this photo (Figure 7.21), is an example. The white color is only possible if the ceramic is made from extremely pure kaolinite. Porcelain is baked, or fired, at very high temperatures. At temperatures of 925 °C and above, metakaolinite converts to a mixture of cristobalite, mullite, and other phases, but it does not melt unless the temperature exceeds 1,600 °C. Prior to firing, small amounts of feldspar or talc are mixed with the kaolinite. When fired at 1,200 to 1,450 °C, the feldspar or talc melt to form a glass, which gives porcelain its glassy luster without melting the kaolinite and destroying the object being made. Porcelain was first developed in China more than 1,000 years ago and slowly moved east through the rest of Asia and to Europe and then the Americas.

7.23 Pyrophyllite 11 cm across

7.22 Talc in a schist 9.7 cm across

Talc, a secondary mineral that forms when Mg-silicates such as olivine or pyroxene are altered, and *pyrophyllite*, an uncommon metamorphic mineral, are often grouped with the clays. Figures 7.22 and 7.23 show examples of each. Both are less variable in their atomic arrangements and composition and contain less H_2O than true clays. They are transitional between clays and micas in structure and, when seen in hand specimen or thin section, are typically easier to identify than clays. Talc is very soft and has a diagnostic greasy feel that generally makes identification straightforward. In contrast, pyrophyllite often looks like many other white minerals, unless it has the characteristic splay of crystals seen in the photo above (Figure 7.23).

7.4.3 Carbonate Minerals

Carbonate Minerals	
Ca-Mg-Fe carbonates	
calcite	$CaCO_3$
aragonite	$CaCO_3$
magnesite	$MgCO_3$
siderite	$FeCO_3$
dolomite	$CaMg(CO_3)_2$
ankerite	$CaFe(CO_3)_2$
Other	
rhodochrosite	$MnCO_3$
smithsonite	$ZnCO_3$
cerussite	$PbCO_3$
strontianite	$SrCO_3$
witherite	$BaCO_3$
azurite	$Cu_3(CO_3)_2(OH)_2$
malachite	$Cu_2CO_3(OH)_2$
hydromagnesite	$Mg_5(CO_3)_4(OH)_2•4H_2O$
natron	$Na_2CO_3•10(H_2O)$

Mineralogists have identified more than 50 different carbonate species; all contain $(CO_3)^{2-}$ groups but some contain other anions or anionic groups. The box lists some examples. The most important carbonates are Ca-Mg-Fe carbonates, especially calcite and dolomite, $CaCO_3$ and $CaMg(CO_3)_2$, respectively. Less common rhodochrosite, smithsonite, cerussite, strontianite, azurite, and malachite sometimes form spectacular mineral specimens. These minerals are also important ore minerals of manganese, zinc, lead, strontium, and copper. The common carbonates have relatively simple compositions and include no hydroxyl groups or H_2O. Some relatively rare species are more complex, however, and examples are at the bottom of the list.

Calcite is the most abundant carbonate mineral. It typically forms by precipitation from oversaturated water. It also occurs in caves, where calcite forms stalactites and stalagmites. Calcite and other carbonate minerals also precipitate from *hydrothermal waters* (warm waters), especially in ore deposits and typically in veins. This is how most azurite and malachite, and some related minerals, are created.

7.24 Maze coral

Many carbonate minerals can have either an inorganic or an organic origin. Inorganic marine carbonate rocks form when either calcite or aragonite precipitate from ocean water. *Marl* may form when carbonates precipitate on lake or stream bottoms. In contrast, organic carbonate rocks form when algae, corals, clams and other organisms create structures and shells from $CaCO_3$ dissolved in seawater. This may produce carbonate rocks directly, or residual shells, bones, and other material can accumulate to produce carbonate clastic rocks. The maze coral seen in this photo (Figure 7.24) builds its structure out of calcite.

7.25 Marble from Tate,

Georgia. 6.7 cm across

Both calcite and dolomite are essential minerals in limestones and dolostones (limestones containing dolomite instead of calcite), and may be clasts in other kinds of sedimentary rocks. Some clastic rocks are held together by fine grained carbonate cement. Both minerals are found in metamorphic rocks such as *marbles* and in rare igneous rocks called *carbonatites*. The photo seen here (Figure 7.25) shows a marble made of coarsely crystalline calcite.

7.26 White hydromagnesite on top of basalt

Many carbonate minerals are secondary minerals formed during weathering or diagenesis. For example, most dolomite is secondary and forms by reaction of calcite with Mg-rich water during diagenesis. Magnesite, ($MgCO_3$), a related carbonate, forms as an alteration product of mafic and ultramafic rocks. Hydromagnesite (a hydrated equivalent of magnesite) forms by weathering of Mg-rich minerals, including olivine, serpentine, and others. Figure 7.26 shows hydromagnesite that has crystallized on the surface of basalt.

The photos below are examples of coarsely crystalline carbonate minerals. Figure 7.27 shows *calcite* crystals (Ca-

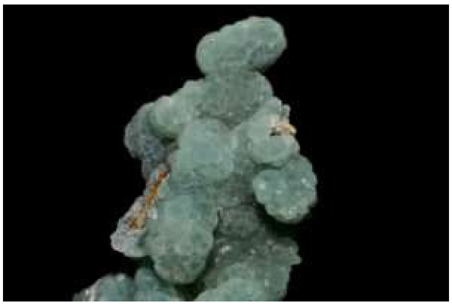
carbonate) on top of siderite (Fe-carbonate). TFigure 7.28 shows *aragonite*, which is a polymorph of calcite. The blue and green specimen in Figure 7.29 contains *azurite* and *malachite*. Both are Cu-carbonates and both are copper ore minerals. The pinkish crystals in Figure 7.30 are *rhodochrosite* (Mn-carbonate). Rhodochrosite is not always this color, but when it is, the color helps identify it. The azurite, malachite, and rhodochrosite come from a well-known mining district in western Colorado. The green crystals in Figure 7.31 are *smithsonite* (Zn-carbonate). Like rhodochrosite, smithsonite comes in various colors, but this green color is typical. The last photo (Figure 7.32) shows crystals of *dolomite* (Ca-Mg carbonate) on top of talc.

7.27 Calcite (white) with siderite (green) from the Pyrenees Mtns., France.

7.28 Aragonite from Sicily, Italy. 7 cm across.

7.29 Azurite (blue) and malachite (Green) from San Juan County., Colorado

7.30 Rhodochrosite with quartz, from San Juan County., Colorado



7.31 Smithsonite from

France

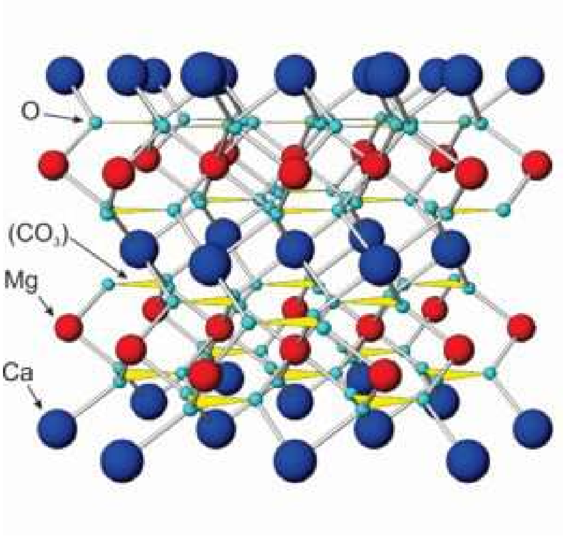
7.32 Dolomite (white) with talc (silvery) from the Pyrenees Mtns., France. 10 cm across.

Unfortunately, most mineral specimens are not as well formed or beautiful as suggested by the photos above. So, below are three more typical examples of calcite. The calcite specimen on the left (Figure 7.33, below) is massive; it is difficult to pick out distinct crystal shapes. The blue calcite in Figure 7.34 and the translucent calcite in Figure 7.35 are cleavage fragments. Calcite cleaves easily into rhombohedral shapes like the ones seen here, and the flat surfaces are cleavage planes, not crystal faces. Blue calcite is rare but translucent calcite is not. Rhombohedral cleavage fragments are exceptionally common.

7.33 Calcite from Tapuli, Sweden. 8 cm across.

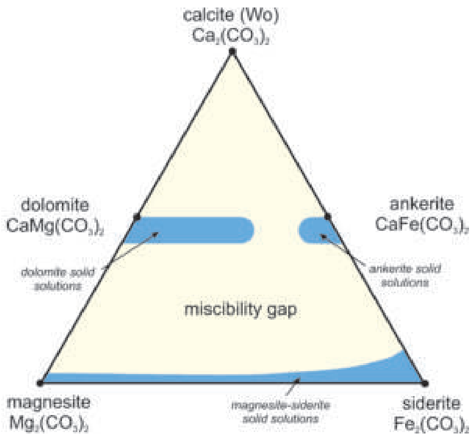
7.34 Blue calcite cleavage fragments

7.35 Rhombs of translucent calcite from England. Crystals are about 3 cm across



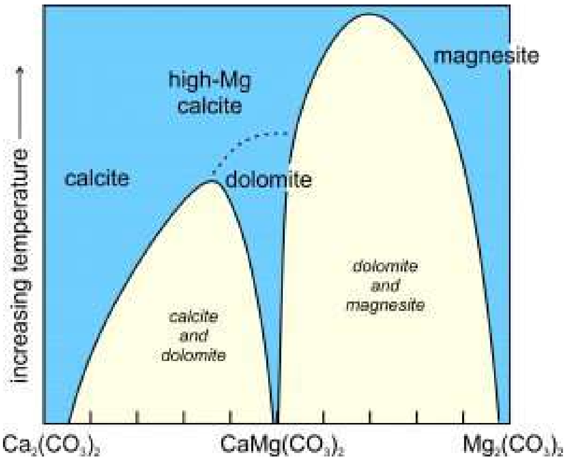
7.36 The atomic arrangement in dolomite

The atomic arrangements in calcite and dolomite, the most common carbonates by far, contain $(CO_3)^{2-}$ groups alternating with Ca^{2+} or Mg^{2+}. In the model of dolomite seen here (Figure 7.36), the blue atoms are calcium, the red ones magnesium, and the small aqua atoms are oxygen. Carbonate $(CO_3)^{2-}$ groups are shown as yellow triangles. Other carbonates have similar structures. They all contain divalent anion carbonate groups and divalent cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, or Zn^{2+}. (Figure 7.36 is not to scale; the size of the carbonate groups is actually larger tham Ca^{2+} and Mg^{2+}.)



7.37 The stable Ca-Mg-Fe carbonates at low temperature

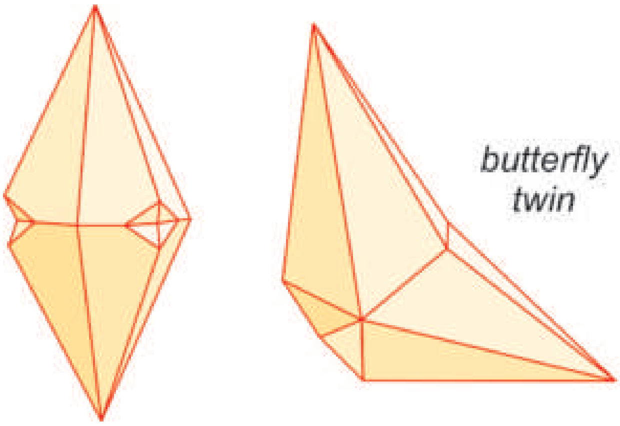
We can plot the compositions of Ca-Mg-Fe carbonates on a triangular diagram (similar to that used for pyroxenes in the previous chapter). Figure 7.37 shows, in blue, the ranges of stable carbonate compositions at low temperature; the stable compositions are limited. A large miscibility gap exists between the Ca-bearing carbonates and the Ca-free ones. It is similar to the gaps between wollastonite, clinopyroxene, and orthopyroxene we have already seen. And, the dolomite-ankerite series does not extend all the way across the diagram. As with the pyroxenes, the size of the miscibility gaps varies with temperature.



7.38 Solvi between calcite and magnesite

Figure 7.38 shows the simplfied schematic solvus relationships between calcite ($CaCO_3$) and magnesite ($MgCO_3$), equivalent to the left side of the triangle above. (It is simplified because melting and decarbonation reactions occur at high temperatures but are not shown.) We can see that the solvi narrow as temperature increases. At the highest temperatures on the diagram, calcite and high-magnesium calcite are stable. They are both Ca-Mg solid solutions of variable composition. Magnesite, an Mg-Ca solid solution, is stable too. At somewhat lower temperatures, high-Mg calcite changes into dolomite by an order-disorder transformation. The miscibility gaps (in yellow) at low temperature, mean that most carbonate compositions will unmix into calcite and dolomite, or dolomite and magnesite, solid solutions. Calcite may contain some extra magnesium, but the other two minerals will be close to end member composition. Calcite sometimes develops exsolution textures that we can see with a thin section and a petrographic microscope.

7.40 Calcite with butterfly twinning 6cm across



7.39 Two common ways that calcite twins

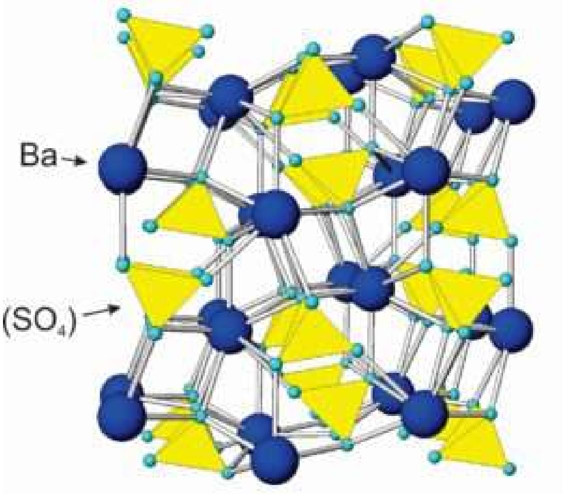
Calcite crystals twin by several different twin laws. The drawings seen here (Figure 7.39) show two common twin appearances. The drawing on the right is called a *butterfly twin*, and the photo in Figure 7.40 shows a good example of this kind of twinning. Calcite also commonly contains microscopic deformation twins that we can only see with a petrographic microscope.

7.4.4 Sulfate Minerals

Sulfate Minerals

gypsum	$CaSO_4 \bullet 2H_2O$
anhydrite	$CaSO_4$
barite	$BaSO_4$
celestite	$SrSO_4$
anglesite	$PbSO_4$

Mineralogists have described more than 100 sulfate minerals. They fall into two main groups: those that contain water (*hydrous sulfates*) and those that do not (*anhydrous sulfates*). Gypsum ($CaSO_4 \bullet 2H_2O$) is the only common hydrous sulfate. Less common species include chalcanthite ($CuSO_4 \bullet 5H_2O$), epsomite ($MgSO_4 \bullet 7H_2O$), and antlerite $Cu_3SO_4(OH)_4$. Examples of anhydrous sulfates include *anhydrite* ($CaSO_4$), *barite* ($BaSO_4$), *celestite* ($SrSO_4$), and *anglesite* ($PbSO_4$). Many others are known, but most are rare.



7.41 The arrangement of atoms in barite

The drawing in Figure 7.41 shows how atoms are arranged in barite ($BaSO_4$). Sulfur atoms bond to four oxygen, creating sulfate tetrahedra with composition $(SO_4)^{2-}$. The tetrahedra are tightly bonded and similar, in some ways, to the $(SiO_4)^{4-}$ groups that characterize silicates. Sulfate tetrahedra, however, do not polymerize. Ba^{2+} cations alternate with anion sulfate and bond to oxygen at tetrahedral corners. The atomic arrangements are the same in the other anhydrous sulfates, with Ca^{2+}, Sr^{2+}, and Pb^{2+} substituting for Ba^{2+} in anhydrite, celestite, and anglesite, respectively. Besides the minerals listed in the blue box, at least a dozen other, but rare sulfates exist. Some are listed in the table of evaporite minerals earlier in this chapter.

7.42 Gypsum crystals in Mexico’s Cueva de los Cristales

The spectacular photo in Figure 7.42 shows a geologist in Mexico’s *Cueva de los Cristales* (Cave of Crystals). The cave contains some of the largest mineral crystals in the world – up to 12 meters long. These crystals are *selenite*, a translucent form of *gypsum*. Gypsum is moderately water-soluble, so it is one of a relatively small number of common minerals that precipitate from natural water, often redissolve, and later reprecipitate somewhere else. Most natural gypsum crystals are centimeters in size or smaller.

However, extremely large crystals, such as those shown here, exist in several places around the world.

● Box 7-3 Gypsum: Ingredient of Plaster and Drywall

7.43 Plaster of Paris

Plaster can be made from different mineral materials. Early Romans used a lime-based plaster (Figure 7.43), but plaster of Paris, which is gypsum-based plaster, was introduced around 1254. At the time, the best and most productive gypsum quarries were in Montmartre, a section of Paris. Modern plasters and sheetrock both contain plaster of Paris. Manufacturers produce it by *calcining* (grinding and heating) gypsum ($CaSO_4 \bullet 2H_2O$) to reduce its water content. Most plasters contain about 25% of the gypsum’s original water. Complete dehydration of gypsum would produce anhydrite ($CaSO_4$), which is not useful as a plaster because it does not recombine easily with water. However, when plaster of Paris is mixed with water, reaction occurs quickly, giving off heat and promoting drying and hardening.

Drywall (also known as *sheet rock*) is composed of gypsum with paper front and backing. A number of different additives may be mixed with the gypsum to promote desired properties, including strength, resistance to mildew, and reduced water absorption. Drywall construction replaced the more classic lath and plaster walls in the mid 1900s.

7.45 Gypsum crystals with swallowtail twins. From Winnipeg, Manitoba 9 cm across

7.44 Translucent blades of selenite on top of hematite from Chihauhua, Mexico

Gypsum, hydrated calcium sulfate, is the most common sulfate mineral. It is found in thick evaporite deposits, in hydrothermal veins, and as precipitates from surface or subsurface waters, hot springs, or volcanic gases. *Anhydrite*, with a composition equivalent to gypsum lacking H_2O, is found in sedimentary rocks but alters to gypsum over time. Anhydrite is also commonly found in evaporite deposits with gypsum.

Common gypsum is white to grey, and translucent, but just about all colors are known. Normal coarse crystals of gypsum form blades or tabs. We call them *selenite* (Figures 7.42 and 7.44). Selenite commonly twins, sometimes forming characteristic *swallow tail* or *fishtail twins*. These two types of twinning are very similar and often not distinguished from each other. Figure 7.45 shows two examples of swallowtail twins. Another example is in Figure 4.39 (Chapter 4).

7.47 Gypsum desert rose from Tunisia 47cm across

7.46 Satinspar variety of gypsum

Satin spar is an especially fibrous variety of selenite (Figure 7.46). Satin spar is often opalescent and is sometimes used in jewelry, although it is soft and not very durable. Sometimes gypsum crystals form a flowery cluster called a *desert rose* (Figure 7.47). The specimen in Figure 7.47 is 47 cm across! In caves gypsum may form *gypsum flowers*, similar in many ways to desert roses. *Alabaster* is very fine grained gypsum that people sometimes carve or polish for building stone or for art.

7.48 Barite from Texas Co, Missouri

7.49 Barite roses from near Norman, Oklahoma 12cm across

Barite, barium sulfate, commonly occurs in hydrothermal deposits with copper, lead, and zinc minerals; it is often associated with anglesite and celestite. Barite is also found in hot spring deposits, and in some evaporite deposits. The cluster of clear to light blue bladed crystals in Figure 7.48 is typical for barite. And, barite sometimes occurs as concretions in sediments and sedimentary rocks, and sometimes as desert roses (Figure 7.49), similar to desert roses made of gypsum.

7.51 Silvery galena with yellow-brown anglesite. 7.5 cm tall specimen from Morocco.

7.50 Celestite crystals

Celestite (also called *celestine*), strontium sulfate, most often occurs in sedimentary rocks associated with gypsum, anhydrite, sulfur, or halite. Commonly it has a diagnostic light blue color as seen in the photo here (Figure 7.50). Celestite is the most common strontium minerals. Strontianite (strontium carbonate) is the only other one of significance.

Some sulfates are common as minor, and rarely major, minerals in ore deposits – typically as replacements for primary sulfides. *Anglesite* ($PbSO_4$), for example, forms during weathering or alteration as a replacement for galena (PbS).

The specimen seen in Figure 7.51 contains light brownish anglesite that appears to have grown from the silver-gray galena.

7.4.5 Halides

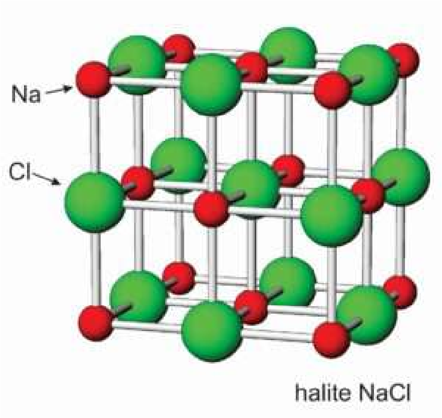
Halide Minerals	
halite sylvite fluorite	NaCl KCl CaF_2

The *halide group* consists of minerals containing a halogen element, generally chlorine or fluorine, as an essential anion. Although many halides exist, only halite and sylvite are common in sedimentary rocks; they are quite rare in rocks of other sorts. Halite is typically found as rock salt in massive salt beds, often occurring with other evaporite minerals such as gypsum or anhydrite, and sometimes with sulfur. Sylvite is much less common than halite. When found, however, it is usually associated with halite. Fluorite, most commonly, is a hydrothermal mineral associated with lead, zinc, and other metal ores. Less commonly, it is found in the vugs or fractures in limestone or dolomite. Other halides are rare and have more complex chemistries.

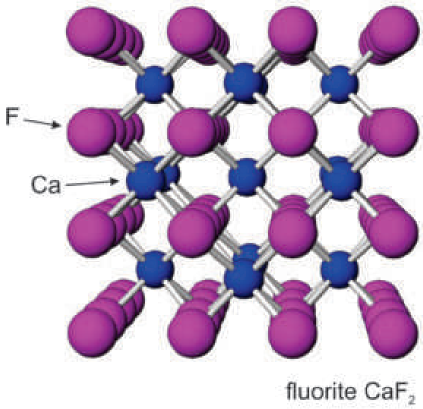
7.53 Blue fluorite crystals from southern France

7.52 Halite crystals from the Great Salt Lake, Utah

The photos seen here show crystals of halite (Figure 7.52) and fluorite (Figure 7.53). Sylvite crystals commonly look the same as the halite crystals here. When euhedral, both minerals form cubic crystals, a reflection of the internal order of their atoms. The most common fluorite is purple, but just about any color is possible for this mineral.



7.54 The atomic arrangement in halite



7.55 The atomic arrangement in fluorite

Figures 7.54 and 7.55 show atomic arrangements in halite and fluorite. In halide minerals, anions and cations alternate and bonds are nearly entirely ionic. In halite (or sylvite), Na^+ (or K^+) and Cl^- alternate in a cubic three-dimensional arrangement. In fluorite, the arrangement of atoms is also cubic, but two F^- are present for every Ca^{2+}.

7.4.6 Zeolites

7.56 Chabazite crystals on top of heulandite. Specimen is 4.4 cm across

This photograph (Figure 7.56) shows orange chabazite crystals on top of heulandite. Both of these are zeolite minerals that occur most commonly in openings within basalt, and less commonly in metamorphic rocks or hydrothermal veins. This sample comes from a classic locality near Wasson Bluff, on the shore of the Bay of Fundy, Nova Scotia, where many outcrops of 200-million year old basalt contain cavities filled with spectacular mineral specimens.

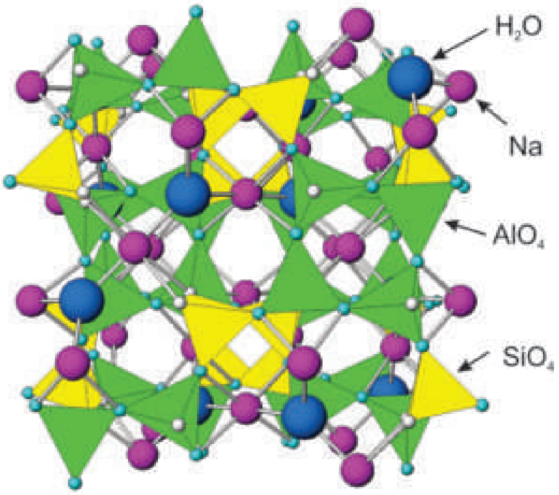
Although zeolites are best known for their occurrences in vugs and other open cavities in volcanic rocks, large volumes are found in volcanic ashes and saline lake deposits. Zeolites also may be present as products of diagenesis or low-grade metamorphism in sediments and rocks.

Zeolite Minerals

natrolite	$Na_2Al_2Si_3O_{10}\bullet 2H_2O$
analcime	$NaAlSi_2O_6\cdot H_2O$
laumontite	$CaAl_2Si_4O_{12}\bullet 4H_2O$
chabazite	$CaAl_2Si_4O_{12}\bullet 6H_2O$
clinoptilolite	$(Na,K)Al_2Si_7O_{18}\bullet 6H_2O$
heulandite	$CaAl_2Si_7O_{18}\bullet 6H_2O$
stilbite	$CaAl_2Si_7O_{18}\bullet 7H_2O$
sodalite	$Na_3Al_3Si_3O_{12}\bullet NaCl$

The zeolite group includes more than 40 minerals. They are, essentially, hydrated feldspars and are framework silicates containing open cavities that can hold loosely bonded large cations and water. Different zeolites have different-sized openings, and in some zeolites the openings connect to form channels. Because of the cavities and channels, zeolites have many industrial applications. See Box 7-4 (below).

The compositions of zeolites seem highly variable, but follow certain patterns. The ratio (Al+Si):O is 1:2. In calcic zeolites, the ratio (Ca:Al) is always 1:2, and in alkali zeolites, the ratio (Na,K):Al is always 1:1. Zeolites and feldspathoids are closely related, but zeolites have more open structures and contain loosely bonded H_2O compared with feldspathoids. Sodalite is sometimes grouped with the feldspathoids rather than the zeolites, but it has a zeolite-type structure and contains loosely bonded NaCl. Analcime, $NaAlSi_2O_6\bullet H_2O$, is also sometimes considered a zeolite, but is closer to leucite and other feldspathoids in structure.



7.57 The atomic arrangement in analcime, $NaAlSi_2O_6 \cdot H_2O$

Figure 7.57 shows the atomic arrangement in analcime – it is similar in most ways to all zeolites. Zeolites contain tetrahedra containing aluminum and silicon cations surrounded by four oxygen anions. Corners of the tetrahedra join to other corners. Analcime and other zeolites contain holes and channels between tetrahedra that can hold or transmit large ions, such as sodium, calcium, potassium, H_2O, or other molecules. This property sets them apart from most other minerals.

● Box 7-4 Industrial Zeolites

7.58 Industrial zeolite

What do water softeners, fish tanks, kitty litter, and people with radioactive poisoning have in common? The answer is *zeolites*.

Zeolites contain water that can be driven off by heat with the basic structure left intact. Removal of water leaves voids that can be filled, making them useful for many purposes, including ion exchange, filtering, odor removal, chemical sieving, and gas absorption. The best-known use for zeolites is in water softeners. Because calcium in water causes it to be “hard,” suppressing the effects of soap, forming scale, or creating other problems, it is often filtered through zeolite. Zeolite charged with sodium ions (generally from dissolved salt) allows water to pass through its structure while exchanging calcium for sodium, thus making the water less hard. This process is reversible, so the zeolite can be flushed and used again.

In a similar way, zeolites can absorb unwanted chemicals, including toxins. For example, zeolites may be components of kitty litter because they absorb cat urine, and zeolites are added to livestock feed to absorb toxins that are damaging or fatal to animals. Additionally, people who have been exposed to radioactive elements ingest zeolites to help rid their system of those dangerous elements, and aquarium hobbyists use zeolites to remove ammonia and other toxins from fish tanks. In the highly-developed countries of the world, most municipal water is processed through zeolites to remove large ions and organic contaminants before public consumption. Manufacturing industries also use zeolites as drying agents, catalysts, and as washing materials. Synthetic zeolites are easily grown in the laboratory, and scientists have synthesized more than 150 varieties. For many applications, synthetic zeolites have advantages over their natural cousins because they can be manufactured to be pure and homogeneous, and to have unique properties not found in nature.

7.4.7 Chert

Chert is a fine-grained (microcrystalline) variety of quartz. It is also the name given to rock composed primarily of fine-grained quartz. So, the name is used in two ways. Chert (the silica mineral kind) may be massive or layered. It is often in nodules or concretions in limestone. Some chert forms by recrystallization of amorphous silica. Chert has many appearances; the five photos below (Figures 7.59 to 7.63) show examples of some of the more common varieties. Common chert is light grey. *Jasper* is chert with a characteristic red color due to hematite inclusions. *Flint*, a darker form of chert, contains organic matter. *Opal* and *chalcedony*, two other types of silica, are often associated with chert deposits. From the Stone Age until the Industrial Revolution, chert and flint were highly valued as weapons, tools, and fire starters.


7.59 Chert

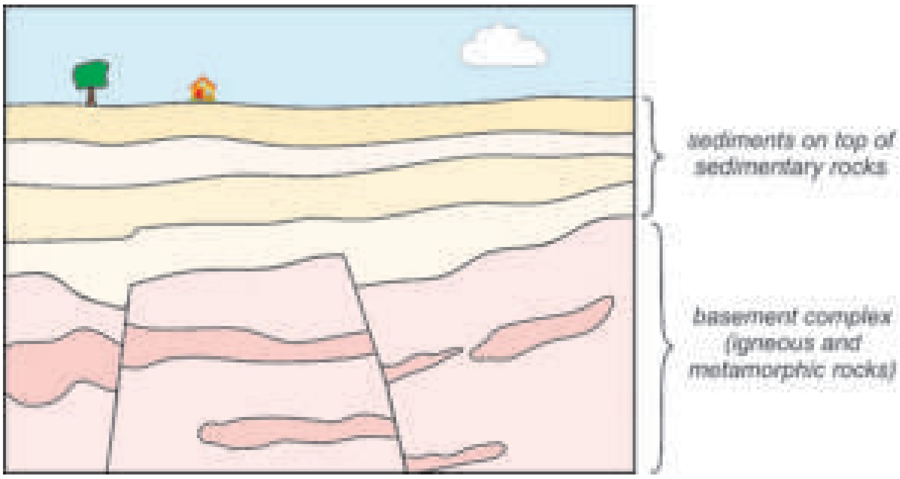

7.60 Jasper


7.61 Flint


7.62 Opal


7.63 Chalcedony

7.5 Common Sedimentary Rocks



7.64 Sediments and sedimentary rocks on top of basement rocks

Sediments and *s*edimentary rocks cover about 80% of all continental areas but are less than 1% of the volume of the Earth’s crust. They are, in effect, a thin blanket on top of igneous and metamorphic *basement rocks*. Yet, we interact with them more than with any other geological materials except, perhaps, soils. Sediments, and rocks derived from sediments, are mostly recycled materials that come from preexisting igneous, metamorphic, or sedimentary rocks. Petrologists usually divide sedimentary rocks into two main groups based on the kinds of material they comprise: *clastic rocks* and *chemical rocks*.

7.5.1 Clastic Sedimentary Rocks

Clastic sedimentary rocks are formed by compaction and cementation of clasts composed of individual mineral grains or pieces of rock. Because their mineralogy varies so much, we generally classify clastic rocks based on grain size rather than composition. Grain size varies from huge clasts and boulders in gravels and conglomerates, to fine “clay size” (<0.004 mm) particles in muds and shales. The table below gives a standard classification scheme for clastic rocks based on clast/grain size. See section 7.2 (above), for more specifics about grain sizes.

Classification of Clastic Rocks Based on Clast Size

clast size	sedimentary rock			major component of unconsolidated sediment	clast sizes
very fine	mudrocks	mudstone	claystone	clay	more than 60% clay-sized
			siltstone	silt, generally quartz	more than 60% clay-sized
		shale		clay	clay- and silt-sized
small to medium		sandstone		sand, commonly quartz	sand
very coarse	conglomerate or breccia			gravel or coarser sediment	pebble
				gravel or coarser sediment	cobble
				gravel or coarser sediment	boulder

In the coarsest clastic rocks, a fine-grained *matrix* separates large clasts that may be of many different compositions. If the clasts are angular, the rock is a *breccia*; if they are rounded, it is a *conglomerate*. Lithic fragments generally dominate the clasts in conglomerate and breccia. Figures 7.65 and 7.66 show a conglomerate and a breccia; both are from Death Valley National Park.

7.65 Conglomerate, Death Valley National Park, California

7.66 Breccia, Death Valley National Park, California

Rocks containing small- to medium-sized grains are generally called *sandstone*. The photos below in Figures 7.67, 7.68, and 7.69 show three examples. Most sandstones contain sand-sized (0.062 to 2 mm in longest dimension) quartz or feldspar grains. Coarser sandstones may contain both lithic fragments and individual detrital mineral grains. Sometimes clays or other minerals are present in a matrix between larger grains. We call a sandstone that is entirely, or almost entirely made of quartz, an *arenite* (Figure 7.67). We call sandstones containing significant amounts of matrix material or lithic fragments *wackes*, or *graywackes* (Figure 7.68). *Arkoses*, like the one seen in Figure 7.69, are sandstones that contain significant amounts of K-feldspar.

7.67 Quartz arenite

7.68 Graywacke with lithic fragments

7.69 Arkose Mt. Tom Massachusetts

Conglomerates and sandstones together account for 20% to 25% of all sedimentary rocks. Finer-grained clastic rocks, generally termed *mudrocks*, are much more common. These fine-grained rocks consist of microscopic (<0.062 mm in longest dimension) clay and quartz grains. Lithic fragments are absent.

7.70 The Marcellus Shale, Pennsylvania

We call the finest grained rocks *shale* if they exhibit *fissility*. Fissility, the ability to cleave into very thin layers, results from parallel alignment of clay grains. This photo (Figure 7.70) shows thin pieces of the Marcellus Shale from Pennsylvania. Those that are not fissile are *mudstones*. We further divide mudstones into *claystones* or *siltstones* depending if they are clay-rich or quartz-rich, respectively.

Minerals in Mudrocks and Sandstones		
Minerals	**Mudrocks average %**	**Sandstones average %**
clay minerals	60	5
quartz	30	65
feldspar	4	10-15
carbonate minerals	3	<1

Since clastic sediments can be derived from any preexisting rocks, they may contain a variety of minerals and rock fragments. However, only a few minerals are common. The table compares the most common minerals in mudrocks and sandstones.

Clays, with subordinate quartz, dominate the mudrocks, but quartz dominates the sandstones.

Quartz, feldspar, and lithic fragments containing quartz and feldspar comprise all but the finest grained rocks because they are resistant to weathering. We call rocks dominated by quartz *quartzose*, while we term those containing large amounts of feldspar *feldspathic*, or (if they are rich in K-feldspar) *arkosic*. In mudstones and shales, clay minerals dominate. In all these rocks, other minerals, including micas, magnetite, rutile, ilmenite, sphene, zircon, apatite, or garnet may occasionally be significant components. Carbonate grains and organic material may be present as well. Because most minerals break down to clay and quartz if exposed at the Earth surface for sufficient time, it should be no surprise that mudstone and shale, which are composed primarily of clay and quartz, are the most abundant sedimentary rocks.

7.71 Examining a rock with a hand lens

In the coarser-grained clastic rocks, the compositions of lithic fragments give clues to the origin of the sediment. In the finer-grained rocks, mineralogical composition is often difficult to determine and interpret. Suppose we look at a sandstone with a hand lens (Figure 7.71). Quartz, and perhaps

K-feldspar, may be easy to find. However, lithic fragments can be confusing and small grains of chert or magnetite may be impossible to identify. For fine sandstones and finer-grained rocks, mineral identification can be problematic, even with a petrographic microscope. Distinguishing quartz from feldspar and telling clay minerals apart may be impossible without using an X-ray diffractometer or other sophisticated equipment.

7.5.2 Chemical Sedimentary Rocks

Chemical sedimentary rocks are formed by precipitation of minerals from water or by alteration of already existing material in place. The most common of these rocks include evaporites, chert, and some varieties of carbonate rocks (limestones and dolostones). In contrast with clastic sedimentary rocks, petrologists name chemical sedimentary rocks based on chemical composition. This is because chemical sedimentary rocks usually include only one or a few minerals — the chemical processes that form them tend to isolate certain elements. The most common precipitated minerals consist of elements of high solubility (for example, alkalis such as sodium or potassium) or elements of great abundance (for example, silicon).

7.5.2.1 Carbonate Rocks

7.72 Crumbling limestone cliffs on the Isle of Purbeck, south coast of England

7.73 The Cairn Formation, a dolostone near Canmore, Alberta. Red Swiss Army knife for scale.

While *limestone* is a general term given to all carbonate rocks, we use the names *dolomite* or *dolostone* for rocks in which dolomite is the dominant carbonate mineral. Limestone and dolostone account for 10% to 15% of all sedimentary rocks. They are mostly composed of calcite or dolomite, one or the other. Surprisingly, rocks with significant amounts of both calcite and dolomite are rare. Besides calcite and dolomite, carbonate rocks often contain detrital quartz or clay minerals and sometimes authigenic minerals of many kinds. Both limestones and dolostones often weather or dissolve, producing distinctive textures such as seen in Figures 7.72 and 7.73. Cracks appear enlarged, and edges are rounded.

Distinguishing limestone from dolostone, based on appearance, can be difficult or impossible in outcrop. On a fresh surface calcite and dolomite may look the same, although weathering sometimes alters dolomite to a yellow-brown color that is distinctive. Field geologists carry dilute hydrochloric acid – which reacts only with calcite or powdered dolomite – or chemical stains to help identification of carbonate minerals. Aragonite, a polymorph of calcite, exists in some very young carbonate deposits, but never in old rocks because it changes to calcite over time. In contrast, for reasons that are not completely clear, dolomite is rare in modern carbonates but is common in Paleozoic and Precambrian rocks.

7.74 Fossiliferous limestone from East Lothian, Scotland

When $CaCO_3$ precipitates to form limestones, it may be as fine-grained lime muds, resulting in microcrystalline calcite, called *micrite*. It also precipitates as coarser *sparry calcite*, with crystals that may be clear and easily visible with the naked eye. However, most carbonate rocks are detrital. They form from organic debris deposited in shallow marine environments, where most biological activity occurs. These rocks often contain fossils amidst clastic grains. The fossils can be of many different sorts. The limestone in Figure 7.74 contains conspicuous ribbed *brachiopods*.

7.5.2.2 Evaporites

Earlier in this chapter, we discussed evaporite deposits. Such deposits may contain thick beds of halite or gypsum many meters thick. Rocks composed of these two minerals are found in many places. Halite deposits may be 1000 m thick or more but gypsum rock deposits are generally much thinner. Both kinds of deposits form during evaporation of inland seas or other isolated waters. For example, halite and gypsum are mined in Michigan and Ontario where the minerals collected when water trapped in an inland basin, called the *Michigan Basin*, evaporated 360-440 million years ago. The world's largest underground salt mine is in Goderich, Ontario, on the edge of the basin.

7.5.2.3 Chert

7.75 Folded chert beds, Glen Canyon Park, San Francisco

We talked about varieties of mineralogical chert in Section 7.4.7 above. *Chert* is also the name given to hard sedimentary rock composed of fine quartz crystals. The rock seen in Figure 7.75 is an example. Chert (the rock) is usually of biological origin, being the petrified remains of siliceous ooze, the biogenic sediment that covers large areas of the deep ocean floor. Chert often contains microscopic skeletal remains of diatoms, silicoflagellates, and radiolarians made of silica. Depending on its origin, chert can contain either microfossils, small macrofossils, or both. Chert (the rock) varies greatly in color (from white to black), but most often manifests as gray, brown, grayish brown and light green to rusty red (occasionally dark green too). Its color is an expression of trace elements present in the rock, and both red and green colors are most often related to small amounts of iron (in its oxidized and reduced forms respectively). Thick beds of chert, up to several hundred meters thick, underlie most of the southern plains states of the United States and parts of California. For poorly understood reasons, thick chert beds are especially common in Precambrian rocks.

7.5.2.4 Organic Sedimentary Rocks

7.76 Coquina, Cayo Costa Island, Florida

Some sedimentary rocks are formed largely from biogenic (organic) debris. We classify such rocks as *organic sedimentary rocks*, separate from chemical and clastic sedimentary rocks. Examples are limestones formed from shell or skeletal remains, *coquina* (a sedimentary rock made of shell fragments), *diatomite* (a sedimentary rock made of the remains of diatoms), and *coal*. This photo (Figure 7.76) shows an example of coquina.

Much overlap exists between chemical, clastic, and organic sedimentary rocks. Many chemical sedimentary rocks contain clastic material, and many clastic sedimentary rocks are held together by chemical cements precipitated from water. Both chemical and clastic rocks may contain biogenic components.

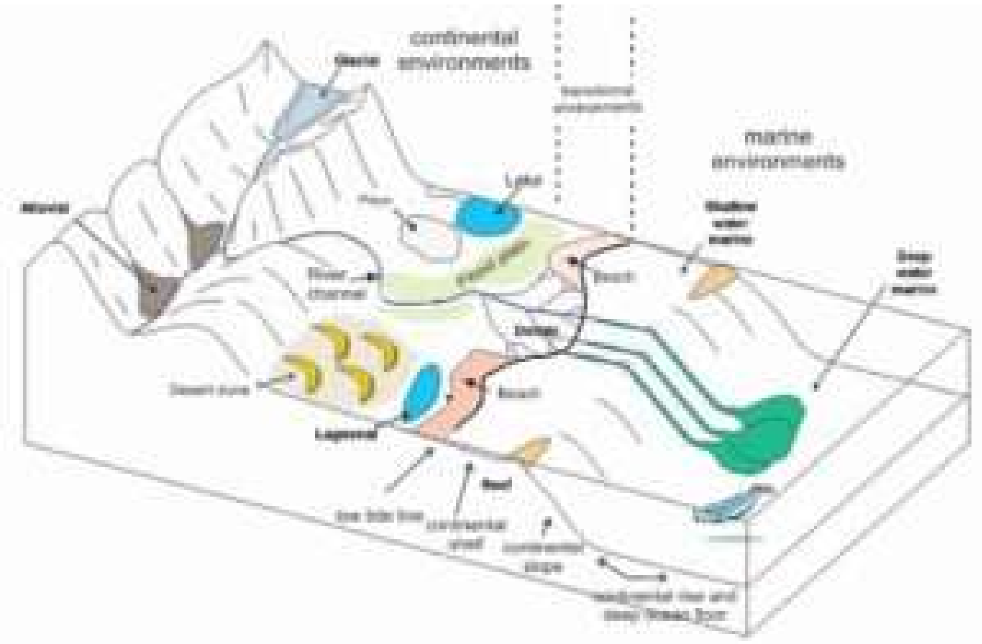
7.5.2.5 Other Chemical Sedimentary Rocks

Many other types of chemical sedimentary rocks and minerals exist. They are not abundant, but they may be important as sources of ore. For example, *collophane*, a cryptocrystalline form of apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, is found in small amounts in many kinds of sedimentary rocks. It has an organic origin. In rocks called *phosphorites*, apatite may comprise nearly the entire rock. Major phosphorite deposits are in Wyoming and Idaho, where mines produce phosphate, an important component of fertilizers.

7.77 Banded iron formation, northern Minnesota

Iron formations, most Precambrian in age, are mined for iron in the Mesabi Range of Minnesota and elsewhere. Iron oxides and hydroxides, including hematite (Fe_2O_3), goethite ($FeO(OH)$) and magnetite (Fe_3O_4), or Fe-carbonate (siderite, $FeCO_3$), are the most common iron minerals in iron formations. Occasionally, iron silicates (*e.g.*, fayalite, Fe_2SiO_4) or sulfide (pyrite, FeS_2) may be present. The outcrop seen in Figure 7.77 is iron formation that contains layers rich in red chert alternating with layers rich in specular hematite (silver grey). Iron formations form from sediments originally deposited in shallow marine conditions. Young manganese deposits, similar to iron formations, have been dredged from ocean floors.

7.6 Sedimentary Environments and Facies



7.78 Some of the many environments where sediments may be deposited

The processes that form sedimentary rock occur in many environments, and different minerals or rocks can characterize each. In many places, however, the rate of sediment deposition is slow. In other places, erosion removes sediment as fast as it is deposited. Consequently, most of the sedimentary rocks and minerals that we see are associated with a few special environments where the rate of deposition is relatively fast, and the volume of sediments deposited was relatively large. The most significant such environments are large basins on continents, and shallow seas. Lesser amounts of sedimentary rocks are associated with other environments such as shorelines, rivers, lakes, deserts, and glaciers. Because different environments are different physically, chemically, and biologically, the nature of sedimentary rocks is highly variable. The most significant factors that account for the differences are the energy and biology of the environment, the distance from the source of the sediment, and the way the sediment was transported. Figure 7.78 show some of the many different places where sediments are deposited. Sedimentologists divide all of them into smaller categories that produce distinctive sediments and sedimentary rocks.

Most sedimentary environments vary laterally. Large basins, for example, are not the same everywhere. So different kinds of sediment can be deposited in different parts of a basin simultaneously. We use the term *facies* to refer to the different rocks that characterize a particular process or environment. So, geologists may talk about *continental, transitional*, or *marine facies*. More specifically, they may consider *reef facies, continental shelf facies, deep ocean facies,* and so on. Different contemporaneous facies often grade into each other. Consider, for example, sedimentation at or near a shoreline. Coarse sediments are typically deposited on dry land and on beaches, somewhat finer sediments in shallow water, and the finest materials farther offshore. If the sedimentary environment changes, the nature of sedimentation changes. With rising sea level, for example, fine deep-water sediments may be deposited over coarser shoreline sediments. With failing sea level, the opposite may occur. So, sedimentary facies vary both laterally and vertically (geographically and temporally).

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8 Metamorphic Minerals and Metamorphic Rocks

8.1 Metamorphic rock from Tanzania containing green zoisite, red corundum, and black hornblende

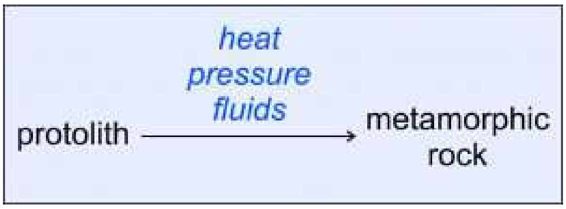
8 Metamorphic Minerals and Metamorphic Rocks

KEY CONCEPTS

- Metamorphic minerals and rocks form when rocks undergo changes in chemistry, texture, or composition.
- Temperature and pressure are the most important causes of metamorphism.
- Different metamorphic textures characterized different kinds of metamorphic rocks.

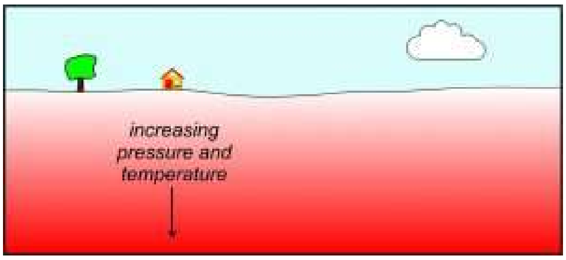
- Chemical reactions of many sorts occur during metamorphism.
- Different parent-rock compositions produce different kinds of metamorphic rocks.
- The composition of the parent rock determines the metamorphic minerals and rocks that may form.

8.1 The Causes of Metamorphism



8.2 Creating metamorphic rocks

Metamorphic rocks, and the processes that create them, are key parts of the rock cycle that also includes igneous and sedimentary rocks and processes. Most metamorphic rocks form when heat, pressure, or chemically reactive fluids cause changes in preexisting rocks. The preexisting, or parent rocks, are called *protoliths*. Protoliths can be igneous, sedimentary, or metamorphic rock of all sorts. The changes that occur during metamorphism may involve changes in rock texture, in the minerals present, and sometimes in overall rock composition. These changes record geologic processes and events of the past. Metamorphic petrologists study metamorphic rocks to interpret those histories.



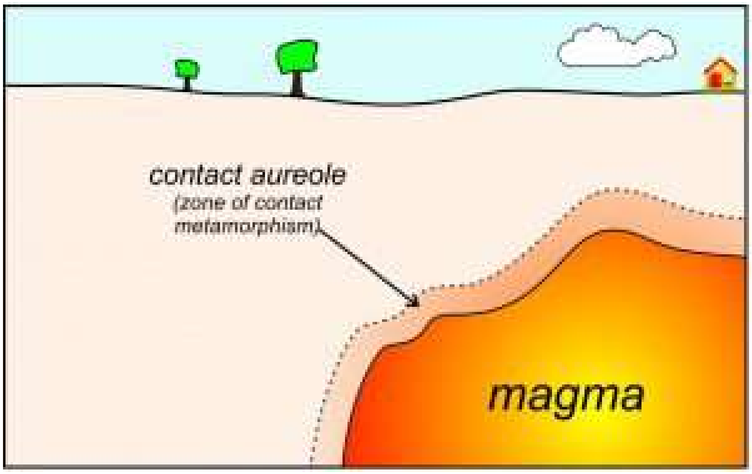
8.3 Regional metamorphism is more intense at depth

The most significant causes of metamorphism are mountain building processes (*tectonism*) that bury, while heating and squeezing, rocks. This kind of metamorphism, called *regional metamorphism*, creates large metamorphic *terranes*, regions characterized by distinctive metamorphic rocks and intensity of metamorphism that may vary laterally. Regional metamorphism occurs because both pressure and temperature increase with depth in Earth (Figure 8.3). The deeper the rocks, the greater the metamorphism. The photos in Figures 8.4 and 8.5 below show two outcrops of regional metamorphic rocks.

8.4 Outcrop of schist, Green Mountains, Vermont

8.5 Outcrop of gneiss near Sudbury, Ontario

Mountain building brings rocks from deep in Earth to the surface. So, many examples of regional metamorphism are found in mountain belts, for example the outcrop in Green Mountains in Figure 8.4, above. Other examples are found in *Precambrian shields*, relatively flat-lying areas that may be thousands of kilometers across, that are the exposed roots of ancient mountains. The gneiss seen in Figure 8.5 is from the Canadian Shield in central Ontario.



8.6 Contact metamorphism around a pluton

Although most regional metamorphism, which accounts for most metamorphism, occurs at relatively deep levels within Earth, metamorphism can also occur at shallow levels or even at Earth’s surface. This occurs when magma that intrudes the crust rises close to, or all the way to, the surface. In such cases, heat from the magma can cause *contact metamorphism* that affects shallow or surface rocks. The effects of contact metamorphism may be profound, because of the high temperature contrast between magmas and upper crustal rocks.

As seen in Figure 8.6, contact metamorphism leads to the development of metamorphic zones called *contact aureoles*, or *skarns*, that wrap around an intrusion. Aureoles and may be anywhere from a few centimeters to many kilometers thick. The formation of contact aureoles frequently involves *metasomatism*, a change in rock composition due to flowing metamorphic fluids. The width of an aureole mainly depends on the size of the intrusion and how much fluid (mostly H_2O and CO_2) it gives off. Aureoles often develop concentric zones or layers, each containing a distinct mineral assemblage that reflects the maximum metamorphic temperature attained and the amount of metasomatism.

Occasionally metamorphism occurs without significant tectonism or magmatism. Metamorphism may occur because of hot water flowing through rock in areas next to hot springs or other geothermal areas. And, sometimes, water flowing through vast regions of the crust alters rocks far from mountain belts. These changes, mostly chemical in nature, can occur without significant increases in temperature and pressure.

8.7 Metamorphism along a fault zone. Knapsack for scale.

8.8 Shatter cones caused by a meterorite impact. Cap-aix-Oies, Quebec

Metamorphism can also occur when rocks grind together in fault zones or when meteorites impact Earth, leading to *dynamic metamorphism*. Dynamic metamorphism, also called *shock metamorphism* or *cataclastic metamorphism*, is an uncommon form of metamorphism. It occurs because of sudden pressure exerted by faults or meteorite impacts. The results are often the fracturing and granulation of rocks and sometimes the creation of high-pressure minerals such as coesite or stishovite, both polymorphs of quartz. The two photos above (Figures 8.7 and 8.8) show examples: metamorphism of rocks along a fault zone, and shatter cones created by a meteorite impact in Quebec. Shatter cones are akin to the damage that a pebble does when it strikes the windshield of your car.

Regional and contact metamorphism account for most metamorphic rocks. Dynamic metamorphism is in a distant third place. Some geologists have also described another kind of metamorphism, called *burial metamorphism*, but it is really just high-temperature diagenesis.

8.1.1 Prograde vs Retrograde Metamorphism

Metamorphic grade is a general term we use to describe the temperature at which metamorphism occurs. Metamorphic grade is important, not just because different kinds of rocks and minerals form at different temperatures, but because temperature affects chemical reaction rates. Rocks metamorphosed at low temperature may change only very slowly, and some changes may not go to completion. Rocks that form at high temperatures generally do not have the same problems. However, there are many kinds of metamorphic rocks, and some of them are more chemically reactive than others.

8.9 Sheared serpentinite with pencil for scale, Marin County, California

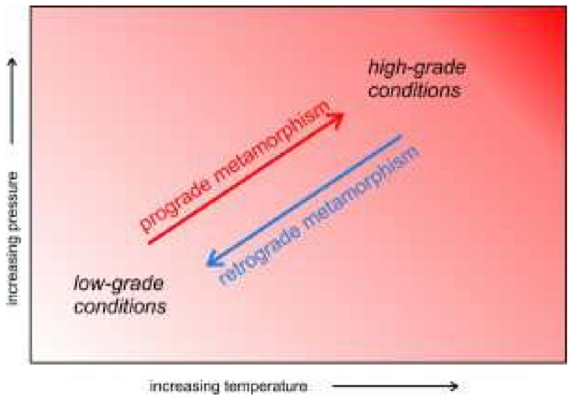
Low-grade metamorphic rocks form at low temperatures, generally between 150 and 450 °C. They mostly form at low pressures, too. At the lower end of this range, diagenesis overlaps metamorphism. Low-grade metamorphic rocks are often fine grained. Because they are hard to study and frequently do not represent chemical equilibrium, many metamorphic petrologists prefer to study higher-grade rocks. The photo in Figure 8.9 shows a serpentinite, an example of a low-grade metamorphic rock. It contains serpentine and chlorite, both hydrous minerals, that formed during metamorphism of a mafic protolith.

Medium-grade metamorphism, forming at temperatures between 400 and about 600 °C, often produces rocks containing conspicuous metamorphic minerals we can easily see and study. Many schists are medium-grade rocks.

8.10 Garnet granulite, a high-grade metamorphic rock

High-grade metamorphic rocks, which form at temperatures greater than about 600 °C, are usually quite coarse-grained and contain minerals easily identified in hand specimen. Most form at high pressures. The high-grade rock shown in Figure 8.10 contains conspicuous cm-sized red garnet, black hornblende, and white plagioclase feldspar.

Depending on its composition, a high-grade metamorphic rock may undergo *partial melting*, also called *anatexis*, so both metamorphic and igneous processes contribute to its evolution. When this happens, the rock, strictly speaking, is no longer a metamorphic rock. We call the resulting partially melted rocks *migmatites*, which means “mixed rocks.” For some composition rocks, partial melting may begin at temperatures as low as 700 °C. Other kinds of rocks, especially those that contain little H_2O, may remain completely solid to temperatures as great as 1100 °C.



8.11 Prograde and retrograde metamorphism

Prograde metamorphism occurs when low-grade or unmetamorphosed rocks change mineralogy or texture in response to a temperature increase. If the metamorphism is gradual and predictable, we call it *progressive metamorphism*. During progressive metamorphism, a series of reactions occur as the degree of metamorphism increases. Rock mineralogy changes multiple times before equilibrating at the highest temperature conditions. While this idea makes a convenient conceptual model, it is not correct for all metamorphic rocks. For example, many metamorphic rocks are deep in Earth where pressure and temperature are great. They were never unmetamorphosed rocks at low pressure and temperature. Other rocks go from low temperature to high temperature, perhaps because of rapid intrusion of a pluton, so rapidly that they skip intermediate stages. Still other rocks may only partially equilibrate during metamorphism. Finally, some metamorphic rocks form by *retrograde* reactions (metamorphism in response to temperature decrease). This is especially true for mafic rocks that were metamorphosed at high-grade conditions. Upon uplift and cooling, retrograde metamorphism may replace original high-temperature mineral assemblages with low-grade minerals. Figure 8.11 compares paths of prograde and retrograde metamorphism.

8.12 A large diamond crystal in kimberlite. The largest crystal is about 7 mm across.

One of the most intriguing questions about metamorphic rocks is: *Why do we find high-grade minerals at the surface of Earth where they are unstable?* The laws of thermodynamics say that rocks will change mineralogy in response to increasing temperature (prograde metamorphism), so why don't they undergo opposite (retrograde metamorphism) changes when temperature decreases as the rock reaches Earth's surface? If rocks always went to equilibrium, we should have no samples of high-grade rocks or minerals to study. Yet, we do. For example, we have samples of diamond-bearing kimberlite, like the specimen seen in this photo, that are unstable and should break down at Earth's surface.

Several considerations help answer these questions:

- Prograde metamorphic events are usually of much longer duration than retrograde events, giving minerals more time to achieve equilibrium.
- Prograde metamorphism liberates fluids not present when retrogression occurs. The fluids act as fluxes to promote prograde metamorphism; their absence may hinder retrogression. And, the absence of fluids means that some low-grade minerals cannot form.
- Prograde reactions are mostly endothermic, which means

they consume heat. The heat that causes metamorphism naturally fuels the reactions. In contrast, retrograde reactions are mostly exothermic – they give off heat. There is no outside energy driving the reactions.

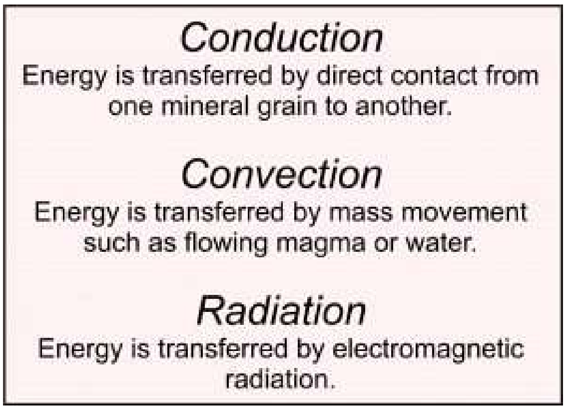
- At low temperature, reactions are very sluggish; they may not have time to reach equilibrium.

- More complex, low-grade minerals often have difficulty nucleating and growing.

8.2 Pressure and Temperature

Metamorphism, which may affect any kind of rock, occurs over a wide range of pressure and temperature conditions. This leads to tremendous variation in metamorphic rocks and the minerals they contain. Most of the metamorphic minerals we see form at temperatures of 150 to 850 °C and at pressures of 1 bar to 10 kbar. Exceptions, however, do exist (see Box 8.1, below).

8.2.1 Heat and Temperature



Conduction
Energy is transferred by direct contact from one mineral grain to another.

Convection
Energy is transferred by mass movement such as flowing magma or water.

Radiation
Energy is transferred by electromagnetic radiation.

8.13 The ways that heat moves

Heat is, perhaps, the most significant cause of metamorphism. Heat is thermal energy that can move (flow) from one place to another or from one substance – such as rock, magma, or water – to another. Thermal energy is high for substances at high temperature and low for substances at low temperature.

Three processes transfer heat: *conduction*, *convection*, and *radiation*; but within Earth, heat transfer by radiation is insignificant. *Conductive heat transfer* occurs when heat flows naturally from a place of high temperature to one of low temperature with no associated movement of matter. Thus, for example, heat is always flowing from Earth’s hot interior to the cooler surface by conduction. And if a (hot) magma intrudes the (cooler) crust, the magma will cool as heat is conducted grain-by-grain into the surrounding rock, causing the surrounding rock to warm while the magma cools. This warming initially occurs only next to the magma body, but, over time, heat is conducted farther away. Magmatic intrusions can affect a large area.

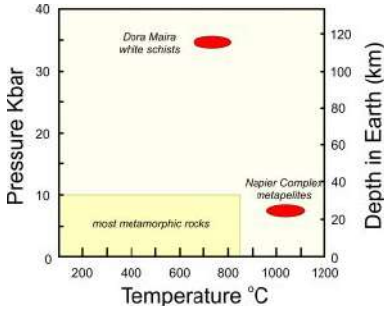
Convective heat transfer, which is more efficient than conductive heat transfer, is the transfer of heat due to the flow of material, such as the flow of hot water or hot air. Within Earth, convection occurs mostly because of flowing water and flowing magmas. Heat transfer by water can have a significant, although generally quite local, effect. Heat transfer by convecting magmas can be much more significant and can warm huge regions of the crust. And in Earth’s mantle, the slow creep of solid rock due to plate tectonics also moves heat by convection.

● Box 8-1: Extremes of Metamorphism

Most metamorphic rocks we see were formed at temperatures of less than 800 to 850 °C and pressures less than 10 kbar. Yet, petrologists do occasionally find rocks that were metamorphosed at pressures greater than 10 kbar or temperatures greater than 850 °C.

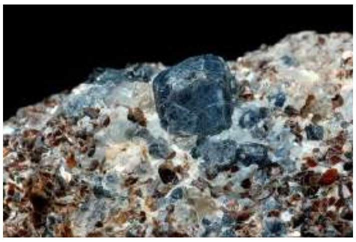
8.14 Talc-kyanite schist from the Dora Maira massif

The talc-kyanite schists from the Dora Maira Massif, Italy, are examples of extremely high-pressure rocks. The Dora Maira rocks have been called *whiteschists* because of their very light color (Figure 8.14). Besides talc and kyanite, they contain pyrope (white to pink Mg-garnet), phengite (a white mica related to muscovite), and quartz as major minerals. Coesite (a high-pressure polymorph of SiO_2) and ellenbergite (another high-pressure mineral) are found as small inclusions in some of the pyrope crystals. Whiteschists are unusual rocks that have been reported from multiple different places.



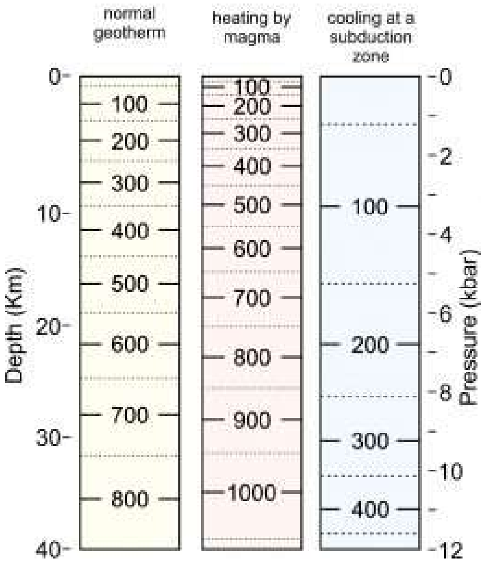
8.15 The Dora Maira whiteschists and Napier Complex metapelites represent extremes of metamorphism

Chopin (1984) and others have concluded that the Dora Maira rocks may have originated as shallow crustal rocks but were subsequently metamorphosed at about 35 kbar pressure and temperatures of 700 to 750 °C. While the temperature is not extreme, the pressure is; 35 kbar is equivalent to a depth in Earth of more than 100 km (see the diagram in Figure 8.15). There are few places where rocks metamorphosed at that depth are found at Earth’s surface – especially if their protoliths originally came from the shallow crust. The Dora Maira rocks were carried to great depth and returned to the surface during the Alpine Orogeny in southern Europe.



8.16 Sapphirine (blue) is a rare high-temperature aluminous mineral. Red garnet and quartz are also seen in this photo.

Metapelites (metamorphosed clay-rich sediments) of the Napier Complex, Enderby Land, Antarctica, are examples of extremely high-temperature metamorphism. An example is found in Figure 8.16. The rocks contain distinctive high-temperature mineral assemblages, which include the relatively rare minerals pigeonite, osumilite, and sapphirine. Several studies concluded that the Napier rocks were metamorphosed at pressures of 7 to 8 kbar and temperatures of more than 1,000 °C, perhaps as high as 1,075 °C. How did these rocks get so hot, and how did they escape melting? The answer to the first question is not known. Some investigators believe that a magmatic heat must have been involved. The answer to the second is that the rocks are of a composition that does not melt easily when water is absent. The Napier rocks were apparently metamorphosed in the absence of water.



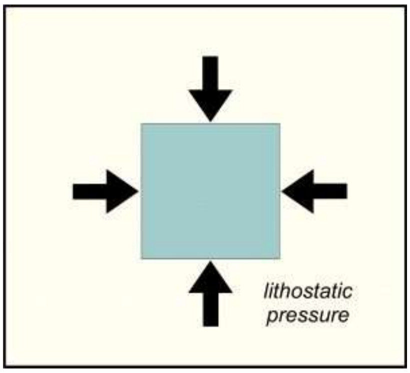
8.17 The temperature increase with depth in Earth in various settings. The numbers in the columns are temperature in °C.

Different places on Earth get their heat by different combinations of conduction and convection. Earth’s *geothermal gradient*, the rate at which temperature increases with depth, averages about 25 to 35°C/km near the surface in most places. This gradient, also called a *geotherm*, is mostly due to conductive heat flow. The left column in Figure 8.17 shows temperature-depth relationships for a normal geotherm typical of regions where all heat transfer is by conduction.

In mountain belts and other places where volcanic activity occurs, convective heat flow due to rising magmas contributes much more heat than normal conduction. Consequently, temperature increases faster with depth than is normal (middle column, Figure 8.17). In some places, next to large igneous intrusions, contact metamorphism occurs and extremely high temperatures may persist for short times before the intrusions cool.

In subduction zones (right column, Figure 8.17), generally cooler temperatures are present. Descending slabs of wet cool ocean lithosphere, which have been continuously carried to depth for millions of years, cool the crust and upper mantle below. So, the rate of temperature increase with depth is less than normal.

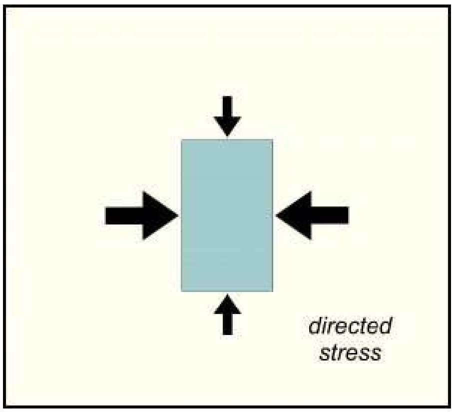
8.2.2 Pressure and Depth



8.18 Lithostatic pressure

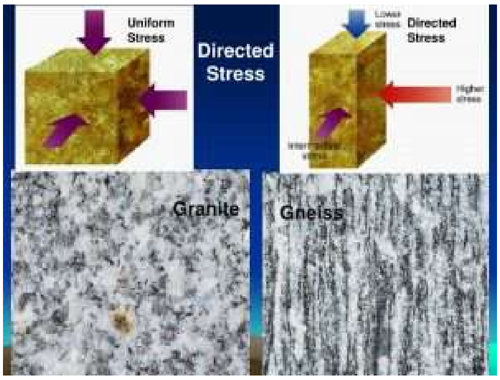
After heat, pressure is the most significant cause of metamorphism. If pressure is applied to a rock, the rock may change size or texture, or perhaps develop new minerals to replace old ones. Burial causes rocks to experience *lithostatic pressure*, also called *confining pressure*. Lithostatic pressure is the same in all directions (Figure 8.18), and thus can cause an object to become smaller without altering its overall shape. This kind of pressure is equivalent to the pressure that swimmers feel on their ears when they go to the bottom of the deep end of a swimming pool. The pressure on a swimmer’s ears accrues because of the weight of water pushing down from above. Within Earth, the weight of rock, which is commonly three times denser than water, causes lithostatic pressure to build up quickly with depth. As shown in Figure 8.17, pressure of around 12 kbar is reached at 40 kilometers depth, although pressure depends, in part, on the density of overlying rocks. Typical metamorphic rocks form at pressures of 0 to 10 kbars, but we find higher pressure rocks in some places. High-pressure rocks are rare because to get to very high pressure requires that rocks are buried to great depth – an uncommon occurrence. Subsequently, getting the rocks back to the surface so we can see them is even more problematic.

8.2.3 Directed Stress



8.19 Directed stress causes deformation

Directed stress, sometimes called *differential pressure*, is also a force applied to an object, but the force is not the same in all directions. For example, when we squeeze a lemon, we are applying directed stress. When we stretch a rubber band, we are also applying directed stress. The drawing in Figure 8.19 shows greater stress being applied horizontally than vertically, causing compression in one dimension. Within Earth, directed stress is common due to plate tectonic processes that push large pieces of lithosphere together or pull pieces apart. Unlike lithostatic pressure, high levels of directed stresses are not sustained for long because rocks deform to reduce the stress. Directed stress, thus, is commonly associated with rock folding or faulting.



8.20 Gneiss may be created when directed stress is applied to a granite

Directed stress can cause new minerals to form within a rock, but much more commonly it produces deformation, fracturing, or textural changes only. Mineral grains may rotate, align, become distorted, or disintegrate. Figure 8.20 shows how directed stress can change granite (igneous rock) into gneiss (metamorphic rock). Directed stress may also cause recrystallization as grains dissolve and regrow in other places, or combine to produce larger crystals. Sometimes, directed stress causes *shearing*, which means that different parts of a rock slide past each other.

8.21 A mylonite, a highly deformed rock from Otrøy in the Western Gneiss Region, Norway

During shearing, mineral grains can become elongated in one direction, and fractures can develop that give a rock a planar texture. This figure (8.21) shows a rock called *mylonite*, a highly deformed kind of rock created when fine sheared material recrystallizes. The sample is from Norway’s Western Gneiss Region. Directed stress, parallel to the layering in this rock, caused feldspar (white) and biotite (black) grains to become elongated as shearing took place. While this was occurring, metamorphism produced wine-red garnet crystals – a single large one is near the left side of the photo and many small ones are scattered throughout. The 1-euro coin is 2.3 cm across, for scale.

8.2.4 Metamorphic Fluids

8.22 Fluid inclusions in a crystal of zoisite

Metamorphism often involves fluids, most commonly water-rich but sometimes dominated by carbon dioxide, sulfur, or other components. Many mineral grains contain fluid inclusions that have trapped samples of fluids that once flowed through them. Figure 8.22 shows a fluid inclusion that contains liquid, gas bubbles, and minerals that crystallized from the trapped fluid. The color is an artifact of the way the photo was taken.

Metamorphic fluids may be *magmatic* (expelled by magmas as they crystallize), *meteoric* (derived from precipitation that infiltrates the ground), released during subduction of wet lithosphere, or products of reactions that release H_2O or CO_2 from minerals. *Hydrothermal metamorphism* occurs when warm fluids significantly alter protolith rocks. This kind of metamorphism can affect large areas and be part of regional metamorphism, or it can be localized and part of contact metamorphism. In either case, the metamorphism involves hot, generally water-rich fluids that flow through cracks and along grain boundaries. The fluids act as catalysts and fluxes that promote reactions and large crystal growth. More important, the fluids may cause metasomatism that changes the composition of the protolith by adding or removing specific elements. The resulting rock may be of a much different composition than its parent. Metasomatism creates many kinds of products. It can, for example, create ore deposits by concentrating minerals (most commonly copper, iron, or lead sulfides) in host rocks where they did not exist previously.

8.3 Metamorphic Textures

8.3.1 Grain size and Porphyroblasts

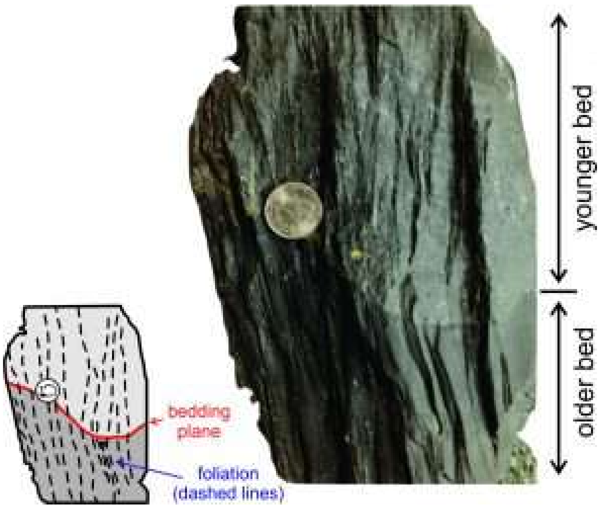
8.23 A garnet-muscovite schist from Syros, Greece. The garnet porphyroblasts are nearly as large as the 1-euro coin.

Textural changes take place as rocks undergo prograde metamorphism, and rocks develop *metamorphic fabrics*. A general coarsening of grain size is typical as small mineral grains recrystallize to form larger ones. This is Ostwald ripening in action (refer to the discussion in Chapter 4). While minerals that are already present recrystallize, new metamorphic minerals may grow and modify rock texture. If minerals develop into large crystals that contrast in size with other minerals in a rock, we call the large crystals *porphyroblasts*. Fine-grained material around the porphyroblasts is the *groundmass*. The garnets in Figure 8.23 are good examples of porphyroblasts surrounded by groundmass.

8.3.2 Lineations and Foliations

Porphyroblasts are one kind of metamorphic fabric, but there are others. In some deformed rocks, mineral grains assume a distinctive arrangement that gives metamorphic rocks a *lineation*, long mineral grains all pointing in the same direction, or a *foliation*, minerals lining up to give a planar fabric. Lineation occurs when amphiboles, kyanite, sillimanite, and other minerals that form long thin crystals, lie parallel in a rock. The photo below in Figure 8.24 shows lineation caused by aligned hornblende (amphibole) crystals.

8.24 Aligned crystals of black hornblende give this rock lineation. The crystals are up to 2 cm long.



8.25 Foliated metamorphic rock (slate) with a bedding plane. A quarter for scale.

Alignment of clays, micas, graphite, or other platy minerals, the separation of a rock into light and dark layers, or parallel fracturing leads to planar fabrics called *foliation*. The photo on the right above (Figure 8.25) shows foliation (vertical fracture traces) that cuts across a bedding plane separating rock of different compositions.

8.3.3 Slate

8.26 Green slate from Pawley, Vermont. About 8 cm across.

Slates, which form during low-grade metamorphism of shales, comprise primarily microscopic clay grains, perhaps with some minor mica. Metamorphism may obliterate the original bedding as foliation develops perpendicular to the direction of maximum stress. This foliation, *slaty cleavage*, gives slates a property called *fissility* – an ability to break into thin sheets of rock with flat smooth surfaces. The photo in Figure 8.25 above shows an example of slaty cleavage. Figure 8.26, seen here, is another example of slate. The minerals in this rock cannot be identified in hand specimen, but in thin section quartz, feldspar, and chlorite can be seen. Slates come in many colors, but various shades of gray are most common. Thin sheets of slate have historically been used for paving or roofing stone.

8.3.4 Phyllite

8.27 Example of a phyllite

Figure 8.27 shows a sample of *phyllite*, a shiny foliated rock created by further metamorphism of slates. The foliation is due to parallel alignment of very small – mostly microscopic – muscovite, chlorite, or other micas, sometimes with graphite. Phyllites, which form at higher metamorphic grades than slates, sparkle because clay minerals have metamorphosed to produce small grains of mica. Thus, foliation of phyllites is different from the foliation in slates that stems from clay mineral alignment, and different from foliation in schists because schists always contain visible mica grains. Like slates, phyllites exhibit fissility.

Phyllites are typically black, gray, or green, and the fine-grained micas and graphite, which are too small to see without a microscope, give phyllites the silky/shiny appearance, or sheen, called a *phyllitic luster*. It is this luster – which is absent from slate and schist – that really defines a phyllite. Additionally, although not seen in Figure 8.27, layering in some phyllites is deformed, giving the rocks a sort of wavy or crinkly appearance.

8.3.5 Schist

8.28 muscovite schist

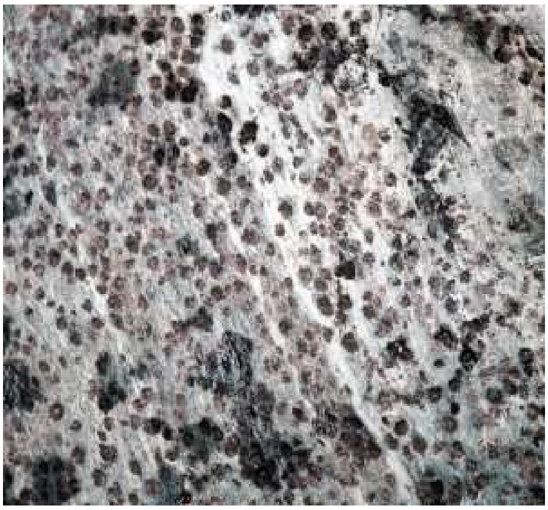
Schists, which form under medium-grade metamorphic conditions, contain medium-to-coarse flakes of aligned mica that we can easily see. This photo (Figure 8.28) shows a typical schist. Schists are higher- grade rocks than phyllites, and most form when phyllites are further metamorphosed. Thus, the precursors of schists are shale, slate, and phyllite. Less commonly, however, schist may form by metamorphism of fine-grained igneous rocks, such as tuff or basalt. Large and aligned flaky minerals, easily seen with the naked eye, define schists. These minerals are most commonly muscovite (such as in this photo) or biotite in parallel or near-parallel orientations that give the rocks *schistosity* – the ability to be broken easily in one direction but not in other directions.

Most schists are mica schists, but graphite, talc, chlorite, and hornblende schists are common. Quartz and feldspar are present in mica schists, often deformed or elongated parallel to the micas, and many other minerals are possible. If schists contain prominent minerals, we name them accordingly. So the schist in Figure 8.23 is a *garnet schist*, and the one in Figure 8.28 is a *muscovite schist*, or simply a *mica schist*. Photos of staurolite schist and kyanite schist are included later in this chapter.

8.3.6 Gneiss

At higher grades, metamorphic rocks may develop compositional layering because different minerals concentrate in layers of contrasting colors. We call such rocks *gneisses*. The defining characteristics of most gneisses, such as the gneisses seen in Figure 8.29 and Figure 8.30, are that the rocks are medium- to coarse-grained and contain alternating layers of light and dark-colored minerals that give the rock foliation called *gneissic banding*. The banding in the garnet gneiss (Figure 8.30) is not particularly well-developed but is present.

8.29 A biotite-quartz gneiss. The specimen is 6.8 cm across.



8.30 A garnet gneiss. The garnets are up to 5 mm across.

Gneisses, the highest temperature-pressure kinds of foliated metamorphic rock, typify many regions that have undergone high-temperature metamorphism. Gneissic banding most commonly forms in response to directed stress. Sometimes, layering may form solely due to chemical processes that concentrate different minerals in different layers. The felsic light-colored layers typically contain quartz and feldspars, and the more mafic darker layers typically contain biotite, hornblende, or pyroxene. Accessory minerals such as garnet are common.

8.31 Deformed granitic gneiss

Sometimes gneissic banding is deformed, as seen in Figure 8.31. This gneiss, from the Czech Republic, contains pink K-feldspar rich layers alternating with darker layers that contain biotite. Metamorphism produced parallel layers of contrasting mineralogy (and color) and subsequent deformation caused the layers to deformed. Figure 8.5 shows another example of a deformed gneiss.

Gneisses are often named based on their protoliths, and petrologists use the general terms *orthogneiss* for gneisses derived from igneous rocks, and *paragneiss* for gneisses derived from sedimentary rocks. More specific names abound – for example, *pelitic gneisses* form by metamorphism of originally clay-rich sedimentary rocks, *granitic gneisses* (such as the one shown in Figure 8.31) form by metamorphism of granites, and *mafic gneisses* form by metamorphism of mafic igneous rocks. Sometimes key minerals are often included in rock names. For example, a garnet gneiss is a gneiss that contains conspicuous garnet crystals.

8.32 Augen gneiss

Some gneisses do not display well-defined dark- and light-colored banding but still maintain less distinct foliation. For example, the foliation in kyanite gneiss may come from alignment of light-colored kyanite crystals in an otherwise quartz- and muscovite-rich rock. An *augen gneiss*, such as the gneiss shown in Figure 8.32, contains large feldspar crystals – “eyes” (*augen* is German for eyes) – stretched in one direction. The gneiss in this photo is oriented so the stretch direction (and, thus, the foliation) is horizontal.

8.3.7 Nonfoliated Metamorphic Rocks

8.33 Biotite hornfels, about 7 cm across, from Riverside County, California

Some metamorphic rocks are fine-grained and lack metamorphic fabrics. For example, *hornfels* are dark colored fine-grained rocks lacking both lineation and foliation. Many hornfels form at low pressure from contact metamorphism of a mudstone or shale. These rocks may contain no visible layering or fractures and appear as a homogeneous mass. Most hornfels are quite hard and durable because constituent grains are tightly bound together. Figure 8.33 shows an example of *biotite hornfels*, the most common kind of hornfels. These rocks are dark brown and sometimes have a slight sheen due to microscopic grains of biotite. Other hornfels may have different colors; the color depends on the minerals present. Some hornfels contain grains that become visible after weathering (because different minerals weather in different ways) but, because of the generally uniform rock color, are invisible otherwise.

8.34 Metamorphosed basalt from near Ely, Minnesota

8.35 Metamorphosed pillow basalt, Italy

Greenstones, which are a specific kind of hornfels, form by metamorphism of basalts. Figure 8.34 shows a 9-cm wide sample of greenstone from Ely, Minnesota. The greenish color is due to chlorite or epidote that grew during metamorphism. Figure 8.35 shows an outcrop of greenstone in Italy. The rock originated as an ocean-floor basalt, and contains rounded structures called *pillows*, indicative of submarine eruption.

8.36 Blue calcite marble from the western Adirondack Mountains, New York

Many nonfoliated metamorphic rocks are dominated by a single mineral. In these rocks, individual mineral grains or crystals, which may start small, recrystallize (grow together) during metamorphism to produce larger crystals. Figure 8.36, for example, shows an 8-cm wide rock consisting only of coarse blue calcite. This rock had a limestone protolith. Petrologists use the term *marble* for all metamorphic carbonate rocks – rocks that form from limestone or dolostone – dominated by calcite or dolomite. (This sometimes leads to confusion because builders and others use the same word to describe any polished slab of rock.)

8.37 An example of quartzite

Quartzite, also a common nonfoliated metamorphic rock, forms by metamorphism of sandstone. Most sandstones comprise mainly quartz and so do quartzites. Figure 8.37 shows a typical example. It consists of small quartz crystals that have grown together so that no grain boundaries are visible without a microscope. The recrystallization produced a typical hard and shiny quartzite (sometimes described as *frosty*), and during metamorphism any original sedimentary textures were erased. Common quartzites are white or gray, but minor components may add color. The pink color in this sample comes from hematite that may have been part of the cement that held the sandstone together. If the protolith sandstone contained minerals besides quartz, so too will the product quartzite. Thus, feldspar, titanite, rutile, magnetite, or zircon may be present in small amounts. And, if the protolith contained some clay, micas and other aluminous minerals may be present.

8.38 Garnet granulite from Lower Silesia, Poland

This figure (8.38) shows an example of a garnet granulite. Many granulites are foliated, but this one is not. Granulites form at the highest grades of metamorphism and can form from many sorts of protoliths. This rock contains black biotite, light-colored K-feldspar and many conspicuous red garnets. The abundant biotite and garnet tell us that the rock is aluminum-rich, suggesting it has a sedimentary origin. Figure 8.10 shows a different granulite; it contains hornblende and plagioclase besides large garnets. The garnet porphyroblasts in Figure 8.10 are 1-2 cm wide. The garnets in this granulite are only a few millimeters wide at most.

8.4 Metamorphic Reactions

8.4.1 Different Kinds of Reactions

Examples of Metamorphic Reactions
Solid-solid reactions:
andalusite = sillimanite
$Al_2SiO_5 = Al_2SiO_5$
grossular + quartz = anorthite + 2 wollastonite
$Ca_3Al_2Si_3O_{12} + SiO_2 = CaAl_2Si_2O_8 + 2\ CaSiO_3$
Dehydration reactions:
muscovite + quartz = K-feldspar + sillimanite + vapor
$KAl_2(AlSi_3)O_{10}(OH)_2 + SiO_2 = KAlSi_3O_8 + Al_2SiO_5 + H_2O$
kaolinite + 2 quartz = pyrophyllite + vapor
$Al_2Si_2O_5(OH)_4 + 2\ SiO_2 = Al_2Si_4O_{10}(OH)_2 + H_2O$
Hydration reaction:
enstatite + 2 H_2O = 2 brucite + 2 quartz
$Mg_2Si_2O_6 + 2\ H_2O = 2\ Mg(OH)_2 + 2\ SiO_2$
Carbonation reaction:
forsterite + 2 CO_2 = 2 magnesite + quartz
$Mg_2SiO_4 + 2\ CO_2 = 2\ MgCO_3 + SiO_2$

As discussed in Chapter 4, under any pressure and temperature, the most stable mineral assemblage is the one with the lowest

Gibbs free energy. So, when a rock is heated or squeezed, chemical reactions occur that may consume old minerals and create new ones. These reactions may be of several types. The table seen here gives examples of different types of metamorphic reactions.

Solid-solid reactions involve no H_2O, CO_2, or other vapor phase. The first example of a solid-solid reaction contains only two minerals, both Al_2SiO_5 polymorphs. This reaction may occur when a metamorphosed shale is heated to high temperature. But most metamorphic reactions involve more than two minerals, and many involve H_2O or CO_2. The second solid-solid reaction is more typical and involves four minerals. Dehydration reactions and decarbonation reactions, such as the examples in this table, liberate H_2O and CO_2, respectively. Hydration reactions and carbonation reactions consume H_2O and CO_2, respectively.

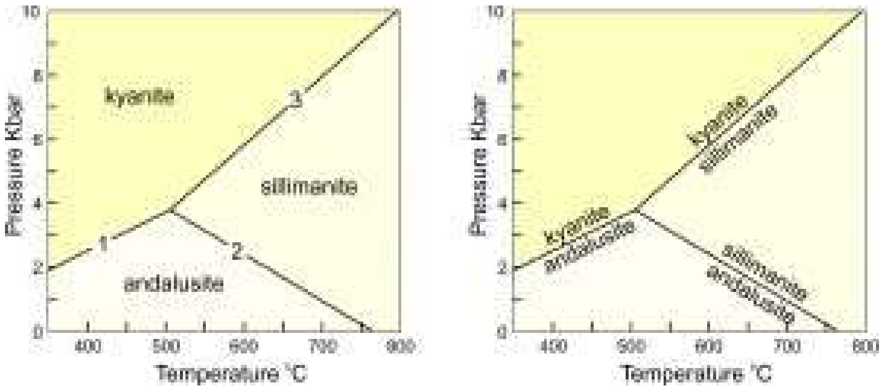
Metamorphic reactions involve changes in mineralogy or in mineral composition. A mineral assemblage is at chemical equilibrium if no such changes are occurring. If the assemblage has the lowest Gibbs free energy possible for the given conditions, it is at *stable equilibrium*. In principle, all rocks tend toward stable equilibrium. Whether they reach it depends on many things, including temperature, grain size, and reaction kinetics. If reactions cease before a rock has reached stable equilibrium, the rock is at *metastable equilibrium*. Many metamorphic rocks contain metastable minerals.

We call a stable mineral assemblage representative of a given set of pressure-temperature conditions a *paragenesis*. When conditions change, metamorphic reactions may create a new paragenesis as some minerals disappear and others grow. Such reactions may be prograde or retrograde. Most of the reactions in the table above are prograde, but the two examples of carbonation and hydration reactions are retrograde reactions that often affect mafic rocks.

Prograde metamorphism involves the breakdown of minerals stable at lower temperature to form minerals stable at higher temperature. Some prograde reactions are solid-solid reactions, but most involve the release of H_2O or CO_2 that flow along cracks or grain boundaries. As temperature increases, minerals containing H_2O or CO_2 become increasingly unstable, causing dehydration or decarbonation, and the release of H_2O or CO_2 as intergranular fluid. If we ignore H_2O and CO_2, we find that most prograde metamorphism is nearly *isochemical*, meaning that the rock is the same composition before and after metamorphism. Sometimes, however, flowing fluids and metasomatism can be the dominant forces controlling metamorphism.

Retrograde metamorphism is, in many ways, just the opposite of prograde metamorphism. H_2O- and CO_2-free minerals react with fluids to produce hydrous or carbonate minerals. Mg-silicates such as forsterite (Mg_2SiO_4), and enstatite ($Mg_2Si_2O_6$), for example, may react to form talc or serpentine (both hydrated Mg-silicates), brucite (Mg hydroxide), or magnesite (Mg carbonate), at low temperature. In contrast with prograde reactions, retrograde reactions are often quite sluggish. They may not go to completion and frequently do not reach stable equilibrium. Sometimes retrogression only affects parts of a rock or parts of some grains in a rock.

8.4.2 Metamorphic Phase Diagrams



8.39 The stability of different aluminosilicate minerals

The laws of thermodynamics allow us to predict which minerals form under particular conditions. We use phase diagrams like the ones seen in Figure 8.39 to show the conditions at which particular minerals or mineral assemblages are stable. The diagram on the left, for example, depicts *stability fields* for kyanite, sillimanite, and andalusite, the Al_2SiO_5 polymorphs. The different fields are the ranges of pressure and temperature where each polymorph is stable. The *reaction lines* separating the fields show the conditions at which chemical reactions occur.

The diagram on the right shows the same information, but the reactions are labeled, not the stability fields. Petrologists use both kinds of diagrams. These diagrams tell us that rocks containing kyanite form at low temperature and high pressure, rocks containing andalusite form at low pressure, and those containing sillimanite form at high temperature. The diagram also allows us to make predictions: for example, if a rock containing andalusite is metamorphosed at high temperature, the andalusite will change into sillimanite.

Phase diagrams for simple chemical systems may only contain a few reactions. The aluminosilicate diagram (above in Figure 8.39) is an example. All the minerals considered have the same composition and are related by three reactions:

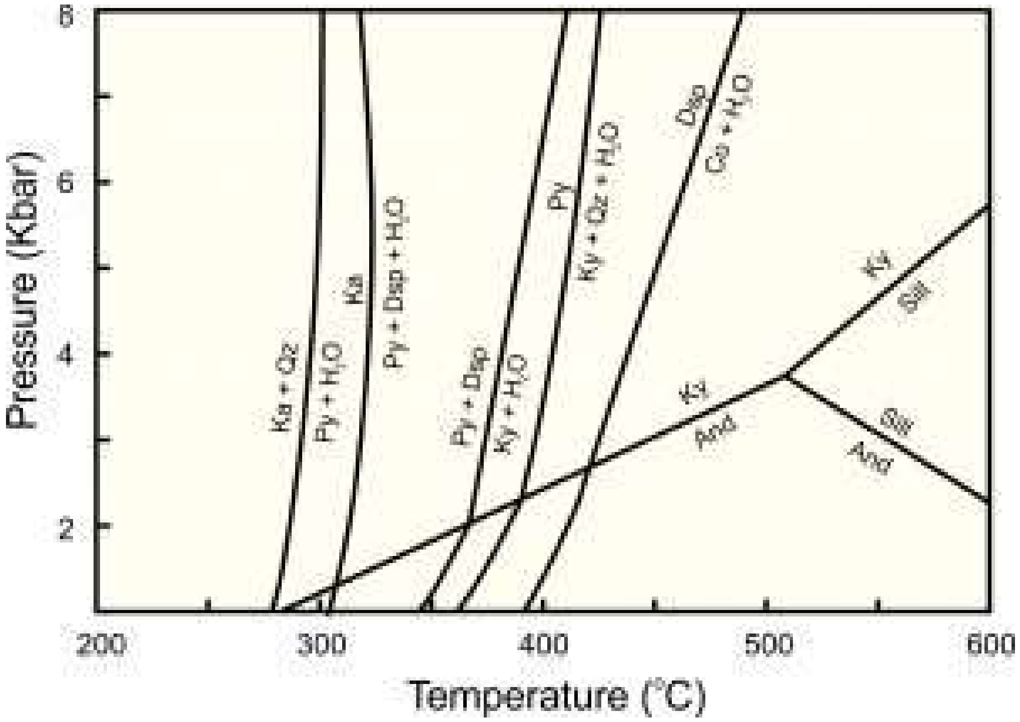
kyanite = andalusite (reaction 1)
$Al_2SiO_5 = Al_2SiO_5$

andalusite = sillimanite (reaction 2)
$Al_2SiO_5 = Al_2SiO_5$

kyanite = sillimanite (reaction 3)
$Al_2SiO_5 = Al_2SiO_5$

Reactions between kyanite, andalusite, and sillimanite are only three of many that involve minerals of Al_2O_3, SiO_2, and H_2O chemical system. Other minerals consist of these same components. The phase diagram seen below in Figure 8.40 is a more complete phase diagram for the system. It includes all stable minerals and reactions. Some of the reactions give off water vapor, labeled as H_2O. Eight minerals are involved but most have restricted stability fields.

Stable Minerals in the System: $Al_2O_3 – SiO_2 – H_2O$	
Mineral	**Formula**
kaolinite (Ka)	$Al_4(Si_4O_{10})(OH)_8$
quartz (Qz)	SiO_2
pyrophyllite (Py)	$Al_2Si_4O_{10}(OH)_2$
diaspore (Dsp)	$AlO(OH)$
kyanite (Ky)	Al_2SiO_5
andalusite (And)	Al_2SiO_5
sillimanite (Sill)	Al_2SiO_5
corundum (Co)	Al_2O_3



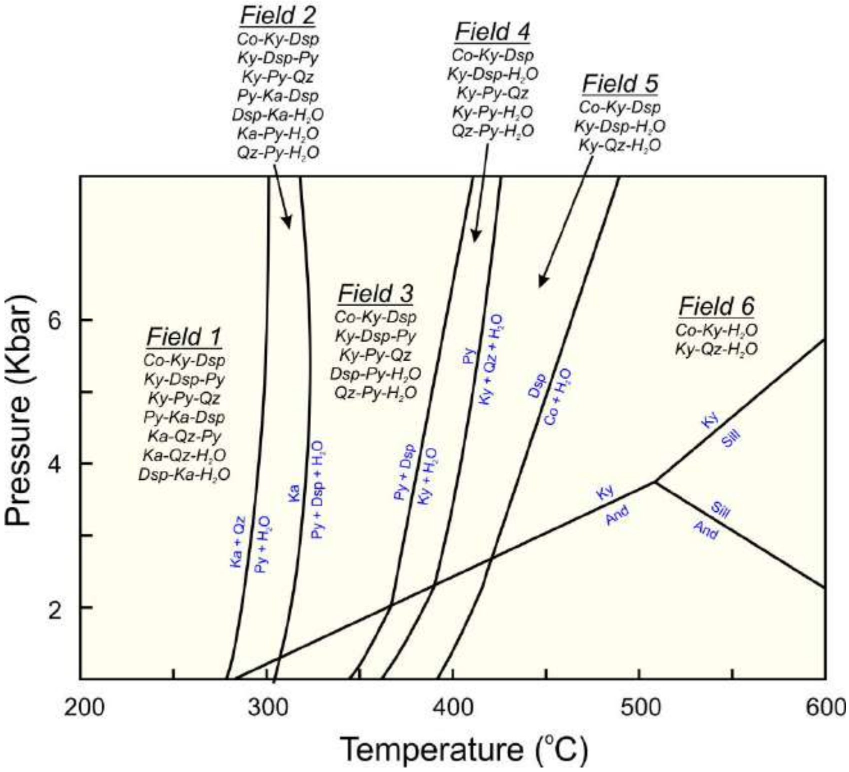
8.40 Minerals and reactions in the system Al_2O_3 – SiO_2 – H_2O

According to this phase diagram, at low temperature, kaolinite (a clay mineral) and quartz are stable together, but as temperature increases to almost 300 Ĉ, kaolinite and quartz react to produce pyrophyllite and H_2O vapor. With a bit more heating, any leftover kaolinite decomposes to pyrophyllite, diaspore, and H_2O vapor. Pyrophyllite itself breaks down at higher temperatures – around 400 Ĉ, so pyrophyllite is only be stable over a limited range of temperature. At temperatures over about 450 °C, the only stable minerals are corundum, quartz, and the three Al_2SiO_5 polymorphs (andalusite, kyanite, sillimanite), but corundum and quartz cannot be found together.

Phase diagrams like this permit prediction of the pressures and temperatures at which individual minerals and specific mineral assemblages will form. Conversely, these diagrams allow us to estimate the pressure and temperature of formation for some rocks containing specific minerals. For example, rocks containing kaolinite and quartz are constrained to have formed at temperatures below about 300 °C. If andalusite accompanies the kaolinite and quartz, pressure is restricted to less than 1 kbar.

● Box 8-2: Using Phase Diagrams

If a rock contains a specific mineral assemblage at equilibrium, we can use an appropriate phase diagram to put restrictions on the conditions at which the rock formed. For example, the diagram in this box is modified from Figure 8.40. It lists all the different 3-mineral assemblages that are stable within fields between reactions. (For simplicity, only assemblages in the high-pressure fields are labeled.) The different assemblages are consistent with the reactions shown.



8.41 Minerals and reactions in the system Al_2O_3-SiO_2-H_2O

But, besides 3-mineral assemblages, different pairs of minerals are stable within the different fields. And individual minerals are stable in different parts of the diagram. In all, there are 87 different mineral combinations stable in different parts of the diagram. If we labeled them all, the diagram would become very messy. This is why most phase diagrams only have reactions labeled.

Consider a rock that contains only diaspore. This diagram says it could have formed in any of the fields 1 through 5. In Field 6, diaspore is not stable and breaks down to corundum and H_2O. Suppose a rock contains diaspore with pyrophyllite. It is stable in Fields 1, 2, and 3, but not at higher temperatures because the two minerals would react to kyanite and H_2O. And, consider a rock that contains pyrophyllite, diaspore, and H_2O. It is stable in Field 3 only. At lower temperature the minerals react to produce kaolinite, and at higher temperature pyrophyllite and diaspore react to produce kyanite. What about four minerals together? Four minerals can only be stable if conditions lie on one of the reaction lines. Thus, we see that the more minerals present, the more restricted the conditions of formation. This is true for all chemical systems at equilibrium, not just minerals in rocks.

8.5 Metasedimentary Rocks and Minerals

Compositional Classes of Metamorphic Rocks

rock class	protolith
metapelites	shale and related sediments
metasandstones	sandstones
metacarbonates	limestone or dolostone
metamorphosed iron formation	iron-rich sediments
metagranites	granitic rocks
metabasalts	basaltic rocks

Metamorphic rocks may contain all the minerals common in sedimentary and igneous rocks, plus many minerals exclusive to metamorphic rocks. The two most important factors controlling mineralogy are the composition of the rock and the pressure-temperature conditions of metamorphism. For convenience, we divide the most common rock types into general compositional classes. The table seen here lists the most important classes considered by petrologists.

The composition of a metamorphic rock, which is the composition of the protolith, is key because it controls the metamorphic minerals that may be present. Metamorphic minerals in metapelites, metacarbonates, metabasites, metagranites, etc., are all different because of differences in rock chemistry. Metapelites typically contain micas and may also contain staurolite, garnet, and other aluminous minerals. Besides containing calcite or dolomite, metacarbonates may contain Ca-Mg silicates. Metagranites usually contain the minerals that igneous granites contain. And, metabasites commonly contain plagioclase, pyroxenes, and amphiboles. In the discussions below, we look at the minerals common in rocks of different compositions. The focus is mostly on prograde minerals, but rocks of any composition may undergo retrograde metamorphism or alteration that produce a variety of low-temperature minerals.

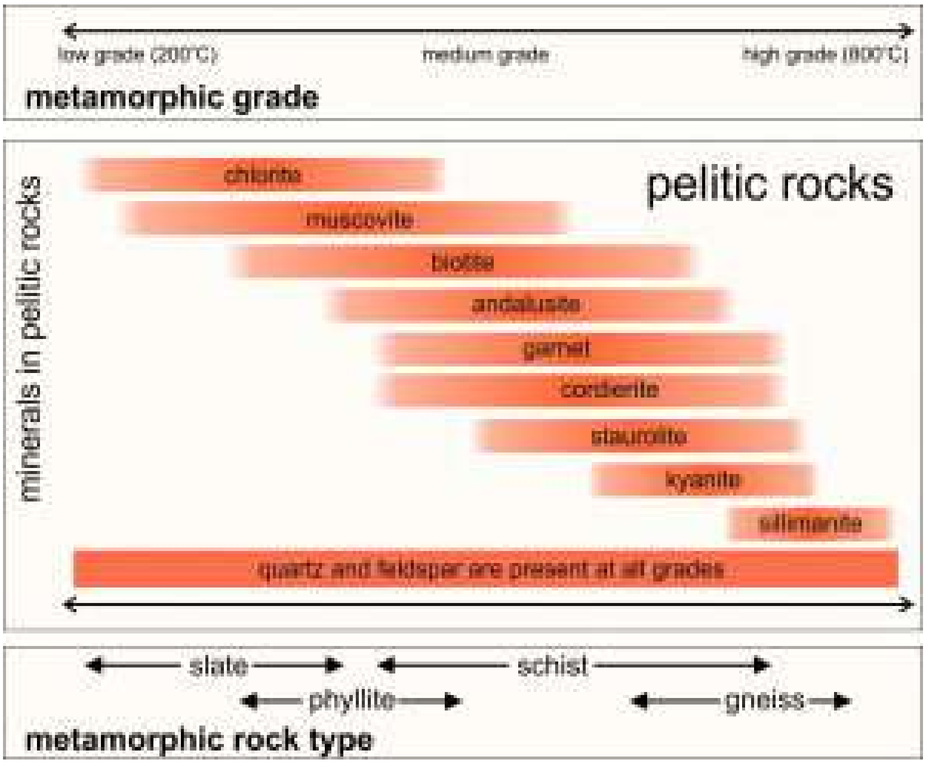
8.5.1 Metamorphosed Pelitic Rocks (Metapelites)

Metapelites derive from the metamorphism of shale and other clay-rich sediments. When metamorphosed, dehydration reactions change clay minerals into new minerals containing less H_2O. At low grade this leads to the formation of chlorite and muscovite. At higher grade, biotite forms. Foliated textures develop as muscovite and biotite crystallize, so metapelites may be slates, phyllites, schists or gneisses depending on grade. Examples are shown earlier in this chapter in Figures 8.23 and 8.26 through 8.30.

Metapelites are rich in Al, Si, and K and may contain substantial amounts of Fe and Mg, so minerals containing these elements dominate metapelitic rocks. The table below lists the most common and important minerals in these rocks. The minerals in the left column may exist in low-grade rocks, those in the right column are exclusively in high-grade rocks, and the ones in the middle are generally in medium-grade rocks.

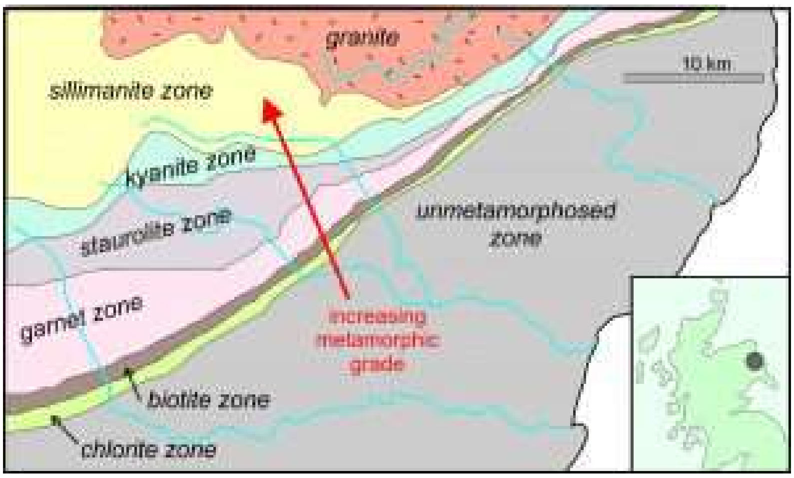
Common Minerals in Metapelites		
low grade	**→**	**high grade**
quartz SiO_2	muscovite $KAl_2(AlSi_3O_{10})(OH)_2$	staurolite $(Fe,Mg)_2Al_9Si_4O_{23}(OH)$
kaolinite $Al_4(Si_4O_{10})(OH)_8$	kyanite Al_2SiO_5	cordierite $(Mg,Fe)Al_4Si_5O_{18}$

pyrophyllite $Al_2(Si_4O_{10})(OH)_2$	andalusite Al_2SiO_5	K-feldspar $KAlSi_3O_8$
chlorite (variable chemistry)	biotite $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	sillimanite Al_2SiO_5
chloritoid $(Fe,Mg)_2Al_4Si_2O_{10}(OH)_4$	garnet (almandine) $(Ca,Fe,Mg,Mn)_3Al_2Si_3O_{12}$	orthopyroxene $(Mg,Fe)_2Si_2O_6$



8.42 Minerals as indicators of metamorphic grade in metapelites

The chart in Figure 8.42 shows typical minerals in metapelites at different grades. Quartz and Na-rich plagioclase are in rocks of all grades. Kaolinite, pyrophyllite and chloritoid may also be present at low grade but are less common and are omitted from this figure. There is a great deal of overlap and many of these minerals exist together. Some persist over a wide range of temperatures. Some are present in low-pressure rocks but not in high-pressure rocks. Either muscovite or biotite are generally present except at the highest grades.



8.43 Barrovian zones of metamorphism. The insert map shows where, in Scotland, these zones are found.

The most classic example of regionally metamorphosed pelites is in the Scottish Highlands where, in the late 19th and early 20th centuries, George Barrow mapped a large region of variable metamorphic grade. The map seen in Figure 8.43 derives from Barrow’s work. In this region, metamorphic grade increases from southeast to northwest. Barrow recognized that the higher-grade metamorphic rocks he was mapping were once unmetamorphosed shales. He mapped different *metamorphic zones* based on the metamorphic minerals that were present. Each of Barrow’s zones is characterized by a particular *index mineral* that reflects metamorphic grade. Thus, the zone names in this map.

Rocks similar to the ones described by Barrow, are found worldwide. They are said to be the results of *Barrovian metamorphism*, a tribute to Barrow. In North America, Barrovian metamorphism is particularly well exposed and studied in the Appalachian Mountains and in the Canadian Shield. Most metapelites in Scotland experienced Barrovian metamorphism, but in an area just north of Aberdeen, metamorphism occurred at slightly lower pressures than classic Barrovian metamorphism. We call this kind of metamorphism *Buchan metamorphism*, named after the Buchan region where it is found. Besides Scotland, other classic occurrences are in Japan and

Spain, but Buchan terranes are found worldwide. Metamorphic rocks in these areas may contain cordierite and andalusite, two low-pressure minerals commonly absent from Barrovian terranes.

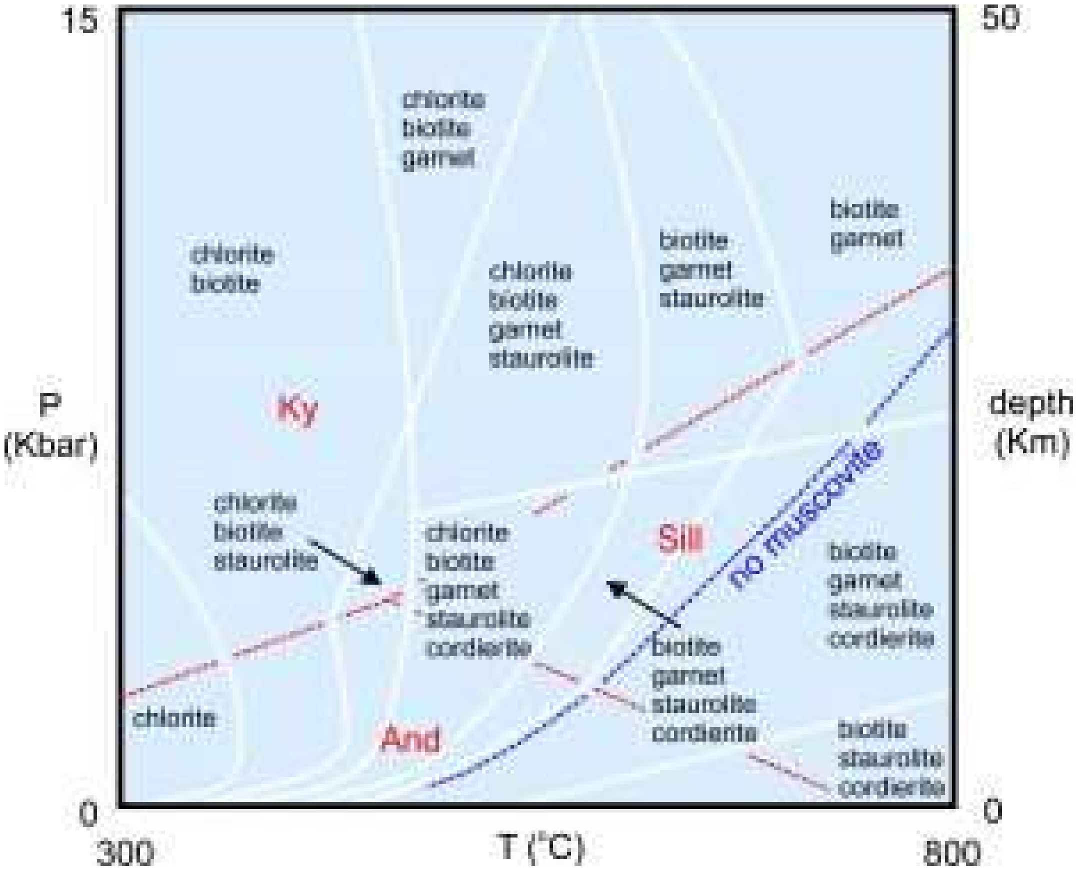
The photos below show typical medium-grade metapelites. Figure 8.44 contains garnet porphyroblasts and Figure 8.45 contains staurolite porphyroblasts. The porphyroblasts in both photos are centimeters across. Muscovite surrounds them. Figure 8.46 contains conspicuous blades of blue kyanite surrounded by quartz, some of which is stained reddish by hematite. Figure 8.47 contains centimeter-sized crystals of blue cordierite. Cordierite can be difficult to identify unless it has this diagnostic blue bottle glass appearance. Figures 8.23 and 8.28, earlier in this chapter, also show examples of typical medium-grade metapelites.

8.44 A garnet-muscovite schist

8.45 A staurolite-muscovite schist from Michigamme, Michigan

8.46 Blue kyanite in a schist

8.47 Blue cordierite with quartz, from Brazil. Centimeter ruler for scale.



8.48 Stable mineral assemblages in metapelites

Figure 8.48 shows pressure-temperature stability fields for common pelitic mineral assemblages. Besides the minerals listed, quartz and plagioclase are present under all conditions. The bounding white lines are really diffuse boundaries and the reactions that relate one assemblage to another are complex.

Many metapelitic rocks contain an Al_2SiO_5 polymorph (andalusite, kyanite, or sillimanite) besides the mineral listed. Red lines and text in this phase diagram show the stability fields for the different polymorphs: kyanite at high pressure, sillimanite at high temperature, and andalusite at low pressure. At medium- or high-grade, Barrovian metamorphism often yields rocks containing kyanite or sillimanite with garnet. At lower pressures, Buchan metamorphism may produce rocks with andalusite, and often cordierite instead of garnet. Muscovite is generally absent at the highest temperatures because it dehydrates to K-feldspar, sillimanite, and water vapor (at temperatures above the blue dashed line). Note that the order of minerals with increasing metamorphic grade in this phase diagram, and in Figure 8.42, matches the order of metamorphic zones mapped by Barrow in Scotland (Figure 8.43).

8.5.2 Metamorphosed Sandstones (Metapsammites)

8.49 Metamorphosed sandstone from South Australia. Sample is 10 cm across.

Compared with metamorphosed pelites, *metamorphosed sandstones*, also called *metasandstones* or metapsammites, are often nondescript. Normal sandstones are mostly quartz, perhaps with some feldspar. When metamorphosed, they still contain quartz and feldspar because these minerals are stable at all metamorphic grades. At low grades, metasandstones typically appear massive and homogeneous, containing light-colored quartz and feldspar grains. The rock seen here (Figure 8.49) is an example. Sometimes small micas and other dark minerals may be scattered evenly throughout.

At higher grades metasandstone may recrystallize with quartz grains growing together and becoming coarser. This produces a quartzite, a hard, nonfoliated metamorphic rock. In quartzites, the once separate quartz crystals become massive quartz with no visible grain boundaries. As this happens, original sedimentary textures are obliterated. Pure quartzites are generally white or light colored (like the one in Figure 8.49) but iron staining often adds a red or pinkish coloration. Figure 8.37, earlier in this chapter, shows another example of an unremarkable quartzite.

So, many metasandstones have unexciting mineralogy, but if the original sandstone contained some clay, any of the minerals that can be in metapelites may be present. For example, the greenish quartzite seen below (Figure 8.50) contains disseminated green chlorite. And the kyanite quartzite in Figure 8.51 contains conspicuous blades of blue kyanite. Quartz usually dominates, and the amounts of other minerals depend on how much clay was in the protolith. Foliation, typical of metapelitic rocks, is usually lacking in these rocks because micas are generally absent.

8.50 Quartzite from Sollières, southeastern France

8.51 Kyanite quartzite from Kapteeninautio, Finland. Sample is 28 cm across.

8.5.3 Metamorphosed Limestones and Dolostones (Marbles)

8.52 Marble from near Tate, Georgia, 7.6 cm across

Geologists generally call metamorphosed carbonate rocks *marbles*, although this term is used in different ways by building contractors and others. The metamorphism of limestone or dolostone composed only of carbonate minerals produces few mineralogical changes. A general increase in grain size may take place – similar to what happens when sandstone turns into quartzite, but no diagnostic minerals can form because of the limited chemical composition and the high stabilities of both calcite and dolomite. The photo in Figure 8.52 shows a marble that contains only course crystals of white calcite. Figure 8.36, earlier in this chapter, showed a marble consisting only of blue calcite.

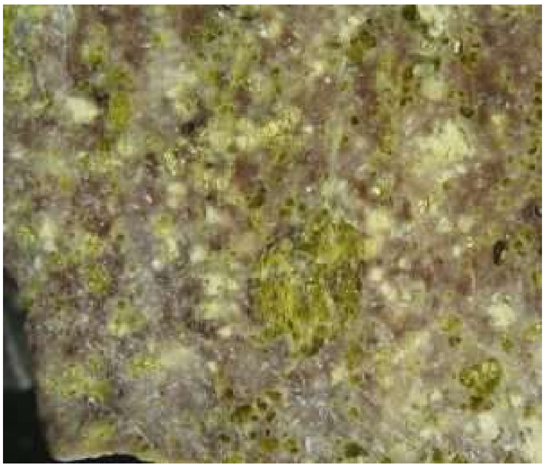
However, most limestones contain some quartz and other minerals besides carbonates. In these rocks, a series of interesting Ca-silicates, Ca-Mg-silicates, and Ca-Al-silicates form as metamorphism progresses. The table below lists the most important of these minerals, roughly in order of their appearance in response to increasing metamorphic grade.

Minerals Common in Metacarbonates		
low grade	**→**	**high grade**
calcite $CaCO_3$	talc $Mg_3Si_4O_{10}(OH)_2$	grossular (garnet) $Ca_3Al_2Si_3O_{12}$
dolomite $CaMg(CO_3)_2$	tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$	periclase MgO
quartz SiO_2	forsterite $(Mg,Fe)_2SiO_4$	wollastonite $CaSiO_3$
phlogopite (Mg-rich biotite) $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$	diopside $CaMgSi_2O_6$	monticellite $CaMgSiO_4$

If quartz is present, the metamorphic reactions in marbles are often decarbonation reactions that involve the breakdown of carbonates to release CO_2. If a pluton intrudes a limestone or dolostone, contact metamorphism may cause CO_2 to flow out of the carbonate and combine with H_2O that comes from the pluton. The CO_2-H_2O fluid can have profound effects on the carbonate nearby, and fluid composition controls the formation of many minerals. Fluids may also cause significant metasomatism and a significant change in rock chemistry.


8.53 Phlogopite in marble from Orange County, New York


8.54 Tremolite and graphite in marble from Franklin, New Jersey


8.55 Forsterite marble


8.56 Diopside marble from the Adirondack Mountains, New York

Phlogopite is typically one of the first minerals to form during carbonate metamorphism. The first photo in the block above (Figure 8.53) shows large, somewhat hexagonal, flakes of phlogopite with calcite behind. The second photo (Figure 8.54) shows gray blades of tremolite in a marble that also contains small (hard to see) specs of graphite. The bottom left photo (Figure 8.55) show a marble that contains green forsterite (olivine). The last photo (Figure 8.56) shows a marble that contains green diopside. These four photos are in order of increasing metamorphic grade. The diopside marble is the highest grade of the four.

8.5.4 Metamorphosed Iron Formations

8.57 Banded iron formation from Dales Gorge, Western Australia

Ironstone is a general name we give to sedimentary rocks that contain more than 15% iron. These rocks may contain iron hydroxides (limonite), oxides (magnetite and hematite), carbonates (siderite), or silicates (chamosite, Fe-rich chlorite). They generally have a uniform, nonfoliated texture. *Iron formations* are similar to ironstones but are mainly Precambrian (ironstones are Phanerozoic). Iron formations generally contain abundant chert and are often well banded with bands ranging from centimeters to meters thick. The bands consist of alternating iron- and chert-rich layers. Figure 8.57 photo shows an example of iron formation from western Australia.

When ironstones and iron formations are metamorphosed, they quickly lose any original hydrous minerals. But any of the other original minerals may persist. At the lowest grades of metamorphism, magnetite and hematite most commonly dominate. If the original rock was rich in carbonate, siderite will be present. And sometimes pyrite is present as well. At higher grades, greenalite, minnesotaite, and glauconite (all iron silicates) may form. At still higher grades, metamorphism may produce actinolite, grunerite, hedenbergite, or fayalite. The table below summarizes these relationships.

Common Minerals in Metamorphosed Iron Formations		
low grade	**→**	**high grade**
quartz SiO_2	pyrite FeS_2	actinolite $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$
hematite Fe_2O_3	greenalite $Fe_{2-3}Si_2O_5OH_4$	grunerite $Fe_7Si_8O_{22}(OH)_2$
magnetite Fe_3O_4	minnesotaite $Fe_3Si_4O_{10}(OH)_2$	hedenbergite $CaFeSi_2O_6$
siderite FeCO3	glauconite $(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	fayalite Fe_2SiO_4

The photos below show minerals common in metamorphosed iron formations. The hematite shown in Figure 8.58 is *specular hematite* (more common hematite has a red earthy color). Actinolite, seen in Figure 8.59, is a calcium-iron amphibole. Grunerite (Figure 8.60) is an iron amphibole. Greenalite (Figure 8.61) is an iron-rich variety of serpentine. Siderite (the brown mineral in Figure 8.62) is an iron carbonate, and pyrite (Figure 8.63) is iron sulfide. The pyrite in this photo is somewhat tarnished.

8.58 Hematite from near Marquette, Michigan

8.59 Actinolite, northern Wisconsin

8.60 Grunerite from near Marquette Michigan. 7 cm across

8.61 Greenalite

8.62 Siderite with calcite from near Roxbury, Connecticut. Photo is about 15 cm across

8.63 Centimeter – sized pyrite crystals in metamorphosed iron formation near Marquette, Michigan

8.6 Metaigneous Rocks and Minerals

8.6.1 Metamorphosed Granitic Rocks

The quartz, K-feldspar, and plagioclase that make up most granites and intermediate igneous rocks are stable at all grades of metamorphism. So, metamorphism of granites may not lead to significant mineralogical changes. However, many granites contain mafic minerals, most commonly biotite and hornblende. These minerals may dehydrate to produce new metamorphic minerals at medium and high grade. The table below lists the most common minerals in metamorphosed granites (also called *metagranites*). At the highest grade, metagranites become *granulites*, defined by the presence of orthopyroxene formed by dehydration of mafic minerals. Figure 8.31, earlier in this chapter, showed an example of a granitic granulite. Accessory minerals found in unmetamorphosed granites may also be present after metamorphism. At high grade, granitic rocks sometimes develop gneissic banding, even if mineralogy has not significantly changed.

Common Minerals in Metamorphosed Granitic Rocks		
unmetamorphosed	**low grade**	**high grade**
Quartz SiO_2	biotite $K(Fe,Mg)_3(AlSi_3O_{10})(OH)_2$	Fe-rich garnet (almandine) $Fe_3Al_2Si_3O_{12}$

K-feldspar $KAlSi_3O_8$	hornblende (complex amphibole)	orthopyroxene $(Fe,Mg)SiO_3$

8.64 Metagranite from western Norway.

The photo above (Figure 8.64) shows a metagranite from the Western Gneiss Region of Norway. During metamorphism, K-feldspar recrystallized to form very large pink crystals. Gray glassy quartz, white plagioclase, and black biotite are also present. This rock shows a significant amount of deformation, recorded by the deformed sheets of biotite. Note the presence of gneissic banding, most notably to the right of the marker pen.

8.6.2 Metamorphosed Mafic Rocks (Metabasites)

Common Minerals in Metabasites

	minerals	rock names
low grade ***high grade***	zeolites (variable Ca-Al silicates) prehnite $Ca_2Al(AlSi_3O_{10})(OH)_2$ pumpellyite (similar to epidote) Ca-rich plagioclase $(Ca,Na)_2(Si,Al)_4O_8$ epidote $Ca_2(Al,Fe)_3(Si_3O_{12})(OH)$ chlorite (variable chemistry) actinolite $Ca_2(Fe,Mg)_5(Si_8O_{22})(OH)_2$ hornblende (complex amphibole) garnet (almandine-pyrope)$(Fe,Mg)_3Al_2Si_3O_{12}$ biotite $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$ augite (pyroxene) $CaMgSi_2O_6$ orthopyroxene (enstatite) $Mg_2Si_2O_6$	*igneous rock with secondary minerals* *greenstone* *amphibolite* *mafic gneiss* *mafic granulite*

Metamorphosed basalts and other rocks of similar composition are commonly called *metabasites*. This is because, geologists once called basalts *basic rocks*. Compared with metasandstones and metapelites, metabasites are relatively poor in Al and Si and rich in Ca, Mg, and Fe. Many different minerals may form, and metamorphic reactions are complex. Plagioclase and augite are stable at all grades but other minerals are not. The most important metamorphic minerals are Ca and Mg silicates. Metabasites are generally more massive and less foliated than pelitic rocks, but at higher grades they do form schist and gneiss.

The table seen here lists the most common minerals in metabasites. Low-grade minerals are at the top of the table, and grade increases downward. Metamorphism often begins with the formation of zeolites, or of prehnite. These minerals may crystallize in vugs or cracks. They are secondary minerals in many igneous rocks, and form by hydration of feldspars when water flows through the protolith. Some petrologists do not consider these minerals to be metamorphic minerals, while others do.

The formation of greenstones is said by many to be the beginning of metamorphism. *Greenstones* are fine-grained, very low-grade metabasites that have a conspicuous light- to dark-gray or green color. The characteristic green color comes from fine-grained chlorite and epidote in the rocks. Greenstones may also contain Na-rich plagioclase (albite), quartz, carbonates, and zeolites. The photo below in Figure 8.65 shows a typical greenstone outcrop in northern Minnesota. Figures 8.34 and 8.35, earlier in this chapter, showed other examples.

At slightly higher grades, metabasites become greenschists, obtaining schistosity from parallel arrangements of the green amphibole actinolite and chlorite. Figure 8.66, below, shows a greenschist from the Homestake Gold Mine in Lead, South Dakota. Although hard to see, the specimen contains native gold near the bottom of the sample. If you enlarge the photo you can see the gold.

At still higher grade, chlorite, epidote, and actinolite break down by dehydration reactions, producing a specific kind of rock called an *amphibolite*. The photo in Figure 8.67 is an example. Amphibolites contain large grains of black hornblende and whitish plagioclase in subequal proportions. Garnet, biotite, and light-colored amphiboles such as anthophyllite or cummingtonite may also be present.

8.66 Greenschist from the Homestake Mine, South Dakota

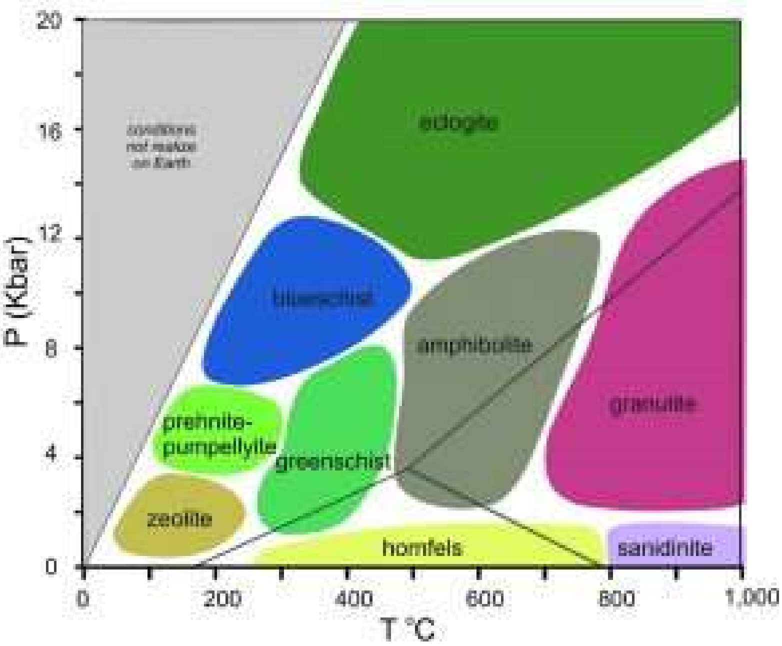
8.65 Greenstone from Ely, Greenstone Belt, Minnesota

8.67 Amphibolite from the Geopark Prague, Czech Republic

With even more metamorphism, mafic rocks may become mafic gneisses. At the highest grades, all amphiboles become unstable and dehydrate to produce pyroxenes. Assemblages including garnet and clinopyroxene, or orthopyroxene, are diagnostic of mafic granulites. Figure 8.10 earlier in this chapter, showed an example of a mafic granulite. Minor minerals at all grades include many that are present in mafic igneous rocks.

8.6.2.1 Metamorphic Facies

Pentti Eskola, a geology professor at the University of Helsinki, introduced the idea of *metamorphic facies* in 1920. He observed that the equilibrium mineral assemblage and texture of metabasites vary with pressure and temperature. Thus, rock mineralogy and texture record the conditions of metamorphism. Eskola defined facies as general ranges of pressure and temperature characterized by a distinct kind of metabasite.



8.68 The P-T ranges for different metamorphic facies

Facies diagrams, such as the one in Figure 8.68, are similar to phase diagrams because they divide P-T space into small areas associated with specific minerals or mineral assemblages. The main differences between facies diagrams and phase diagrams are that facies diagrams involve many chemical components, the locations of different facies in P-T space are not precise, and we often do not know the exact reactions that relate one facies to another. Eskola originally identified eight facies. Other petrologists have divided some to more precisely represent pressure and temperature ranges. Each facies name comes from its most characteristic metabasite minerals or rock types. The table below summarizes key mineral assemblages for each facies.

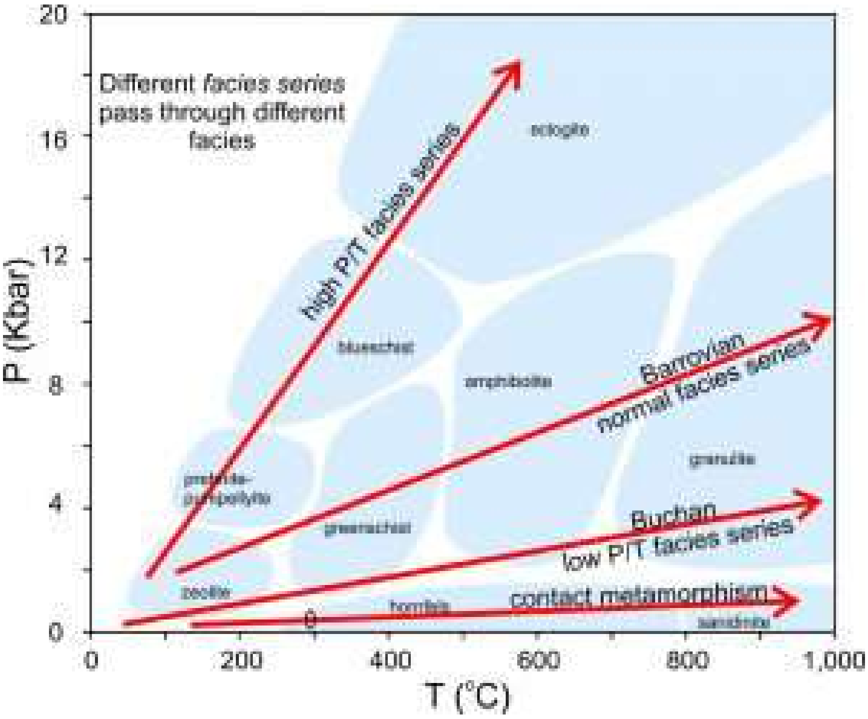
<table>
<tr><th colspan="3">Key Mineral Assemblages in Mafic Rocks of Different Metamorphic Facies</th></tr>
<tr><th>kind of Metamorphism</th><th>metamorphic Facies</th><th>diagnostic Minerals</th></tr>
</table>

contact metamorphism	pyroxene hornfels	orthopyroxene + clinopyroxene + plagioclase
	sanidinite	sanidine or tridymite or pigeonite or glass
low-pressure metamorphism	zeolite	zeolites + quartz
	prehnite-pumpellyite	prehnite or pumpellyite + quartz
	greenschist	chlorite, epidote, albite, quartz
	amphibolite	hornblende + plagioclase
	granulite	orthopyroxene or garnet + clinopyroxene + quartz
high-pressure metamorphism	blueschist	glaucophane
	eclogite	omphacite + garnet ± quartz

Zeolite minerals and clays characterize the *zeolite facies*. This facies represents the lowest grade of metamorphism; it is often hard to distinguish zeolite-facies metamorphism from diagenesis. As temperature rises, the zeolite facies gives way to the *prehnite-pumpellyite facies*, the *greenschist facies*, the *amphibolite facies*, and the *granulite facies*. Contact metamorphism produces two low-pressure, high-temperature facies, the *pyroxene-hornfels facies* and the *sanidinite facies*. The *blueschist facies* and the *eclogite facies* occur at high pressure.

Eskola based his facies names on minerals and textures of mafic rocks. The names of the facies are names of different kinds of metamorphosed mafic rocks. But petrologists use the same names when talking about rocks of other compositions. This leads to some confusion. The table above lists key mineral assemblages in mafic rocks, but the assemblages will never be present in rocks of other compositions. For example, pelitic or calcareous rocks do not form greenschists (green mafic schists) or amphibolites (mafic rocks dominated by amphibole and plagioclase) even when metamorphosed at conditions within the greenschist or amphibolite facies. In addition, for some rock compositions, several different mineral assemblages may be stable within a single facies. Further confusion arises because petrologists use some facies names in a more restricted sense, referring to particular rock types with important tectonic significance. Despite these problems, the facies concept provides a convenient way to discuss general ranges of pressure and temperature, and it receives wide use.

8.6.2.2 Facies Series



8.69 Metamorphic facies series

As a model for progressive metamorphism, petrologists consider different *metamorphic facies series*, the sequences of metamorphic rocks that would form in different metamorphic environments. The PT diagram in Figure 8.69 shows the most important of these series.

Rocks undergoing contact metamorphism experience only low pressure. They pass through the zeolite, prehnite-pumpellyite, low-pressure greenschist, pyroxene hornfels and sanidinite facies with increasing temperature. Such rocks are common anywhere magma has intruded shallow crustal rocks.

Rocks subjected to regional metamorphism during mountain building experience a significant increase in both pressure and temperature. They progress through the zeolite, prehnite-pumpellyite, greenschist, amphibolite, and granulite facies. Sometimes they follow a *Buchan facies series* (lower pressure) and sometimes they follow a *Barrovian facies series* (higher pressure).

Subduction carries relatively cool rocks to depth and high pressures. So, some rocks related to subduction zones follow the *high P/T facies series*, experiencing conditions in the zeolite, prehnite – pumpellyite, blueschist, and possibly eclogite facies. We find these rocks, typically, as blocks in fault contact with greenschist facies rocks. Petrologists have described blueschists from many places, but the two classic examples of the blueschist facies series are rocks of the Sanbagawa metamorphic belt of Japan and of the Franciscan Complex of California.

8.6.3 Metamorphosed Ultramafic Rocks

Common Minerals in Metamorphosed Ultramafic Rocks	
	minerals

low grade	talc $Mg_3Si_4O_{10}(OH)_2$
	brucite $Mg(OH)_2$
	magnesite $MgCO_3$
	serpentine $Mg_6Si_4O_{10}(OH)_8$
	olivine $(Mg,Fe)_2SiO_4$
	anthophyllite $(Mg,Fe)_7Si_8O_{22}(OH)_2$
	garnet (pyrope-almandine) $(Mg,Fe)_3Al_2Si_3O_{12}$
	clinopyroxene (diopside) $CaMgSi_2O_6$
high grade	orthopyroxene (enstatite) $Mg_2Si_2O_6$

Ultramafic rocks come from Earth’s mantle. Sometimes, during tectonism, they make it to the surface so we can study them. Most of the examples of metamorphosed ultramafic rocks that we see are in o*phiolites*, slivers of Earth’s oceanic crust and mantle uplifted and accreted onto continents. The outcrop photo below (Figure 8.70) shows a rock of the Lizard Complex, one of the best-known ophiolites.

8.70 Metamorphosed mantle in the Lizard Complex, Cornwall, England

Mantle rocks are high-temperature, high-pressure rocks that typically contain olivine, clinopyroxene, and orthopyroxene when unweathered. When weathered or metamorphosed at low temperature, the original minerals often react to create low-temperature minerals. Hydration and carbonation reactions occur and produce hydrous and carbonate minerals. Magnesium oxides and hydroxides may also form. Thus, unless metamorphic temperatures are very high, metamorphism of ultramafic rocks produces low-temperature minerals from high-temperature minerals, essentially retrograde metamorphism.

The table above lists the most common minerals in metamorphosed ultramafic rocks. Low-grade minerals are at the top of the table and high-grade minerals at the bottom. Ultramafic rocks are very Mg-rich, and often contain much olivine. Because of their chemistry, Mg-silicates such as talc, serpentine, anthophyllite, diopside, and enstatite are also common in these rocks.

8.71 Outcrop of metamorphosed ultramafic rock at Pyke Hill, western Ontario

Low-grade metamorphism or alteration of olivine-bearing rocks often produces a brownish, highly weathered, appearance, such as seen in this outcrop photo (Figure 8.71). Typically, these rocks contain serpentine that developed by hydration of olivine. We call rocks rich in serpentine *serpentinites*. Figure 8.9, near the beginning of this chapter showed another example. Serpentine has three polymorphs: antigorite, lizardite, and chrysotile. The photos below show examples of each.

8.72 Outcrop of a serpentinite containing primarily antigorite

8.73 Lizardite with stichtite from Tasmania. The specimen is 8.6 cm across

8.74 Chrysotile, the most common asbestos mineral

Antigorite, the most common serpentine mineral that forms during metamorphism of ultramafic rocks, is stable over a wide range of metamorphic conditions. The weathered outcrop in Figure 8.72 is a typical occurrence. *Lizardite* (Figure 8.73), named for occurrences in the Lizard Complex, Cornwall, and *chrysotile* (Figure 8.74) are less common and form exclusively at low pressures or at Earth’s surface. The green lizardite in the middle photo above contains pinkish inclusions of *stichtite*, a rare magnesium chrome carbonate. Chrysotile is one of the few recognized asbestos minerals; fine fibers are easily seen in Figure 8.74. The other asbestos minerals are amphiboles.

While serpentine commonly dominates very low-grade ultramafic rocks, several other minerals may also be present. The photos below show talc (hydrated Mg-silicate), brucite (Mg-hydroxide), and magnesite (Mg-carbonate). These minerals, common in metamorphosed ultramafic rocks, can also form in metacarbonates.


8.75 7 cm wide sample of talc


8.76 Brucite


8.77 Magnesite forming from ultramafic rock near Turin, Italy

At higher metamorphic grades, ultramafic rocks may contain olivine, anthophyllite, enstatite, periclase, or spinel. And, at the highest grades, garnet and pyroxene become stable. Minerals in high-grade ultramafic rocks are the same as the minerals in rocks of the mantle (where pressure and temperature are great). In effect, such rocks originated as high-grade metamorphic rocks. We saw photos of several examples in Chapter 6 (Figures 6.118, 6.119, and 6.120).

8.7 High-Pressure Rocks and Minerals

Common Minerals in Metamorphosed High-Pressure Rocks	
	minerals
low grade	glaucophane $Na_2(Fe,Mg)_3Al_2Si_8O_{22}(OH)_2$
	lawsonite $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$
	epidote $Ca_2(Al_2Fe)_3Si_3O_{12}(OH)$
	jadeite $NaAlSi_2O_6$
	aragonite $CaCO_3$
	kyanite Al_2SiO_5
high grade	garnet (pyrope-almandine) $(Mg,Fe)_3Al_2Si_3O_{12}$
	omphacite $(Ca,Na)(Mg,Fe,Al)Si_2O_6$

Because of their tectonic significance, petrologists group high-pressure metamorphic rocks into a class unrelated to rock composition. These rocks include mainly blueschists and eclogites, both quite rare. They come from deep in Earth, and special conditions are required to create them and bring them to Earth’s surface. *Blueschist* is a name given to one type of rock that forms at conditions within the *blueschist facies*, a facies characterized by high pressure and relatively low temperature. Blueschist chemistry is variable. Compositions range from pelitic to mafic. No matter their compositions, they contain conspicuous mineralogy.

A blue amphibole, called *glaucophane*, is responsible for the name of the facies. The blueschist seen below in Figure 8.78 is mostly glaucophane. Other common blueschist minerals include a colorless to green Na-pyroxene called *jadeite*, green or white lawsonite, and pale aragonite (the high-pressure polymorph of calcite). Epidote, garnet, zoisite, quartz, and other accessory minerals may also be present. Because they form at low temperature, blueschists are often fine grained, poorly crystallized, and difficult to study.

Eclogites, such as the one seen below in Figure 8.79, are mafic rocks metamorphosed at high pressure and moderate-to-high temperature. They contain the essential minerals pyrope (Mg-rich garnet) and the green Na-rich clinopyroxene called *omphacite*. Orthopyroxene may also be present in significant quantities. Accessory minerals include kyanite, quartz, spinel, titanite, and many others. Eclogites originate in the deep crust or in the mantle. Many mantle xenoliths, carried up as nodules within magma, are eclogites. Eclogites are also found as layers or bands associated with some peridotites. Quite commonly, eclogites undergo retrograde metamorphism and so become partially changed into blueschists.

8.78 Blueschist from Marin County, California. 4.7 cm across.

8.79 Eclogite from Almenning, Norway. About 7.5 cm across.

The photos below show some additional examples of high-pressure minerals. The light-colored crystals in Figure 8.80 are *lawsonite*. Lawsonite has about the same composition as anorthite. But plagioclase (including anorthite and albite components) becomes unstable at high pressure, so the anorthite part hydrates and we get lawsonite instead. The green *jadeite*, in Figure 8.81, is an Na-rich pyroxene that is only stable at high pressure. It forms because the albite component in plagioclase changes by solid-solid reaction into Na-pyroxene. *Glaucophane,* the inky blue mineral in the lower left photo (Figure 8.82) is an Na-rich amphibole. Like omphacite, it incorporates its sodium component from albite. In this specimen, a silvery and greenish chrome mica, *fuchsite*, accompanies the glaucophane. The green omphacite in the lower right photo (Figure 8.83) is a pyroxene that includes a few high-pressure components. And the pyrope (red garnet) in the same sample formed by solid-solid reactions involving pyroxenes.

8.80 Lawsonite crystals from Marin County, California. The specimen is 5.5 cm across

8.81 Emerald green jadeite from Myanmar

8.82 Glaucophane with fuchsite from Brittany, France. The specimen is 6.5 cm across

8.83 Green omphacite and red pyrope from Nordfjord, Norway. The specimen is 10 cm across

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8.59 Actinolite, Wisconsin Geological Survey
8.60 Grunerite, geology.today
8.61 Greenalite, erocks.com
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9 Ore Deposits and Economic Minerals

9.1 Golden pyrite with silvery hematite from Elba Island, Italy. The specimen is 12 cm wide.

9 Ore Deposits and Economic Minerals

KEY CONCEPTS

- We mine many minerals from Earth.
- Some ores are valued for their mineral properties, some for the elements they contain, and others because they contain valuable gems.
- The best ore deposits are those containing large amounts of ore minerals.
- The best metal ore minerals are those that contain large

amounts of metals of value.
- Most metallic ore minerals are native elements, sulfides, sulfosalts, oxides, or hydroxides.
- Ore deposits are highly variable in nature and origin.
- The most important kinds of ore deposits are magmatic, hydrothermal, or sedimentary.

9.1 Mineral Commodities

9.1.1 Mineral Resources

Earth gives us many mineralogical resources, also called *mineral commodities*. Fewer than a dozen minerals and eight or nine elements dominate the crust – we use most of them in our daily lives. Other elements and minerals that exist only in small amounts and have uneven distributions, are equally vital. We mine some ores because they contain elements that have the metallic properties of conductivity, strength, or shiny appearance. We mine industrial minerals such as halite, gypsum, clays, calcite, asbestos, micas, and zeolites to make salt, plaster, ceramics, construction materials, electronic components, chemical filters, and many other things. We also quarry large quantities of limestone (to make cement) and building stone, and energy companies produce large amounts of coal, oil, gas, uranium and other energy resources.

9.2 The Diavik Diamond Mine in the Northwest Territories, Canada

We mine diamond and other potential gem minerals for jewelry and also for use in industry. The photo in Figure 9.2 shows the Diavik Diamond Mine in remote Canada. This mine has produced about 10 million carats of rough diamond since it began operations in 2003. When we think of diamonds, we generally think of gems, but gem diamonds are rare. Most natural diamonds, called *industrial diamonds*, have little gem quality. Because of diamond’s great hardness, industrial diamonds have many important uses. Most commonly they are used as an abrasive or polishing agent. But they are also incorporated into grinding wheels, saw blades, and drill bits used to manufacture products from very hard materials. Thus, diamonds and many other mineral commodities are used in many different ways.

Ore deposits and ore minerals fall into several main commodity groups: metallic and semimetallic elements, nonmetallic elements, gems, construction and manufacturing materials, fertilizer and chemical minerals, and energy resources (table below). We take energy resources and construction materials from Earth in the greatest quantities. We also mine large amounts of salt and fertilizer components. Of the metals, only iron is removed from Earth at rates comparable to these components.

Groups of Mineral Commodities	
group	**examples**
metallic and semimetallic elements	gold, silver, copper, iron, manganese, aluminum
nonmetallic elements	potassium, sodium, phosphorous, sulfur
gems	diamond, sapphire, agate
industrial materials: construction and manufacturing	sand, clay, building stone, diatomite, talc, mica, zeolites

industrial materials: fertilizer and chemicals	limestone, phosphate, potash, salt, nitrate, fluorite
energy resources	coal, oil, gas, uranium

Many different mineral commodities are important to modern society. However, when mineralogists think about mining, they are generally thinking of ore minerals that are the sources of important metals, or of minerals that have specific, highly valued properties (*e.g.*, asbestos, micas, potash, and gems of all sorts). That is what we will focus on in most of the rest of this chapter.

9.1.2 The History of Mining

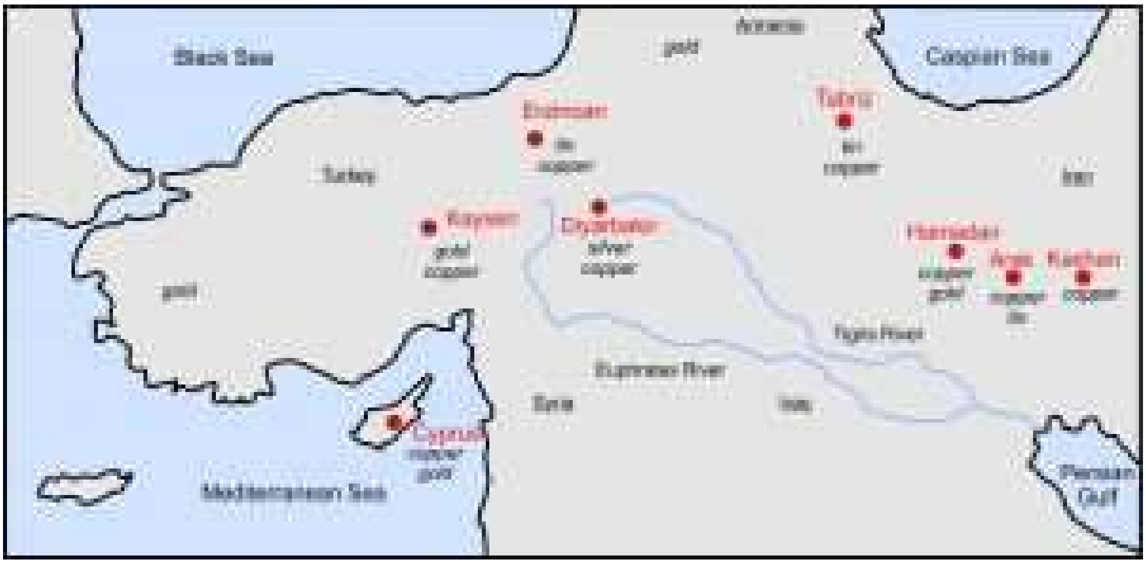
Mining is nothing new. People have practiced mining and quarrying since ancient times. The first mineral known to be mined was flint, a fine-grained variety of quartz used to make weapons. Early peoples mined other things, such as ochre, for use as pigment in art and religious ceremonies. Archaeologists and anthropologists define major periods of human civilization based on resources used. There is a great deal of overlap and different regions moved from one period to another at different times.

9.3 Chalcolithic Age artifacts from a cave at Nahal Mishmar, near the Dead Sea, Israel

The late *Stone Age*, also called the *Neolithic Age*, was followed by the *Chalcolithic Age* from 4,500 to 3,500 BCE (Before Common Era). During the Chalcolithic Age, humans began using copper (the name *chalcolithic* is derived from the Greek word *khalkos* for copper) for both decorative and utilitarian purposes. One of the largest collections of chalcolithic artifacts was discovered in a cave in Israel's Judean Desert in 1961 (Figure 9.3). Because copper could be found as malleable pure copper nuggets, people could shape it with available stone tools – a property that no other common minerals possessed. A rise in consumption of copper coincided with the development of a socioeconomic hierarchy, and the wealthy citizens possessed more copper than the proletariat.

9.4 Axe heads and other Bronze Age artifacts

Figure 9.4 shows artifacts from the Bronze Age, the age that followed the Chalcolithic Age and lasted from about 4,200 to 1,000 BCE. Use of bronze first developed in the Mesopotamian civilization of Sumeria and became common in other places later. This was a period characterized by a rapid rise of resource consumption and increasing diversification of products made by metalworking. Perhaps the most significant advancement in metal use was the discovery of how to make bronze, an alloy created by melting and combining the metals copper and tin. Although tin melts at a relatively low temperature (232 °C), copper melts at 1,983 °C, a temperature too great to be easily achieved at the time. However, clever metal workers discovered that a mix of one part tin and three parts copper melts at 1,675 °C, which was low enough to make bronze manufacturing possible in many places.



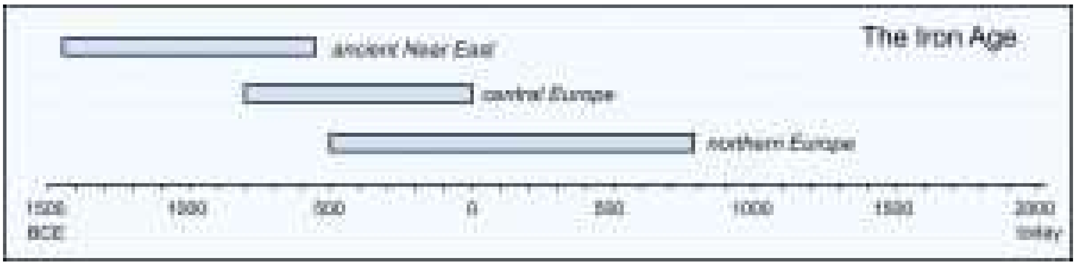
9.5 Sites of resource extraction in the Bronze Age

9.6 The Skiriotissa Copper Mine in Cyprus

The map in Figure 9.5 shows the location of Bronze Age mines that provided metals used throughout much of the Middle East. Most of the copper came from the Troodos Mountains of Cyprus, where copper could be found in loose sediments at Earth’s surface. Even today, a great deal of copper mining takes place in Cyprus, although most operations have moved underground. Figure 9.6 shows the Skiriotissa Mine, which was the site of

Bronze Age mining and is an active mine today. Although some copper and other metals came from mines on Cyprus and on the Asian mainland, tin deposits were generally small or hard to produce. The scarcity of tin in the Middle East and other areas of the Mediterranean region, meant that tin ores came from as far away as the British Isles, which the Greeks named the *Cassiterides*, that translates to *Tin Islands*.

A key property that allowed humans to work with bronze is that, after pouring the molten bronze into stone molds and allowing the liquid to cool to a solid, the copper-tin alloy could be formed and shaped using hammers at room temperature, a process called *cold working*. And, because bronze is much stronger than copper, people could make many improved products, including knives, shields and swords, and tools that led to more productive agriculture.



9.7 Time of the Iron Age in different places

The *Iron Age* followed the Bronze Age beginning around 1500 BCE, when the Hittite society of ancient Anatolia (modern day Turkey) discovered how to process iron. Their technological breakthrough was to add a small amount of charcoal (carbon) to rocks that contained iron. Pure iron melts at 1,538 °C, but adding carbon results in a carbon-iron mixture that melts at 1170 °C. The Hittites also figured out that iron-carbon alloys could not be cold-worked like bronze but had to be hammered and shaped while hot. Thus, they invented the art of modern blacksmithing. The iron and alloys produced, once cooled, were much stronger and harder than bronze was. After the time of the Hittites, it took another 500 to 1,000 years for the iron age to reach central and northern Europe (Figure 9.7).

The source of iron used by the Hittites was metallic meteorites. Meteorites also contained a small amount of nickel that improved metal properties. Because iron-rich meteorites were not in abundance, the Hittites carefully guarded their invention of iron metal working for several centuries. During those centuries, the Hittites exercised military superiority over much of the Middle East and Egypt, where the weaker bronze was used in battle. However, by 1200 BCE, iron metal working technology had spread across the Middle East, North Africa, Europe, and to Asia; people discovered new sources of iron; and the Hittite empire disappeared.

9.8 Georgius Agricola

Egyptians mined native metals, including gold, silver, and copper, from stream beds as early as 3700 to 3000 BCE. Around 2600 BCE they began to quarry stone to build the Great Pyramids. By the Middle Ages, mining was common in Europe. Georgius Agricola (Figure 9.8), a German physician, wrote the first widely read book about mining, *De re metallica*, published in 1556. Agricola's work is said by some to represent the beginning of the science of mineralogy.

Mineral resources literally put places on the map of the ancient world. If a region contained abundant amounts of copper, silver, tin, or gold, and later iron, it soon became populated and prosperous. Civilizations established trade routes and developed commercial systems, shipping commodities over increasingly longer distances. If resource supplies became depleted in one location, people sought new sources. Thus, exploration was needed to sustain production and consumption of valuable resources. These same dynamics operate today: when new mineral deposits are discovered, new communities and industries may appear. When old deposits become depleted, communities and industries wane. And, always, mining companies are exploring to find new sources of economically viable minerals.

Copper, tin, iron, and nickel were all important during the early ages of humans, and they are equally important today. Those same metals – and many others – are key parts of a seemingly infinite number of products. For example, Figure 9.9 (below) shows the many minerals that provide elements that are in a smart phone. Copper makes up about 10% of the weight of a smartphone, and that copper is the key to moving around the electricity that powers the phone. Tin is used to make the liquid crystal display (LCD) screen and to solder electrical connections that transmit digital information. Iron is combined with the metals neodymium and boron to make magnets that are part of the microphone and speaker. And those are not the only elements in a smartphone; there are about 75 elements in all. Without any one of these elements, smartphones would not exist as they do. Nearly everything that we manufacture contains mineral resources, and the sources for these resources are mineral deposits.

Display

A mobile device's glass screen is very durable because glassmakers combine its main ingredient, **silica** (silicon dioxide or quartz) **sand**, with ceramic materials and then add potassium.

Layers of indium-tin-oxide are used to create transparent circuits in the display. Tin is also the ingredient in circuit board solder, and **cassiterite** is a primary source of tin.

Gallium provides light emitting diode (LED) backlighting. **Bauxite** is the primary source of this commodity.

Sphalerite is the source of indium (used in the screen's conductive coating) and germanium (used in displays and LEDs).

Electronics and Circuitry

The content of copper in a mobile device far exceeds the amount of any other metal. Copper conducts electricity and heat and comes from the source mineral **chalcopyrite**.

Tetrahedrite is a primary source of silver. Silver-based inks on composite boards create electrical pathways through a device.

Silicon, very abundant in the Earth's crust, is produced from the source mineral quartz and is the basis of integrated circuits.

Arsenopyrite is a source of arsenic, which is used in radio frequency and power amplifiers.

Tantalum, from the source mineral **tantalite**, is added to capacitors to regulate voltage and improve the audio quality of a device.

Wolframite is a source of tungsten, which acts as a heat sink and provides the mass for mobile phone vibration.

Battery

Spodumene and subsurface brines are the sources of lithium used in cathodes of lithium-ion batteries.

Graphite is used for the anodes of lithium-ion batteries because of its electrical and thermal conductivity.

Speakers and Vibration

Bastnaesite is a source of rare-earth elements used to produce magnets in speakers, microphones, and vibration motors.

Banner image courtesy of freevector-archive.com

9.9 Minerals that go into a smartphone

9.1.3 Mineral Deposits, Ore Deposits, and Mining

A *mineral deposit* is a place in Earth's crust where geologic processes have concentrated one or more minerals at greater abundance than in the average crust. An *ore deposit* is a mineral deposit that can be produced to make a profit. Thus, all ore deposits are mineral deposits, but the reverse is not true.

Many factors control the profitability of an ore deposit. We call the amount of known ore in a deposit the *reserves*. The concentration of a commodity in the ore (the "richness" of the ore) determines the *ore grade*. When calculating the profitability, amount of reserves and ore grade are the most significant geological factors, although economic factors such as extraction costs, processing costs, and market price are often more decisive. A high-grade ore deposit may be uneconomical to mine if the reserves are low, because start-up costs could consume all profits. A large high-grade deposit may be uneconomical to mine if it is in a remote area. Even large, developed deposits can become uneconomical if the market price falls, perhaps due to the discovery of a better deposit somewhere else.

9.10 The Bingham Canyon Mine, with Salt Lake City in the background

Mining operations have many guises. Surface mining involves uncovering resources by removing overburden. This is done in several ways but, for metal deposits, open pit mining is most common. The Bingham Canyon Mine (Figure 9.10, above), near Salt Lake City, is the world’s deepest open pit. It is 4.5 km by 1.3 km in area and is 1.2 km deep. Since mining began just over 100 years ago, the Bingham Canyon open-pit mine has produced 24 million tons of copper, 790 tons of gold, 6,600 tons of silver, and 425,000 tons of molybdenum. To put these numbers in perspective, consider that, in total, the people of the world consume about 30 million tons of newly mined copper, 2,750 tons of newly mined gold, 30,000 tons of newly mined silver, and 250,000 tons newly mined molybdenum *every year*.

So, the cumulative amounts of copper, gold, silver and molybdenum mined from Bingham Canyon over an entire century are insufficient to satisfy peoples' needs for even one year. Thus, to maintain our societies and lifestyles, without recycling metals, the world's people need many mines like the one at Bingham Canyon.

9.11 Site of the Mponeng Gold Mine, South Africa

When open pit mining cannot get to valuable resources, mining may move underground. Underground mining involves digging tunnels and shafts to reach buried ore bodies. This takes on many forms depending on the nature of an ore deposit. The Mponeng Gold Mine (Figure 9.11), southwest of Johannesburg, South Africa, is the deepest mine in the world. Its deepest workings are more than 3.5 km below Earth's surface. Figure 9.11 shows the mine buildings on the surface; the tall towers are head frames where lifts descend to depth where the actual mining takes place.

9.12 Asbestos mine tailings at

the Thetford Mines, Quebec

After mining, processing separates and concentrates valuable minerals from the ore. This involves crushing the ore rock, followed by gravity and chemical separation. Any unwanted rock and minerals, called *waste rock* and *gangue*, respectively, are usually discarded in tailings piles. This photo (Figure 9.12) shows tailings at a mine just south of Quebec City, Quebec. Besides piling discarded material on the surface, sometimes miners return wastes to abandoned portions of a mine to fill voids left by ore removal.

9.13 Acid mine drainage flowing from a collapsed mine adit near Joggins, Nova Scotia

Mining commonly comes with some significant environmental costs because disposal of mine waste can lead to significant problems. And, abandoned mines also pose environmental problems. Runoff from waste piles or mine sites may create soil, groundwater, or surface water contamination. Many ore bodies, for example, are rich in sulfide minerals. After mining ceases, sulfur from the minerals can react with water and air to create acid mine drainage (Figure 9.13) or acid runoff from tailings piles. The resulting sulfuric acid may kill vegetation and fish in nearby lakes and streams. Contamination may also occur because of non-natural chemicals used during mineral production. And, there may be terrain costs. After mining ceases it is often impossible to restore the mined land to anything like its pre-mining condition. Open pits remain forever and so do tailings piles. Mining sometimes also leads to increased erosion or the formation of sinkholes.

9.14 Reclaimed coal mine land near Cannock Chase, central England

Most mining companies are responsible and do their best to reduce impacts while mining takes place, but eliminating them all is impossible. And, many mining companies do a good job of cleaning up after they are done. The photo seen in Figure 9.14 shows a site near Cannock Chase, England, that was once a coal mine. The area was restored and is now used for picnicking, walking and cycling. The United States, like many other countries, has enacted laws to limit the damage caused by mining. These laws, however, are often controversial because they may drive up the price of mined commodities. Communities that rely on mining for employment, in particular, worry that regulations may lead eventually to loss of jobs.

● Box 9-1 Mining, the Environment, and Politics

9.15 Gold mining on public land in 1898

Mining, especially public land mining, is sometimes a controversial environmental issue. For example, the 1872 Mining Law gives U.S. citizens and corporations the right to stake claims and mine public lands if they can show that the mining is profitable. The claims last forever, provided miners invest $100 in the property each year. Claim holders have the right to purchase the surface and mineral rights at very low cost through a process called patenting, often at $5 an acre or less. Miners pay no royalties, in contrast with those who develop coal, oil, or gas on public lands. In 1999, mining corporations took more than $1 billion worth of minerals from public lands without paying anything back to taxpayers. So, the 1872 law is a federal subsidy for mining.

Many environmental groups want to see Congress change the 1872 law. They argue that public lands are for the public, not mining corporations, and they point out that mining is incompatible with other uses such as wildlife habitat, hiking, and camping. Furthermore, mining leaves scars on the land and may cause long-term environmental degradation. According to a 1998 article in the journal *Environmental Law*, “there are over 550,000 abandoned hard-rock mines, most of which have been left for government-funded clean-up efforts at an estimated cost of $32 to $72 billion.”

The mining industry argues that we need the 1872 law to ensure a flow of mineral resources to our citizens. They point out the importance of mining to some local western economies and say they can mine in an environmentally friendly way. They also accuse many mining opponents of having a “NIMBY” (not in my backyard) mentality.

The mining industry is correct when they argue that we need mineral resources and they have to come from somewhere. Despite industry’s claims, however, mining always has a cost to the environment. A visit to active or abandoned mines confirms this. Besides scars on the land, less obvious problems include air, water, and soil pollution. All these problems can be limited, but not eliminated, by following the best mining practices.

In today’s industrial world we need mineral resources. The real questions are where are they going to come from and how much are we willing to pay? Those who seek reform of the 1872 law argue that some areas should be off limits to mining, that mining companies should pay more in royalties, and that there should be strict antipollution and land reclamation requirements. If enacted by Congress, these changes might affect the price of mineral commodities, but most economists think the effect would be very small.

9.1.4 Natural Abundances of Elements

Oxygen, silicon, aluminum, iron, calcium, sodium, potassium, magnesium, and titanium make up 99% of Earth’s crust. We saw a histogram of this distribution in Figure 2.2 (Chapter 2). It is no wonder, then, that humans have developed ways to use these elements in industry, agriculture, and manufacturing. Less abundant elements have also become important to modern society. These include metals, radioactive elements such as uranium or thorium, and fertilizer components including, most importantly, nitrogen and phosphorous. As shown in the table below, some important elements make up very small percentages of Earth’s crust; nevertheless, natural processes concentrate them in particular minerals and in particular places.

Natural Abundance, Economical Ore Grade, and Concentration Factors for Some Metals			
ore resource	**metal concentration in average crustal rock**	**minimum ore grade for profitable extraction**	**economical concentration factor**
aluminum	8.2 wt%	30 wt%	4
iron	5.6 wt%	20 wt%	4
sodium	2.4 wt%	40 wt%	17
manganese	0.09 wt%	35 wt%	370
chromium	0.01 wt%	30 wt%	2,940
nickel	0.008 wt%	0.5 wt%	60
zinc	0.007 wt%	4.0 wt%	570
lead	0.001 wt%	4.0 wt%	2,900
copper	0.006 wt%	0.5 wt%	80
tin	0.0002 wt%	0.5 wt%	2,500

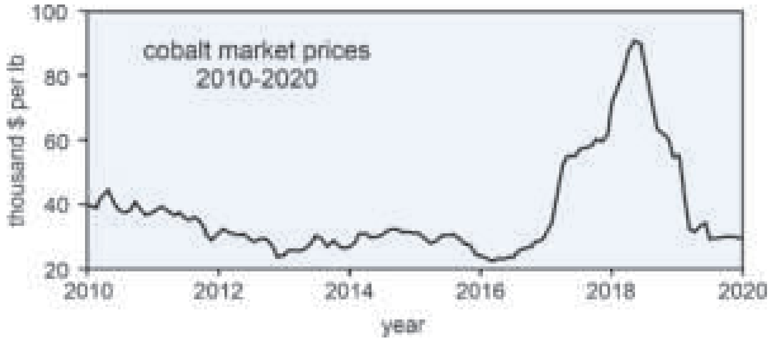
The economical concentration factor listed in the table above is the ratio of typical minimum economical ore concentration to average crustal concentration. For example, the average crustal abundance of chromium is about 0.01 wt %. Chromium ore can sometimes be profitable if it contains 30 wt % chromium. The necessary concentration factor is therefore nearly 3,000 – chromium must be concentrated at least 3,000 times to create profitable ore. The table compares economical concentration factors for a dozen different metals. They are ordered from those most abundant (top) to those that are rare (bottom). Concentration factors range from 4 for aluminum and iron, to nearly 3,000 for tin, chromium and lead.

Elements that occur in high abundance do not need a high concentration factor to make mining economical. In contrast, less common chromium, lead, tin, and zinc require great concentrations to be profitably mined (see the table above). We mine relatively common elements, such as iron and aluminum, in many places worldwide; we mine rarer elements, including tin, chromium, or lead, in far fewer places.

9.16 Gold flakes associated with a hydrothermal vein in gray quartz, Nalunaq, Greenland. The field of view is 1.9 cm across.

Although the table does not include prices, there is a correlation between the economical ore grades and the price of a given resource. Gold, for example, is much more expensive than the metals listed, although the demand for gold is less than for the others. This price difference exists because the natural processes that concentrate most commonly used metals are much more common than the processes that concentrate gold, so there are fewer high-quality gold deposits than there are other kinds of deposits. Many gold mines can remain profitable even if the ore contains less than 0.1 ounces of gold in a ton of rock. Figure 9.16 shows an example of gold ore from Greenland. The gold flakes are small – the entire photo is less than 2 cm across.

The market for metals can be extremely volatile. Geopolitics, wars, economic sanctions, and other things may cause major market disruptions. But, trends in technology may, over the long run, be even more significant. For example, beginning about 5 years ago, many predicted that the demand for electric vehicles (EV) was going to skyrocket. A growing EV industry means that demand for lithium-ion batteries will increase. So, in 2016, the average market price for lithium began rising and doubled in two years.



9.17 Cobalt market prices

But, lithium-ion batteries also include other key metals besides lithium, for example cobalt. Between 2016 and 2018, cobalt prices increased from just over $20,000 to $95,000 per tonne (Figure 9.17). But, since spring of 2018, prices have collapsed as cobalt lost 75% of it value. Why did this happen? Several things are undoubtably important. Perhaps most significant is that the projected increase in EV sales and demand for lithium-ion batteries did not occur as rapidly as predicted. Additionally, when things looked good, the world’s major cobalt mines, most of which are in the Democratic Republic of the Congo, greatly increased production. At the same time, smaller independent operators started new mines.

So now we have a market surfeit of cobalt, and prices are about the lowest they have been in a decade. Still, market prognosticators say that with the inevitable increase in demand for EVs, and for rechargeable batteries in general, prices for cobalt, nickel and graphite, and other key components of lithium-iron batteries can be expected to increase soon.

9.1.5 Worldwide Distribution

Geological processes that concentrate minerals are not unusual. But, the processes that create economically productive ore deposits are rare. If they were not, market prices would fall, decreasing profits and putting some mines out of business. The largest and most easily produced mines control market prices. Old mines shut down and new mines open up when new discoveries are made. Today, however, new discoveries are generally smaller than in the past because the largest deposits, which are more easily found than smaller deposits, have already been developed.

9.18 The Climax Mine near Leadville, 130 km southwest of Denver, Colorado

Because the geology of Earth varies, the distribution of ore deposits around the globe is uneven, and the minerals industry flourishes in some places and not in others. Some regions of the world contain most of the supply of certain commodities; this can affect international politics. For example, the United States controls about half the world’s molybdenum. Figure 9.18 shows the Climax Mine in Colorado. This mine has historically been the largest producer of molybdenum in the world. Production started in 1915, but the mine temporarily shut down between 1995 and 2012 due to low molybdenum prices. Nonetheless, the US has sufficient supply of molybdenum.

Unfortunately, many other important minerals are not produced in the United States. We call these minerals *critical minerals*, or *strategic minerals* (See Box 9-2). Additionally, we import many mineral commodities, that we might produce ourselves, because it would cost too much to mine them in our own country; tungsten is a good example.

Australia produces about a quarter of the world's aluminum, and Zaire half the cobalt. China accounts for 95% of all rare earth production, although significant reserves are found in other countries. South Africa, a country rich in mineral commodities, controls 90% of the world's platinum, half the world's gold, and 75% of the chromium. Much of the world's tin comes from Bolivia and Brazil.

9.19 Outcrop of metamorphosed basalt in the Barberton Greenstone Belt, South Africa

9.20 Pillow basalts in the Temagami Greenstone Belt near Sudbury, Ontario. The largest pillow structure is about 65 cm in long dimension.

9.21 Outcrops in the Kilimafedha greenstone belt, Tanzania

South Africa is, arguably, the number one mining country in the world. Most South African ore deposits are associated with regions called *Precambrian greenstone belts*, ancient volcanic terranes. Similar greenstone belts in Canada account for many of North America's metallic ore deposits. Figures 9.19, 9.20, and 9.21, above show rocks of greenstone belts in Africa, Canada, and Tanzania. Various other types of geological terranes are associated with ore deposits, too. Most economical metal and semimetal deposits are found near margins of continents, or the former margins of continents, where mountain building and igneous activity have occurred. Still, other types of deposits are found in continental interiors.

● Box 9-2 Strategic Minerals and Metals

We use many different minerals and metals to maintain our lifestyles and provide military security. Some of these commodities are not found or produced in the United States in sufficient quantities to meet demand. Consequently, we must import them from other nations. And sometimes supplies are problematic. During the Cold War, for example, the former Soviet Union and its allies stopped exporting minerals commodities to the Untied States. At various times since then the United States has stopped importations from Cuba, Iran, Iraq, Libya, and North Korea. So, sources of strategic metals are controlled by politics as well as geology.

Consider the push to expand the use of electric vehicles (EVs). The Netherlands, United Kingdom, France and some other countries have announced ambitious plans to completely eliminate gasoline and diesel vehicles. China is moving in that direction as well. But EVs need batteries and, although battery technology continues to evolve, lithium and cobalt are key components. Only eight countries produce lithium, and most of it comes from only three countries. Cobalt supplies are even more limited. The Democratic Republic of the Congo produces just about all of the world's cobalt. Batteries also require rare earth elements (REEs), and China controls the market – accounting for 95% of total REE production. The last functioning rare earth mine in North America closed for financial reasons in 2015 (Figure 9.22, below). Thus, the United States is heavily reliant on just a few countries if we are to expand electric vehicle technology and keep up with the rest of the world.

9.22 The Mountain Pass rare earth mine near Las Vegas, Nevada

Further complicating the picture is that the United States is both an importer and an exporter of some key metals and minerals. Today, the US relies entirely on imports for the following important element and mineral commodities:

arsenic, asbestos, cesium, fluorite, gallium, graphite, muscovite, niobium, rare earth elements, rubidium, scandium, strontium, tantalum, thorium

The United States is partially reliant on imports to meet needs for these element and mineral commodities:

aluminum, antimony, barite, beryllium, bismuth, chromium, cobalt, copper, diamonds, germanium, hafnium, indium, lithium, magnesium, manganese, nickel, platinum group metals, potash, rhenium, silver, tellurium, tin, tungsten, uranium, vanadium, zirconium

The United States is a net exporter of:

boron, clays, diatomite, gold, helium, iron, kyanite, molybdenum, selenium, titanium, trona, wollastonite, zeolites

9.2 Ore Minerals

Some Common Ore Minerals		
metal	**mineral**	**formula**

Al	gibbsite boehmite diaspore	$Al(OH)_3$ $AlO(OH)$ $AlO(OH)$
Fe	magnetite hematite goethite siderite pyrite	Fe_3O_4 Fe_2O_3 $FeO(OH)$ $FeCO_3$ FeS_2
Cu	copper chalcopyrite bornite chalcocite covellite	Cu $CuFeS_2$ Cu_5FeS_4 Cu_2S CuS
Ni	pentlandite garnierite	$(Ni,Fe)_9S_8$ $(Ni,Mg)_3Si_2O_5(OH)_4$
Zn	sphalerite wurtzite zincite franklinite	ZnS ZnS ZnO $ZnFe_2O_4$
Mn	hausmannite polianite pyrolusite cassiterite	Mn_3O_4 MnO_2 MnO_2 SnO_2
Cr	chromite	$FeCr_2O_4$
Pb	galena cerussite	PbS $PbCO_3$
Ag	gold calaverite	Au $AuTe_2$

Ores and ore minerals vary greatly in quality. Ideal ores contain 100% ore minerals. Such ores do not exist, but some come close. Ideal *ore minerals* contain 100% of the commodity of interest. Native copper, for example, is an ideal copper ore mineral. Ideal ore minerals are, however, uncommon. The most commonly mined ores are not ideal. Instead they are rich in ore minerals that can be processed relatively inexpensively to isolate desired components.

The table seen here lists common ore minerals for various metals. The minerals include the native metals copper and gold, and many sulfides, oxides, and hydroxides. Minerals in these groups are generally good ore minerals because they contain relatively large amounts of the desired elements. Furthermore, processing and element extraction are usually straightforward and relatively inexpensive. That is why we mine Cu and Cu-Fe sulfides for their copper content and iron oxides for their iron content.

Silicate minerals, although common, are generally poor ore minerals and are not included in the table. For example, although aluminum is found in many common silicates, tight bonding makes producing metallic aluminum from silicates uneconomical. We obtain most aluminum from Al-hydroxides found in bauxite deposits.

We discussed igneous and sedimentary minerals in previous chapters. In the following section, we focus on economic minerals that belong to other groups.

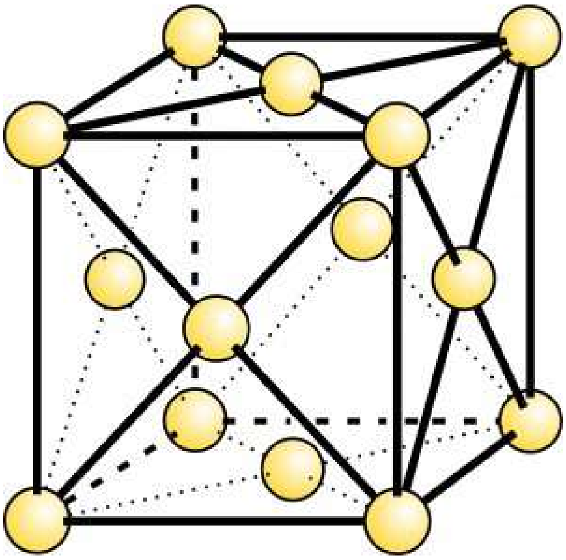
9.2.1 Native Elements: Metals, Semimetals, and Nonmetals

Native Metals	
gold	Au
silver	Ag
copper	Cu
platinum	Pt
Native Semimetals	

arsenic	As
antimony	Sb
bismuth	Bi
Native Nonmetals	
graphite	C
diamond	C
sulfur	S

Native elements have high value because they may require no processing before being used in manufacturing, as currency, or for other purposes. The first metals ever used by humans were native minerals. Only later did humans develop refining techniques for the extraction of elements from more complex minerals. We conveniently divide native elements into metals, semimetals, and nonmetals based on their chemical and physical properties. The table to the right includes the most common minerals of each group.

Within the metal group, the principal native minerals are gold, silver, copper, and platinum. These four minerals all contain weak metallic bonds. Gold, silver, and copper have further commonality in their chemical properties because they are in the same column of the periodic table. Gold and silver form a complete solid solution; we call compositions containing both gold and silver *electrum*. But, because copper atoms are smaller than gold and silver atoms, solutions are limited between copper and the precious metals. Native gold, silver, and copper may contain small amounts of other elements. For example, native copper frequently contains arsenic, antimony, bismuth, iron, or mercury. Native platinum is much rarer than gold, silver, or copper. It typically contains small amounts of other elements, especially palladium. The native semimetals arsenic, antimony, and bismuth are also rare.



9.23 The arrangement of atoms in some native metals

Native copper, gold, silver, and platinum have atomic structures with atoms arranged in a cubic pattern (Figure 9.23). Iron does, too, although native iron is rare, except in meteorites, and the atomic arrangement in native iron is not quite the same as in the other metals. Nonetheless, euhedral crystals of any of these minerals may be cubic or, as we will explain in the next chapter, octahedral. More typically, however, these minerals crystallize in less regular shapes. Native zinc, a very rare mineral, has a hexagonal atomic arrangement and so forms crystals of different shapes. The photos below (Figures 9.24 through 9.29) show examples of native gold, silver, copper, platinum, antimony, and sulfur.

Gold, sometimes mined as nuggets or flakes (see the example in Figure 9.17), is also found as wires or scales. Large, visible specimens, like the one seen below in Figure 9.24 are, however, unusual. Most gold and other precious metal ores contain very fine subhedral metal grains, often microscopic. Silver sometimes occurs in a wire-like or *arborescent* (tree-like) form (Figure 9.25). It also easily tarnishes and so has a gray color in this photo. Most bedrock gold and silver deposits are in quartz-rich hydrothermal veins. Pyrite (*fool's gold*) and other sulfides are often associated with native gold and silver in these veins. Besides hard-rock deposits, gold and silver are also found in *placers* (accumulations in river, stream, or other kinds of sediments), and native silver is found in several other types of deposits. Box 9-3 (below) describes the Witwatersrand gold deposits, the largest gold deposits in the world. Section 9.3.3.1, later in this chapter, gives more detailed information about placers.

 9.24 Native gold on quartz from the Sierra Nevada foothills. The sample is 4 cm tall.	 9.25 Native silver with calcite, Valenciana Mine, Mexico	 9.26 Native copper with malachite from near White Pine, Michigan
 9.27 Placer platinum nuggets from southern British Columbia. The largest are about 2 mm across.	 9.28 Native antimony with quartz from southern Germany	 9.29 Native sulfur from Sicily

Native copper occurs in a variety of ore deposits associated with mafic volcanics and in some sandstones. Copper is found as branching sheets, plates, and wires, and as massive pieces. In Figure 9.26, it is in a discontinuous sheet that has partially altered to malachite, copper carbonate. We mine native platinum primarily from ultramafic igneous rocks, but platinum is also found in placers – Figure 9.27 shows examples placer platinum nuggets. Platinum is also a secondary product of Cu- or Ni-sulfide refining. Native antimony (in Figure 9.28), is rarely pure. It is usually in solution with arsenic and may contain small amounts of other metals. Untarnished specimens are metallic and silvery, but antimony typically tarnishes to a gray color as seen in this photo.

Graphite, diamond, and sulfur are examples of nonmetallic native elements. Figure 9.29 shows an example of native sulfur. Figure 3.49 (Chapter 3) contains another photo. Sulfur deposits are associated with volcanoes, often concentrated at fumaroles. Sulfur is also found in veins in some sulfide deposits and in sedimentary rocks where it is found with halite, anhydrite, gypsum, or calcite. Native sulfur deposits only account for about half the world’s sulfur supply. Most of the rest is separated from sulfides during processing to recover metals.

Both graphite and diamond consist only of carbon. We discussed the nature of the two minerals in Box 3-3 of (Chapter 3). Graphite is common as a minor mineral in many kinds of metamorphic rocks, including marbles, schists, and gneisses. The origin of the carbon is usually organic material in the original sediments. Graphite also occurs in some types of igneous rocks and in meteorites. Diamond only forms at very high pressures associated with the lowermost crust or mantle of Earth. We mine it from kimberlite pipes, where rapidly moving, sometimes explosive, mafic magmas have carried it up to the surface. After formation, diamond sometimes concentrates in river and streambeds where we mine it from placer deposits. Although some diamonds are of gem quality, most are not. We call lower-quality diamonds *industrial diamonds* or *bort* (if the diamonds are small and opaque). See section 9.2.4, later in this chapter, for more information about diamonds and other gems.

● Box 9-3 The Witwatersrand Gold Deposits

9.30 Very high-grade Witwatersrand gold ore

Gold occurs in many different ore deposits. The world’s largest, the Witwatersrand deposit of northeastern South Africa, dominates world production. 40% of all the gold ever mined came from Witwatersrand ores. Figure 9.30 shows an example of very high-grade ore from the Blyvooruitzicht Gold Mine of that region. The yellow grains are gold, and the black material is uraninite. This ore, like many Witswatersrand ores, is quite radioactive.

The Witwatersrand deposits are paleoplacer deposits, meaning that they were placers when originally deposited. They occur in an area about 100 km by 40 km. The origin of the Witwatersrand deposits is a bit of a mystery. Placers form when hard-rock deposits are eroded, and sedimentary processes concentrate ore. Yet today we know of no hard-rock gold deposits of sufficient size to account for the volume of the Witwatersrand placers.

The Witwatersrand gold prospects were discovered in 1852, but the discovery was kept secret. It was not until 1886 that significant production began. A booming mining industry led to the rapid growth of Johannesburg, a central town in frontier South Africa. Within a decade, Johannesburg was the largest city in the country. When miners reached a zone of pyrite in 1889, the mining slowed because it was not known how to extract gold from sulfides at the time. Subsequently, John MacArthur, Robert Forrest and William Forrest, three Scotsmen working for the Tennant Company in Glasgow, developed a dissolution process involving cyanide that would extract gold from sulfides. So, Johannesburg flourished once more.

9.2.2 Sulfides and Sulfosalts

Sulfide and Sulfosalt Ore Minerals	
sulfides	
pyrite	FeS_2
chalcopyrite	$CuFeS_2$
molybdenite	MoS_2
sphalerite	ZnS
galena	PbS
cinnabar	HgS
acanthite	Ag_2S
chalcocite	Cu_2S
bornite	Cu_5FeS_4
pyrrhotite	$Fe_{1-x}S$
millerite	NiS
pentlandite	$(Fe,Ni)_9S_8$
covellite	CuS
realgar	AsS
orpiment	As_2S_3
stibnite	Sb_2S_3
marcasite	FeS_2
Sulfosalts	
cobaltite	(Co,Fe)AsS
arsenopyrite	FeAsS
pyrargyrite	Ag_3SbS_3
tetrahedrite	$Cu_{12}Sb_4S_{13}$

enargite	Cu_3AsS_4

Metallic ore deposits contain many different sulfide and related ore minerals. Most are quite rare. The table seen here lists the more important species. Pyrite (iron sulfide) is most common. Other relatively common sulfides include chalcopyrite (copper iron sulfide), molybdenite (molybdenum sulfide), sphalerite (zinc sulfide), galena (lead sulfide), and cinnabar (mercury sulfide). The others in the table are less abundant but are occasionally concentrated in particular deposits.

Sulfide minerals (such as pyrite) contain one or several metallic elements and sulfur as the only nonmetallic element. Bonding is either covalent, metallic, or a combination of both. Other very uncommon minerals grouped with the sulfides (because of similar properties) contain selenium (the *selenides*), tellurium (the *tellurides*), or bismuth (the *bismuthides*) instead of sulfur. A related group of minerals, the *sulfosalts*, contains the semimetals arsenic and antimony in place of some metal atoms. Because many sulfides have similar atomic arrangements, solid solutions between them are common. The same holds true for the sulfosalts.

Primary sulfide minerals consist of sulfur and reduced metals. When exposed to oxygen rich-groundwaters, or to the atmosphere at Earth’s surface, they easily oxidize or break down in other ways. Oxidation can alter the original mineral’s color or texture. It can also create new minerals. So, iron-bearing sulfides may turn into iron oxide (magnetite or hematite), iron hydroxide (limonite or goethite), or iron carbonate (siderite). Galena (lead sulfide) may become cerussite (lead carbonate). Copper sulfides may become azurite or malachite (both hydrated copper carbonates).

Sulfide minerals often form in common associations. Pyrite, sphalerite, and pyrrhotite are frequently found together, as are chalcopyrite, pyrite, and bornite or pyrrhotite. In some carbonate-hosted deposits, sphalerite and galena occur together. We can depict sulfide associations using triangular composition diagrams. Box 9-4 (below) presents a detailed discussion of Cu-Fe-S ore minerals and explains how we use triangular diagrams to show solid solution compositions.

Unlike other mineral groups, especially the silicates, color is sometimes a good way to identify sulfide minerals. The reason is that transition metals often control color, and the color of sulfides is often due to the metals they contain. So, color is helpful. Sulfide minerals, however, show lots of variation in appearance, especially if they are tarnished. Space does not permit including photos of all the different sulfides, but some examples are below.

The most common gold and goldish sulfides are pyrite, chalcopyrite, and pyrrhotite (shown in Figures below). They can be very hard to tell apart. Pyrite, also called *fool's gold*, is seen in Figure 9.31. The specimen in the photo has pyrite's typical metallic golden color. Figures 3.2 and 3.42 (Chapter 3) show other views of golden pyrite. Chalcopyrite, in contrast with pyrite, contains copper and easily tarnishes – often to a yellow green color. The photo of chalcopyrite below (Figure 9.33) shows multiple colors due to tarnishing. Figures 3.22 and 3.43 (Chapter 3) also show tarnished chalcopyrite. Chalcopyrite is much softer than the other two minerals which also sometimes helps identification. Pyrrhotite, seen in Figure 9.32, is the only one of the three that is magnetic, and sometimes that can distinguish it from the others. Some pyrrhotite has a more silvery color than pyrite which helps identification.

9.31 Pyrite crystals from Huanzala, Peru

9.32 Pyrrhotite from eastern Russia

9.33 Tarnished chalcopyrite

Many sulfides have a gray color, sometimes with metallic luster. The photos below show examples of galena (Figure 9.34), molybdenite (Figure 9.35), and stibnite (Figure 9.36). The lusters of the samples in these photos are not particularly metallic, but many specimens of these minerals are. For example, Figure 3.21 (Chapter 3) shows a spectacular example of metallic stibnite, and Figure 3.40 (Chapter 3) shows a hexagonal flake of metallic molybdenite..

9.34 Galena cubes on top of chalcopyrite and dolomite from Joplin, Missouri

9.35 Molybdenite from the Swiss Alps

9.36 Stibnite from Xinhuang, China

The three photos below show copper minerals. Copper minerals are often characterized by strong colors. Bornite, which is unremarkable and hard to identify if unoxidized, commonly oxidizes to form what we call *peacock ore* (Figure 9.37). Covellite (Figure 9.38) is usually identified by its blue, commonly metallic color. We include a photo of azurite and malachite here (Figure 9.39) because of the color similarity to the other two minerals. But azurite and malachite are secondary copper carbonate hydroxides and not sulfide minerals. Figure 3.47 (Chapter 3) shows another specimen containing azurite and malachite.


9.37 Bornite is brown to copper red when fresh but easily tarnishes to produce what is called peacock ore


9.38 Covellite from Butte, Montana


9.39 Azurite (blue) and malachite (green) from Bisbee, Arizona. Both minerals are hydrated carbonates.

Sphalerite (ZnS) is a mineral that has many different appearances; the three photos below show examples. In Figure 9.40, the sphalerite is dark colored and bordering on metallic. In Figure 9.41, two prominent calcite crystals accompany the sphalerite, which has a characteristic brown resinous appearance. In Figure 9.42, the sphalerite is almost gemmy. Gray galena and orange dolomite are also present in the photo. Because of its many different appearances, sphalerite can be hard to identify unless it is brown and resinous as in Figure 9.41, and in Figure 3.26 (Chapter 3). For example, Figures 3.45 and 3.46 (Chapter 3) showed clear green and yellow sphalerite that looks nothing like the samples seen below. The many different colors of sphalerite are due to trace amounts of iron and other elements in the zinc sulfide. In laboratories, pure manufactured zinc sulfide is white.

9.40 Sphalerite (black) with quartz (clear) and siderite (yellow)

9.41 Resinous brown sphalerite with two large calcite crystals

9.42 Translucent brown sphalerite with galena (gray) from Peru

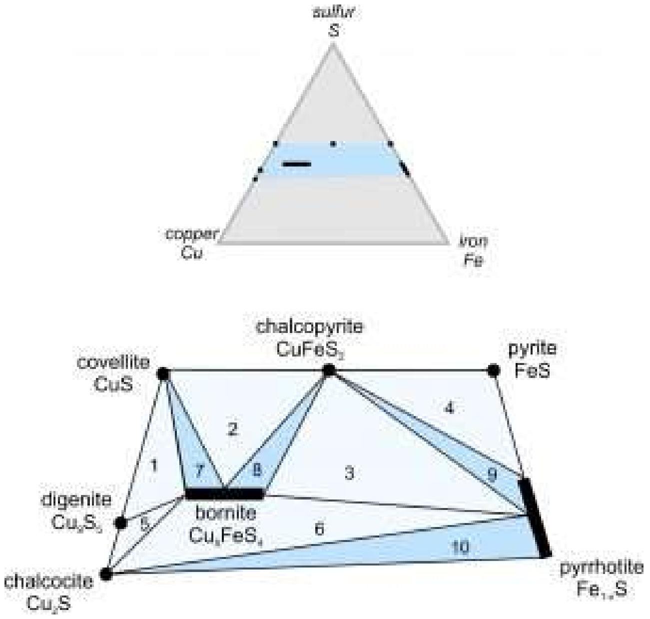
The photos below show three of the most colorful sulfides: cinnabar (HgS), realgar (AsS), and orpiment (As_2S_3). We typically identify these minerals by their color. Cinnabar (Figure 9.43) is generally a red-pink color, although the color is sometime diluted by other minerals present. Realgar (Figure 9.44) has a bright orangey-red color, and orpiment (Figure 9.45) is one of two common minerals (the other is sulfur) that is yellow. Note that the orpiment contains a small amount of orange realgar; their compositions are nearly identical. Figure 3.39 (Chapter 3) contains a photo of orpiment with calcite.

9.43 Cinnabar from Mirabel Springs, California

9.44 Realgar (red) , galena (silver gray), and minor orpiment (yellow) from Peru

9.45 Orpiment from Nevada

● Box 9-4 Cu-Fe Sulfide Minerals



9.46 The Cu-Fe-S system

We can use a triangular diagram to plot the compositions of copper-iron sulfide minerals in the same way we plotted feldspar, pyroxene, and other silicate compositions in Chapter 6. The small gray triangular diagram in the top of Figure 9.46 depicts the Cu-Fe-S system. The blue region in the center of the triangle is where compositions of the most important ore minerals plot. The quadrilateral below the triangle is an enlargement of that blue region.

The quadrilateral shows seven minerals. Bornite and pyrrhotite, which have variable compositions appear as bars that show the variation. Different specimens of bornite may contain different amounts of copper and iron, and so bornite plots as a horizontal bar. Pyrrhotite contains variable amounts of iron and sulfur and so plots as a bar pointing at the iron and sulfur corners of the triangle. The other minerals do not vary much in composition and so appear as dots. The phase rule (discussed in Chapters 4 and 8) tells us that the number of minerals that can coexist is generally quite small for simple chemical systems. This triangle depicts a simple system with only three chemical components. Tie lines and triangles on the quadrilateral show minerals that may be found together. If, for example, a rock has composition that plots where the number 3 is, it will contain bornite, chalcopyrite, and pyrrhotite.

Cu-Fe sulfide mineralogy is complex because many minerals have similar compositions. The quadrilateral shows 10 triangular fields (numbered 1 through 10). Those in light blue are 3-mineral fields – any composition that plots within them will contain three sulfides. The darker blue triangles only connect two minerals; they are 2-mineral fields. Compositions that plot within them will contain only two sulfides. The assemblage present in a specific deposit depends on the Cu:Fe:S ratio. In Fe-poor ore deposits, for example, sulfide assemblages will include covellite, digenite, or chalcocite, but not pyrite or pyrrhotite. Diagrams such as the one in this box (Figure 9.46) are useful ways to describe complex mineral relationships without words, and we use them to predict and interpret ore deposit mineralogy.

9.2.3 Oxides and Hydroxides

Oxide and Hydroxide Minerals	
oxides	
corundum	$AlsO_3$
periclase	MgO
magnetite	Fe_3O_4
hematite	Fe_2O_3
pyrolusite	MnO_2
rutile	TiO_2
cassiterite	SnO_2
ilmenite	$FeTiO_3$
spinel	$MgAl_2O_4$
chromite	$FeCr_2O_4$
hydroxides	
gibbsite	$Al(OH)_3$
diaspore	$AlO(OH)$
brucite	$Mg(OH)_2$
goethite	$FeO(OH)$
manganite	$MnO(OH)$

We often group oxides and hydroxides together because they have similar compositions and atomic arrangements. The table to the left lists the most common of these minerals. These minerals often have similar properties, and most have relatively simple and related formulas. Oxide minerals consist of metal cations bonded to O^{2-}. Hydroxide minerals contain $(OH)^-$ anion molecules in place of all or some O^{2-}. We group quartz, the most common oxide, with silicate minerals, so it is not considered here.

A primary difference between oxides and hydroxides is the temperatures at which they form and are stable. Hydroxides are unstable at high temperature; they exist in low-temperature environments and are commonly products of alteration and weathering. Other oxide minerals – magnetite and ilmenite, for example – are high-temperature minerals generally associated with igneous or metamorphic rocks. In fact, most igneous and metamorphic rocks contain oxide minerals. Typically they are present in minor amounts, are easily overlooked, and may be difficult to identify.

Oxides and hydroxides have properties distinct from silicates and sulfides. They are often dominated by ionic bonding, and anions (O^{2-}or OH^{-}) do not control their structure and properties as anions do for other mineral groups. Oxides and hydroxides also are distinct from carbonates, sulfates, and other ionic minerals that often have relatively high solubilities in water.

Simple oxides contain one metal element and have formulas R_2O, RO, or R_2O_3, where R is the metal cation. The different formulas reflect different valences of the metal cations. More complex oxides contain two different metals and have formulas XYO_3 or XY_2O_4, where X and Y denote the metals. Oxides with general formula XY_2O_4 (spinel and chromite in the table) belong to the *spinel group*; they all have similar atomic arrangements but contain different elements. Magnetite, which contains both Fe^{2+} and Fe^{3+}, also has a spinel structure and belongs to this group.

Some oxide minerals, for example corundum and spinel, come in many colors. Figure 3.41 (Chapter 3) shows red ruby and two different colored sapphires (blue and tangerine); all three are corundum. Sapphire may be other colors too, including white, pink, yellow, or orange. The photos below show four different colored spinels that were cut as gems. Pure spinel (which is rare) is clear or light gray like the stone in Figure 9.47 (below left), but most spinel contains trace metals that lead to a wide range of colors. Spinels may be various shades of red, purple, blue, yellow, orange, pink, or black, but red is most common. Some examples are in Figures 9.48, 9.49, and 9.50, below.


9.47 Clear spinel


9.48 Red spinel


9.49 Purple spinel


9.50 Blue spinel

Dark colored oxides can be particularly difficult to tell apart, especially because the same mineral can have many different appearances. Some typical samples are in the photos below. The top row contains iron oxides/hydroxides. Magnetite (Figure 9.51) is generally silvery or black. It is the only strongly magnetic mineral, which aids identification considerably. Hematite may have a metallic silver color (Figure 9.52) or may be dull to bright red (Figure 9.53) but, in either case, has a red streak. Figure 3.13 (Chapter 3) shows another example of red botryoidal hematite, and Figure 3.48 (Chapter 3) shows hematite's red streak. Goethite (Figure 9.54), the most common component of rust, may be yellow-brown, black or reddish.


9.51 Magnetite (Fe_3O_4) with pyrite from near Turin, Italy. The photo is 11.2 cm across


9.52 Specular hematite (Fe_2O_3) with quartz. 16 cm across


9.53 Botryoidal hematite (Fe_2O_3) from northeast Spain


9.54 Goethite ($FeO(OH)$) from Cornwall, England


9.55 Ilmenite ($FeTiO_3$) from Mont-Saint-Hilaire, Quebec. The photo is 8 cm across


9.56 Cassiterite (SnO_2) from Bohemia. 7.4 cm tall


9.57 Manganite ($MnO(OH)$) from Cape Town, South Africa. 4.3 cm tall


9.58 Millimeter wide pyrolusite (MnO_2) dendrites on limestone

Figure 9.55 shows ilmenite, iron titanium oxide. It sometimes looks like an iron oxide (magnetite or hematite) but is nonmagnetic and has a black streak. The hexagonal flakes of ilmenite in Figure 9.55 are spectacular but rare. Cassiterite, tin oxide, is shown in Figure 9.56. It is harder than the other minerals shown and often has an adamantine luster. Manganite, a manganese oxide/hydroxide, is shown in Figure 9.57. It shares properties with the other three minerals. The black arborescent mineral in Figure 9.58 is dendritic pyrolusite, manganese oxide, that crystallized along a fracture surface in limestone. Dendritic pyrolusite is sometimes mistaken as having an organic origin. Pyrolusite has other appearances and may be difficult to distinguish from other dense dark-colored minerals. But, it is the only common mineral that forms dendrites like the ones shown.

9.2.4 Gems and Gem Minerals

Mineral Gems and the Most Important Producing Countries and Regions

mineral	gem	source
beryl	emerald	Colombia, Brazil, Russia, Egypt, East Africa

beryl	aquamarine	Brazil, Afghanistan, Pakistan
chrysoberyl	alexandrite	Russia, Brazil
corundum	ruby	Cambodia, Myanmar, Afghanistan, India, Australia, Thailand, Sri Lanka, Brazil
corundum	sapphire	
diamond	diamond	Australia, South Africa, Namibia, Russia
jadeite	jade	Myanmar, China
K-feldspar	moonstone	many sources
olivine	peridot	Egypt, Myanmar, Australia
opal	opal	Australia, Hungary, Mexico
quartz	amethyst	Russia, Sri Lanka, India, Uruguay, Brazil
quartz	citrine	
topaz	topaz	Brazil, Sri Lanka, Russia, India
tourmaline	tourmaline	Namibia, Brazil, United States, Russia
turquoise	turquoise	United States, Egypt, Australia
tremolite – actinolite	nephrite (jade)	Russia, China, Taiwan, Canada
zircon	zircon	Sri Lanka

Gems are precious or semiprecious stones and related substances that we can cut or polishe to use for ornamentation. There are many kinds, and they may be natural or synthetic. Most gems are natural materials; they can be either minerals or nonminerals.

The term *gemstone* is sometimes used to refer to gems that are minerals. The table lists the common gemstones and their most important countries of origin. Only one or two countries dominate production of many gems, including diamond. Because gems differ in appearances from common minerals, they often have names different from their mineral names. The table contains some examples.

Diamond, emerald (a variety of beryl), and ruby (a variety of corundum), have been, historically, the most valuable gemstones. Sapphire (another variety of corundum) and alexandrite (a variety of chrysoberyl) are nearly as valuable. The most expensive gem on record sold for $71.2 million during a 2017 auction in Hong Kong. It was a unique oval-shaped diamond with a vivid pink color, weighed about 60 carats, and was almost 2 cm in longest dimension.

It is not the composition of gems that makes them valuable, but rather their appearance. Most are varieties of common minerals that exhibit spectacular color, clarity, brilliance, or play-of-color. The hardest gems – for example diamond, ruby, and sapphire – are especially highly valued because they are most durable. Besides its beauty, a gem’s rarity and uniqueness are important to some people, and gems sometimes have snob appeal.

Common beryl, is opaque with a nondescript blue color. For an example, see Figure 6.89 (Chapter 6). But exceptional beryl crystals are beautiful translucent or transparent gems, including emerald (green), aquamarine (blue), morganite (pink), helidor (yellow), goshenite (clear), and several other varieties. The four photos below (9.59 through 9.62) show gemmy examples of emerald, aquamarine, heliodor, and morganite that could be cut to make colorful gemstones. Although common beryl has no value as a gem, it is sometimes mined as a beryllium ore mineral. Other photos of gemmy beryl were seen in Figures 1.12, 1.13, and 1.14 (Chapter 1).


9.59 Emerald (green beryl) with quartz and sulfide minerals. The green crystal is 2 cm long


9.60 Aquamarine (light blue beryl) on top of muscovite


9.61 Heliodor (yellow beryl)


9.62 Morganite (pink beryl)


9.63 An opal pendant surrounded by diamonds


9.64 Diamond showing play of colors

Some gems, such as the opal shown in Figure 9.63, show *fire*, a type of play-of-color that appears as changing flashes of different colors when we view a gem from different angles. Fire is most apparent in minerals that exhibit *dispersion* – the ability to separate white light into different colors that pass through the mineral along slightly different paths. Diamond best exhibits this property (Figure 9.64) but other minerals, including sphene, zircon, and a green garnet called *demantoid garnet* sometimes also display fire. Fire is most notable in clear gemstones and may be completely masked in strongly colored stones. Fire may also be seen in amber or pearls – which we call gems although they are not minerals. Proper polishing or cutting can enhance play-of-color in gems of many sorts.

We saw other examples of minerals that exhibit play-of-color in previous chapters; all are common gemstones:
•Figures 1.2 (Chapter 1) and Figure 3.52 (Chapter 3) – opal
•Figures 3.51 (Chapter 3) – limonite
•Figures 3.53 (Chapter 3) – labradorite
•Figures 3.54 (Chapter 3) – moonstone

9.65 Irradiated topaz from Pakistan; 4 cm tall.

Gems and other minerals derive their color from many different things (see Chapter 3). Common minerals may have little value as gems, but if we can alter or enhance colors, even common quartz may become valuable. Gemologists, therefore, often treat gems and minerals, natural or synthetic, to change or enhance their color and increase their value. The vast majority of gems on the market today have had their appearances enhanced in some way.

For instance, quartz crystals from the Hot Springs area of Arkansas are irradiated to disrupt their atomic structure and give them a smoky, purple, or black color. Irradiation is also used to induce color changes in diamond and topaz. Figure 9.65 shows a remarkable blue colored topaz crystal. The strong color was produced by irradiation.

Gemologists also change a stone’s color using dyeing or heat treatment, although dyeing only affects gems such as jade and chalcedony, that are porous. Gemologists have successfully used heat treatment – which changes elemental valences or alters atomic structures – on quartz, beryl, zircon, and topaz, although the results are not always predictable.

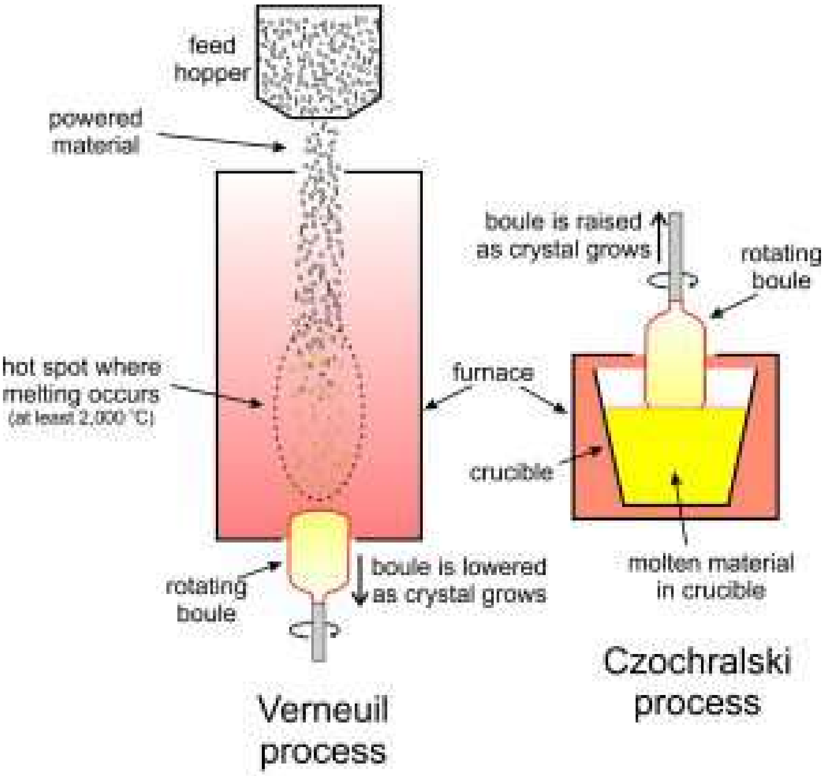
9.2.4.1 Synthetic Gems

9.66 Synthetic sapphire, ruby, and emerald. Each stone is 9 mm across.

Today, it is routine to synthesize gems of many sorts, including diamonds, and also varieties of quartz, beryl, corundum, and garnet. Chrysoberyl, opal, rutile, spinel, topaz, and turquoise are also synthesized. We saw photos of both natural and synthetic topaz and ruby in Figures 1.16, 1.17, 1.18, and 1.19 (Chapter 1). The photos seen here in Figure 9.66 show synthetic sapphire, ruby, and emerald.

9.67 Cubic zirconia (CZ)

Several synthetic compounds with no natural equivalents are used as simulants for gems. Foremost among them are yttrium aluminum garnet (YAG; $Y_3A1_5O_{12}$) and cubic zirconia (CZ; ZrO_2), both used as imitation (or “genuine faux” from the French for “fake”) diamonds. This photo (Figure 9.67) shows different examples of (synthetic) cubic zirconia. Today, clear CZ – two examples are seen in the photo – is the most common diamond simulant. CZ can have just about any color and so is a common simulant for other, darker-colored, gems as well.



9.68 The Verneuil and Czochralski processes for making synthetic gems

Gem manufacturers use several different methods to produce synthetic crystals. The Verneuil process and the Czochralski process both involve crystallizing gems from molten material (Figure 9.68). In the more common Verneuil process, powdered starting materials pass through a hot furnace and melt to produce droplets that add to a growing *boule*, a single elongated crystal, at the bottom of the furnace. The boule is slowly withdrawn from the furnace as it grows. This technique produces large synthetic rubies, sapphires, spinels, and other gems. The synthetic rubies are often key components of lasers.

In the Czochralski process (also shown in Figure 9.68), a seed crystal is placed in contact with a melt and allowed to grow. As it grows, the crystal is raised from the melt and so grows even longer. The photo on the left, below in Figure 9.69, shows synthetic corundum, including red ruby, made using the Verneuil process. The other colored stones are generically called *sapphire*. The stones in the bottom of the photo have been faceted to be used as ornamental gems. The photo on the right, in Figure 9.70, shows ruby being synthesized using the Czochralski process. The Czochralski process can produce 40 cm, or longer, ruby boules.

9.69 Corundum crystals created using the Verneuil process

9.70 Ruby being created by the Czochralski method

A third approach, the *flux method*, has sometimes yielded large synthetic crystals, notably ruby, sapphire, alexandrite, and emerald. A *flux* is a material that promotes reaction and crystal growth but is not incorporated in crystal structures. A mixture of chemicals – including those needed to make the desired mineral and others to act as the flux – is ground together and heated above its melting point. As the temperature is lowered, crystals begin to grow. After the melt solidifies, water or other reagents remove the flux, leaving the desired crystals. Most synthetic rubies and emeralds are created this way, but the process is very slow and may take many months. A related approach, called the *hydrothermal method* produces synthetic quartz and a few other gems. The method involves heating water that contains the necessary dissolved elements, and letting the crystals grow as the solution cools. It is a very slow process, like the flux method.

Mineralogists synthesize minerals in other ways, but they rarely produce gems of great value. For example, synthetic minerals may be grown from hydrothermal solutions in high-pressure reactor vessels called *bombs*. Synthetic quartz, corundum, and emerald have all been made this way. Synthetic diamond and a few other high-pressure minerals are made using a *solid state* (no melt or water) approach. This process involves a cylinder of starting material, enclosed in a graphite heater, squeezed between two pistons. Electricity passing through the graphite heats the material to temperatures at which crystals will grow. Chemists at General Electric have perfected this technique for making gem-quality synthetic diamonds.

9.2.4.2 Cutting and Polishing Gems

Most gems have shapes that do not resemble natural crystals. Sapphire, a variety of corundum, generally grows as hexagonal crystals, but when sapphires are to be incorporated into jewelry, gem cutters shape and polish them to increase their beauty and value. Figure 9.71 below shows natural sapphire from Madagascar and Figure 9.72 shows the Logan sapphire, a famous gemstone originally from Sri Lanka. Twenty diamonds surround the sapphire. Gem cutting affects value as much as the quality of the raw material. Cutting and polishing takes place in many parts of the world. Israel and Belgium dominate diamond cutting; the United States, India, Hong Kong, Thailand, and Brazil also cut significant amounts of various gems.

9.71 Natural sapphire from Madagascar

9.72 The Logan sapphire in the Field Museum of Natural History, Washington DC

9.73 Tourmaline cabachons of different colors

Gemologists shape gems in several ways. Agate, opal, chalcedony, and onyx may be tumbled in a cylinder with a polishing/abrading agent. The cylinder rotates until the stones have smooth surfaces. The stones become polished, but often have irregular shapes. Alternatively, gemologists shape stones using a wet grinding wheel made of quartz sandstone (for relatively soft minerals) or metal impregnated with diamonds (for harder minerals). After shaping and polishing, the stones are called *cabochons*. They have a smooth, domed top and, usually, a flat base. Until the Middle Ages, most gems were cut as cabochons. The gems shown in Figure 9.73 are all varieties of the mineral tourmaline, shaped and polished as cabochons.

9.74 Faceted orthoclase from Madagascar, 2 cm across

While most soft gemstones receive a cabochon cut, many hard gemstones are faceted. *Facets* are small, polished, planar surfaces that give the stones attractive shapes and light properties. With proper cutting, originally dull stones can sparkle. Facets are usually symmetrically arranged in geometric shapes. Gemologists create them by mounting stones on a holder, called a *dop*, and grinding the stone with a diamond-impregnated wheel. As with cabochons, the gems are polished after being ground. Figure 9.74 shows a faceted example of orthoclase from Madagascar. Figures 9.47-9.50 (spinel), 9.64 (diamond), 9.66 (synthetic sapphire, ruby, and emerald), 9.67 (cubic zieconia), and 9.69 (synthetic ruby and sapphire) contain other photos of faceted gems.

9.3 Types of Ore Deposits

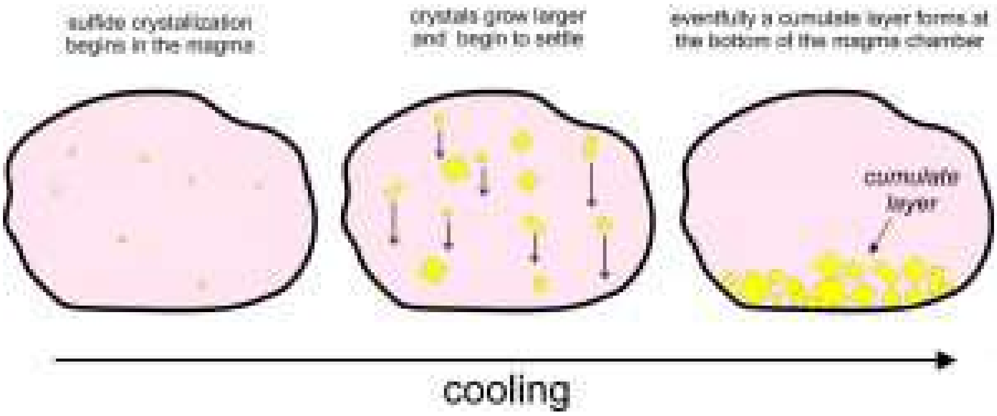
9.3.1 Magmatic Ore Deposits

9.75 Gold-bearing quartz vein at the Nalunaq Gold Mine in Southern Greenland. Meter stick for scale.

Minerals containing elements of economic value are generally present in all igneous rocks, but the elements may not be concentrated enough to make mining economical. Only in relatively rare circumstances are they in sufficient abundance so that mining is profitable. If the minerals are scattered throughout a host rock, but in sufficient amounts to mine profitably, we call the deposit a *disseminated deposit*. Disseminated deposits produce most of the world's diamonds, copper, and molybdenum and also large percentages of the available tin, silver, and mercury. Often, disseminated ores consist of minerals scattered randomly in a host rock. Sometimes geological processes concentrate ore minerals in *vein deposits* consisting of veins that are centimeters to meters thick. If ore is distributed in many small veins, geologists call the deposit a *lode deposit*. Vein deposits account for most of the world's gold and silver mines, and also some copper and lead-zinc mines. Figure 9.75 shows a meter wide quartz vein that is the source of gold at Nalunaq Gold Mine in southern Greenland. In still other kinds of igneous deposits, ore minerals become concentrated in layers. Below, we look at some of the most important kinds of igneous deposits.

9.3.1.1 Magmatic Sulfides and Cumulates

Mafic and ultramafic magmas, like all common magmas, contain the major elements oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. But they typically also contain other elements including sulfur, nickel, and less common metals such as platinum, palladium, and chromium. As these magmas cool and crystallize, the first minerals to form are plagioclase, pyroxene, and olivine – all made of major elements. Consequently, the concentrations of sulfur and other minor elements increase in remaining melt. Eventually, sulfur concentration becomes great enough so that sulfide minerals begin to crystallize. The sulfide minerals, typically containing iron and nickel, may also contain relatively high concentrations of platinum, palladium, and other minor metals.



9.76 Forming a cumulate deposit

Sulfides have greater densities than silicate minerals and the mafic or ultramafic melts. So, the denser sulfide minerals will, over time, begin to sink, as shown in Figure 9.76 above. Eventually, after more cooling and crystallization, significant deposits of sulfide minerals may accumulate on the bottom of a magma chamber. The deposits, which may form centimeters-, or meters-thick layer called a *cumulate*, are often entirely, or nearly entirely, composed of sulfide minerals. This process produces *magmatic sulfide deposits*, which are the most important sources of platinum, palladium, chromium, and several other metals. Cumulate sulfide minerals include pentlandite $(Fe,Ni)_9S_8$, chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$), and pyrite (FeS_2).

9.77 Chromite layers in the Bushveld layered mafic intrusion, South Africa

Cumulate sulfide deposits account for almost 60% of the world's nickel production and more than 95% of platinum and palladium production. These deposits are associated with mafic and ultramafic magmas but not, generally, with felsic magmas, because felsic magmas are so viscous that they cool and crystallize before dense minerals can settle.

Sulfides are not the only kind of mineral that can become concentrated in a cumulate deposit. Oxides – including magnetite (Fe_3O_4), ilmenite ($FeTiO_3$), and chromite ($FeCr_2O_4$) – may settle and collect at the bottom of a magma chamber, too. South Africa's Bushveld Complex is the most significant and important example of oxide mineral cumulates. Figure 9.77

shows Bushveld chromite layers surrounded by a feldspar-rich rock. These chromite cumulates produce not only significant amounts of chrome, but also very large amounts of platinum, palladium, and related elements.

9.3.1.2 Pegmatites

9.78 A pegmatite containing a large black tourmaline crystal withe K-feldspar and quartz

During crystallization, some minerals crystallize before others. Consequently, a late-stage magma will not be the same composition as an original magma. *Pegmatite* is the name given to coarse-grained igneous rocks that form during the final stage of magma crystallization. Common pegmatites have an overall granitic composition and comprise mostly quartz, feldspar, and mica. But pegmatites share another important characteristic. They also commonly contain minerals made of relatively rare elements that did not go into the early formed minerals. Figure 9.78, for example, contains the common minerals K-feldspar (white) and quartz (gray), but also contains tourmaline (black), a boron mineral. (Biotite is also present but is hard to see in the photo.) So, pegmatites are often mined for minerals rich in boron, cesium, lithium, molybdenum, niobium, tantalum, tin, tungsten, or other elements. For example, pegmatites are sometimes sources of spodumene (an important lithium mineral) and beryl (an important beryllium ore mineral).

Additionally, pegmatites may be a source of gem minerals. Gems from pegmatites include emerald and aquamarine (varieties of the mineral beryl), amazonite (variety of feldspar), apatite, chrysoberyl, garnet, spodumene, lepidolite, topaz, tourmaline, zircon, and others. Most pegmatite mines make their money from mineral specimens and gems rather than from the ore minerals they contain. The minerals in Figures 9.59 – 9.62, earlier in this chapter came from pegmatites, and we saw other examples of pegmatite minerals in Chapter 4 and Chapter 6:

- Figure 4.1 – Aquamarine and tourmaline
- Figure 4.12 – Riebeckite (an amphibole) with K-feldspar and quartz
- Figure 4.13 – Tourmaline
- Figure 4.30 – Emerald (beryl) on quartz
- Figure 6.108 – Tourmaline from a pegmatite

9.3.1.3 Kimberlites

9.79 The Big Hole at Kimberly, South Africa

Kimberlites, named after the town of *Kimberly*, South Africa, where they were first described, are volcanic rocks that originate in Earth’s mantle. They are mined exclusively for diamonds. The photo in Figure 9.79 shows the “Big Hole” at Kimberly. The Hole was mined from 1871 to 1914 and reached a depth of 240 m below the surface. Subsequently it filled with water.

Kimberlite eruptions are gas-powered explosive events. The magmas originate at depths of 150 to 450 km, deeper than other igneous rocks. Most kimberlites are in small vertical columns called *kimberlite pipes* although some rare sills are known. These pipes are the most important source of diamonds today. If kimberlite weathers and erodes, the diamonds may become concentrated in sedimentary deposits. Some kimberlites bring mantle xenoliths (pieces of mantle rock) to the surface; petrologists use these samples to study mantle chemistry and mineralogy.

Kimberlites are ultramafic rocks, having high magnesium and low silicon contents, and are rich in potassium. Mg-rich olivine and carbonate minerals generally dominate, but some kimberlites contain significant amounts of phlogopite (Mg-rich biotite). Lesser amounts of serpentine, ilmenite, garnet, clinopyroxene, enstatite and chromite may be present. Most kimberlites are very old, having erupted between about 80 million and 2.5 billion years ago. A few younger ones, 10-20,000 years old, are in Tanzania and Democratic Republic of the Congo.

Figure 8.11 (Chapter 8) showed a kimberlite that contained diamonds. Not all kimberlites do. The photo below in Figure 9.80 shows a sample of kimberlite from Baffin Island, Canada. The dark material consists of pyroxene and olivine. The obvious bright green minerals are chrome diopside. Harder-to-see smaller wine-red minerals are Mg-rich garnet. The large light-colored fragments are limestone that got caught up in the kimberlite magma during eruption.

9.80 Kimberlite from Baffin Island that contains coarse crystals of chrome diopside, small crystals of red garnet, and include fragments of limestone

9.3.2 Hydrothermal Ore Deposits

As a melt cools and crystallizes, hot, water-rich fluids may be released. These hydrothermal fluids are rich in sulfur, sodium, potassium, copper, tin, tungsten, and other elements with relatively high solubilities. Hydrothermal fluids dissolve other elements as they flow through rocks and eventually cool to deposit minerals in *hydrothermal deposits*. These deposits fall into four or five categories: *porphyry deposits*, *skarn deposits*, *volcanogenic massive sulfide deposits*, *sedimentary exhalitive deposits*, and *epigenetic deposits*. We discuss the different types in sections below – they have distinctly different origins and vary in size from huge networks of veins covering many square kilometers to small veinlets only centimeters wide. Hydrothermal deposits generally form at mid-ocean ridges, in subduction zone, or next to plutons. In all these settings, there is a source of heat that drives fluid circulation. The exceptions are epigenetic deposits that may form in continental interiors.

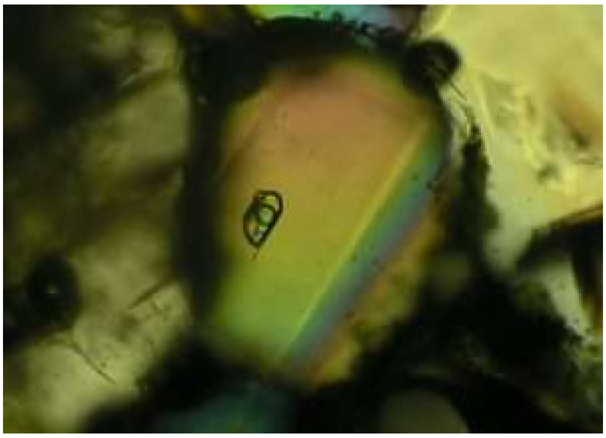
The Nalunaq gold shown in Figure 9.17 is an example of hydrothermal gold. Two other examples of hydrothermal mineralization are below in Figures 9.81 and 9.82: molybdenite ore from the Keystone Mine in Colorado and gold ore from the Sierra Nevada Mountains.

9.81 Hydrothermal veins of molybdenite from the Keystone Mine, Colorado

9.82 Hydrothermal gold from the Mother Load of the Sierra Nevada Mountains

Many minerals trap droplets of hydrothermal fluids that we can analyze to get information about their origins (Box 9-5). But, hydrothermal fluids may travel long distances before they deposit ore. So, determining the source of the fluid and of the ore elements is often difficult or impossible. Explaining deposition, however, is easier. It usually occurs in response to cooling, pressure changes, or changes in pH or other chemical factors.

● Box 9-5 Fluid Inclusions and Hydrothermal Ore Deposits

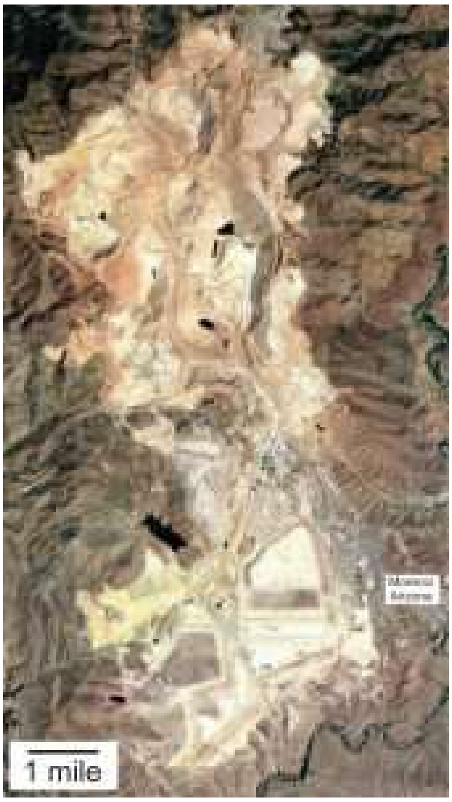


9.83 Microscope view of a fluid inclusion in an apatite crystal

Many minerals contain fluid inclusions, small bubbles that are typically 0.1 to 1 mm in diameter, left over from the time the minerals formed. Usually we need a microscope to see them. Inclusions are found in igneous, sedimentary, and metamorphic minerals, and are of particular importance when studying hydrothermal ore deposits. Fluid inclusions are also found in deep ice cores from Greenland and the Arctic. By studying their composition climatologists gain information that helps them reconstruct the past climate record.

When trapped as inclusions, fluids are at relatively high temperatures. As the fluid cools, it contracts, and a gas bubble may form. So, many fluid inclusions contain both a liquid and a vapor bubble. If the fluid contained abundant dissolved ions, minerals such as halite, sylvite, or hematite may precipitate as well. The inclusion in Figure 9.83 contains a gas bubble, a solid crystal, and some liquid. By heating an inclusion slowly and measuring the temperatures at which any gas bubble disappears and salts dissolve, ore petrologists can often determine the conditions under which an ore deposit formed.

9.3.2.1 Porphyry Deposits



9.84 The mine workings at Morenci, Arizona

Porphyry deposits are a special kind of hydrothermal deposit. They form when hydrothermal fluids, derived from magmas at depth, carry metals toward the surface and deposit minerals to create disseminated ore deposits. These deposits are important sources of copper, molybdenum, and gold. They may also yield tungsten or tin.

In porphyry deposits, ore minerals are in small veins within a hydrothermally altered host rock, generally a porphyritic felsic to intermediate composition intrusive rock. Porphyry ores are not particularly high-grade, but the deposits are commonly large and so are profitably mined. These deposits are common in the mountains along the west coast of North and South America, and in islands of the southwest Pacific, north of Australia.

The Morenci deposit in Arizona is a porphyry deposit. Figure 9.84 shows a satellite image of the mine. The town of Morenci (pop 1,489) is in the lower right of the photo. Copper minerals were first discovered at Morenci by an Army battalion in 1865; mining began in 1872. Today, the mine, with pits that total almost 130 square kilometers, is the largest copper producer in North America. The workings extend beneath and between several large mountains next to the Morenci town site. Pyrite and chalcopyrite, both sulfide minerals, are the primary copper ore minerals, but chrysocolla (copper oxide/hydroxide) and malachite (copper carbonate) are found and mined from oxidized ore zones. Although copper minerals are by far the most important ore minerals, the mine also produces lesser amounts of sphalerite (zinc ore), galena (lead ore), and molybdenite (molybdenum ore).

9.3.2.2 Skarn Deposits

9.85 Underground mining in the Cantung Mine in Canada's Northwest Territories

As described in Chapter 8, *skarns* are contact metamorphic zones that develop around an intrusion. They may be thin or thick, and their formation often involves metasomatism. Skarns can form in any kind of rock, but most are associated with limestone or dolostone. Common skarn minerals include calcite and dolomite, and many Ca-, Mg-, and Ca-Mg-silicates. Some skarns, however, are valuable mineral deposits containing copper, tungsten, iron, tin, molybdenum, zinc, lead, and gold. Skarns account for nearly three quarters of the world's tungsten production. Less commonly, skarns produce manganese, nickel, uranium, silver, boron, fluorine and rare-earth elements. Porphyry deposits and skarn deposits are both the results of hydrothermal activity, and a continuum exists between the two types. The photo in Figure 9.85 shows underground mining in a major skarn that yields tungsten, Canada’s Cantung Mine in the Northwest Territories.

9.3.2.3 Volcanogenic Massive Sulfides and other Exhalitive Deposits

9.86 The Kidd Mine near Timmins, Ontario

When hydrothermal fluids create ore deposits at, or near, Earth’s surface, we call the deposits *exhalitives*. The Kidd Mine, shown in Figure 9.86, is an example. The mine is in eastern Ontario, near Timmins; it is the world’s deepest *base metal* (a term referring to industrial metals excluding iron and precious metals) mine and extends to a depth of more than 3,350 meters. The bottom of the mine is said to be the closest a person can get to the center of Earth.

The Kidd Mine started producing in 1966. It was initially an open pit but soon went underground. The moneymaking metals are mostly copper and zinc, but silver, gold, lead, and other metals are important too. Ore minerals – mostly pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena – were deposited when warm, metal-rich hydrothermal waters combined with ocean waters in sediments and rocks of the ocean floor. The resulting deposits are in pods or sheets within sedimentary rock layers that, in places, contain nearly 100% ore.

The Kidd ore deposit is an example of a *volcanogenic massive sulfide (VMS) deposit*. Most such deposits are small, and, although the Kidd Mine is large, it is not the largest. The largest VMS deposits, about twice the size of the Kidd, are the Windy Craggy deposit in British Columbia, discovered in 1958, and the Rio Tinto deposit in Spain, discovered in 1972. The quality of the ore in massive sulfide deposits is high, host rocks are generally greater than 60% ore minerals, so even if they are small, massive sulfide deposits are alluring mining prospects. The photo below in Figure 9.87 shows one of the main pits at the Rio Tinto Mine. The name of the mine translates to Red River, and the photo in Figure 9.88 shows the acid mine drainage that gives the river its color today. Runoff from the mine has caused major environmental problems.

9.87 Rio Tinto Mine. The view is 10 km across.

9.88 Acid mine drainage from the Rio Tinto Mine

9.89 A black smoker on the ocean floor
Click this link to see a 4 minute YouTube video of a black smoker near the Galapagos Islands.

What makes VMS deposits especially intriguing is that we can see them being created today. This photo (Figure 9.89), and the spectacular YouTube video that is linked below it, show a *black smoker* on the ocean floor. At these smokers, hot hydrothermal waters, mixing with ocean waters, create fine particles of sulfide minerals and produce massive ore deposits. The iron sulfides that are the most common minerals created, are black, so the name. The ores mined from the Kidd, Windy, Craggy, Rio Tinto, and other massive sulfide deposits owe their origins to black smokers such as the one seen here. The smokers cover huge regions of the ocean floor and did so in the past. After forming, they later became uplifted and incorporated into the continents where we find them today. As seen in the video, black smokers are also sites of abundant marine life.

Black smokers occur at all mid-ocean ridges and is potentially minable. Prospecting of ocean floors is occurring today, and some mining companies have developed tentative plans for mining operations. To date, however, the water depth has proven too great for direct mining. Some areas near black smokers contain sulfide ooze that might, perhaps, be picked up with a vacuum. The Papua New Guinea (PNG) government invested more than $100 million in the Solwara 1 project, a planned mining operation that was to target mineral-rich hydrothermal vents on the ocean floor just north of PNG. The project had significant funding problems and met with much local and environmental opposition. It was cancelled in 2019.

9.90 Chalcopyrite and bornite from the Rammelsberg deposit, Germany

Sedimentary exhalitive (SEDEX) deposits are close cousins to VMS deposits. The difference is that host rocks in SEDEX deposits are sedimentary rocks. These deposits are rare compared with the other deposit types already discussed. They have produced significant amounts of zinc, lead, silver and sometimes copper. But, most of them are not economical to mine. Figure 9.90 shows copper ore (mostly chalcopyrite and bornite) from the Rammelsberg SEDEX deposit in Germany. At Rammelsberg, the hydrothermal ores are in shale. The Rammelsberg mine once produced silver, copper, and lead but is closed today.

9.3.2.4 Epigenetic Deposits

When a hydrothermal deposit is not directly associated with a pluton, we call it an *epigenetic* deposit. Often, the hydrothermal fluids have traveled so far that their original source is unknown. For example, some flat sedimentary rocks in the interior of the United States have strata of limestone that contain ore minerals. These include mineral deposits of the Southeast Missouri Lead District and related deposits in Iowa, Wisconsin, and Illinois. The deposits are especially concentrated in a curved zone called the *Viburnum Trend* in southeast Missouri. Similar deposits are found at Pine Point in Canada's Northwest Territories, in northern, England, and in a handful of other places around the world. We call all these deposits *Mississippi Valley type (MVT)* deposits.

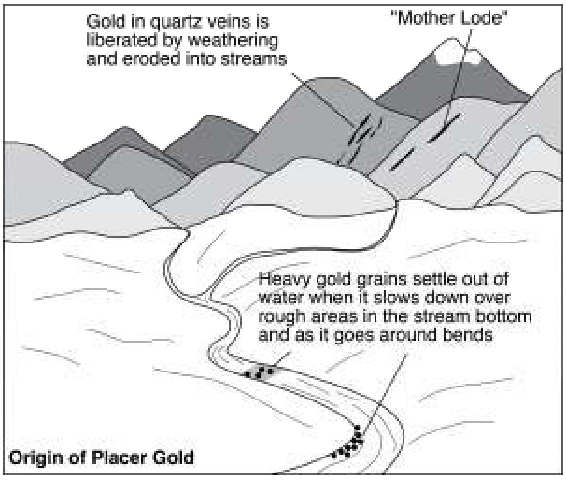
9.91 Galena, calcite, and fluorite from the Rogerley Mine, County Durham, England

This photo (Figure 9.91) shows a museum specimen from an MVT ore deposit in the North Pennines of England. This sample is mostly green fluorite, but also contains silver-gray cubes of galena and white and salmon-colored calcite.

Primary ore minerals in MVT deposits are generally galena (PbS) and sphalerite (ZnS). Fluorite (CaF_2) is common but has little economic value. Weathered or altered MVT ores may contain anglesite (PbSO4), cerussite ($PbCO_3$), smithsonite ($ZnCO_3$), hydrozincite (also a type of zinc carbonate), and secondary galena or sphalerite. Flowing groundwaters deposited both primary and secondary ore minerals long after limestone formation, but the origins of the groundwaters are unknown. According to some geologists, the metal-rich ore fluid came from oxidized clastic iron-rich rocks.

9.3.3 Sedimentary Ore Deposits

9.3.3.1 Placer Deposits



9.92 Formation of placer gold deposit

Gravity may be an important force that concentrates economic minerals. Heavy minerals, weathered from igneous, sedimentary, or metamorphic rocks, can be picked up and rivers may transport them long distances before they become concentrated in placers. So, placer deposits, also just called *placers*, form when one or more minerals concentrate in this way to become an ore deposit. The word *placer* is Spanish for *alluvial sand*.

Typically, placers form where a stream’s velocity slows on point bars, in braided streams, or in alluvial fans (Figure 9.92). Other similar deposits are in beach sands or gravels on ocean and lake shores. And some placers, although not commonly mined, form in offshore marine environments on continental shelves.

9.93 Placer mining for gold in California. Published in The Century illustrated monthly magazine in 1883.

Placer gold set off the historically important California Gold Rush of 1849 (Figure 9.93). The original sources of minerals in placers are often difficult to determine but, in California, the source has been identified. The California gold weathered from extensive vein deposits, called the *mother lode*, in the Sierra Nevada Mountains. The lode is in a zone east of Sacramento and San Francisco that is 1 to 6 km wide and extends almost 200 km north-south. Mother Lode gold is in quartz veins up to 20 meters thick and thousands of meters long. Many prospectors told stories of finding and mining the mother lode, but in actuality, most of it eroded away long before the miners arrived.

The California gold rush resulted in California being admitted to the United States in 1850 and later provided a name for a San Francisco football team (the *49ers*). Although once one of the most productive gold-producing districts in the United States, the Mother Lode is presently mostly a tourist destination and the home of wineries.

9.94 Placer gold in the Draper Museum of Natural History, Cody, Wyoming

Placer minerals must be both dense and durable to be deposited and remain in place without decomposing. Native metals such as copper or gold, sulfide minerals such as pyrite or pyrrhotite, and oxide minerals such as magnetite or ilmenite are all dense and likely to be found in placers. Metal oxides, especially magnetite (iron oxide), are common and especially dense and durable, and often dominate such deposits. And gold is dense and extremely resistant to any kind of weathering and so can accumulate in stream and river sediments. Gold in placer deposits is found as nuggets that range from microscopic size to basketball size. The photo seen here (Figure 9.94) shows millimeter and finer-sized placer gold nuggets from an unknown origin.

Other important metals besides gold come from placers. As discussed previously, during the Bronze Age, people of Mesopotamia and Greece obtained their tin from what is today England. That tin came from tin placers in the modern-day area of Cornwall. The tin is in cassiterite (SnO_2) that derived from the weathering of nearby granites. People mined the Cornwall tin deposits, placer and underground, for more than 4,100 years, beginning about 2150 BCE. The last mine, the South

Crofty Mine, closed in 1998. Other important minerals found in placers include diamond, garnet, ilmenite and rutile (titanium ore), ruby, sapphire, monazite, and zircon.

9.3.3.2 Iron Ores

9.95 The Soudan Iron Formation in northern Minnesota. Hammer for scale.

Sedimentary ore deposits also form by chemical precipitation; *banded iron formations (BIF)*, found in Precambrian shields, are examples. Photos of BIF are seen here in Figure 9.95, and also in Figure 7.77 (Chapter 7). Banded iron formations are massive in scale, in places covering hundreds of square kilometers, and perhaps being tens to hundreds of meters thick. If they contain especially significant amounts of magnetite and hematite, they are profitably mined.

Typical banded iron formation contains repeating layers of black to silver iron oxide (magnetite), and red chert (microcrystalline quartz). The overall red color is because the chert contains inclusions of hematite. The outcrop shown in Figure 9.95 is in the Mesabi Iron Range of Minnesota. It formed during the Precambrian Eon, 2.1 billion years ago, and is 2 meters high, 3 meters across, and weighs 8.5 tons.

Banded iron formations include oxides, silicates, and carbonates of iron. They are most commonly rich in magnetite (Fe_3O_4) and hematite (Fe_2O_3) but goethite ($FeO(OH)$), limonite

($FeO(OH)\cdot n(H_2O)$) and siderite ($FeCO_3$) are sometimes ore minerals. Other minerals in BIF include the carbonate *ankerite* (similar to siderite with impurities), and iron silicates such as *minnesotaite* (an iron amphibole), *greenalite* (Fe-rich serpentine), or *grunerite* (also an iron amphibole). Changes in the composition of Earth's atmosphere more than two billion years ago caused deposition of these minerals. They are commonly associated with very old fossil algae which likely caused the atmospheric change. BIFs are found on all the world's major continents, and, where they are found, mining often occurs.

9.96 Iron mine at Tom Price, Western Australia

Australia contains many large iron mines where hematite is the main ore mineral. Most large hematite deposits formed by alteration of banded iron formations. These deposits are less common than magnetite-rich banded iron formation but easier to mine and process.

Australia dominates the world iron market, producing 36% of all iron ore. Brazil and China each produce about 16%. Figure 9.96 shows an iron mine at Tom Price in Western Australia. The bedrock and the soil have the typical reddish color associated with oxidized iron minerals, such as hematite and goethite, that typifies iron formations.

9.3.3.3 Evaporites

When a body of water is trapped, evaporation can lead to precipitation of halite and other salts. Thick *evaporite deposits* of halite, *sylvite*, gypsum, and sulfur have formed in this way. Section 7.3.2 (Chapter 7) discussed the formation of these deposits and evaporite minerals. Evaporites are mined for many things, most notably halite, sylvite, and gypsum. They also produce boron- and lithium-mineral ores.

9.3.3.4 Laterite Deposits

The weathering of preexisting rock may expose and concentrate valuable minerals. Over time, water leaches rocks and soils, dissolving and carrying away soluble material. The remains, called *residuum*, may be rich in aluminum, nickel, iron, or other insoluble elements. In tropical climates extreme leaching has produced soils called *laterites*, which are rich in aluminum or, sometimes, nickel. If aluminum-rich laterite lithifies to become rock, we term it *bauxite* . We mine laterites and bauxites from open pits to produce nickel and aluminum and, sometimes as a secondary commodity, iron. Chapter 7 discussed the formation of laterites and bauxites. See especially Box 7.1.

9.3.3.5 Phosphorites

9.97 Cormorants on a guano island

Phosphorus, like potassium, is an essential nutrient for all living things and people have used it as a fertilizer for centuries. In the 18th century, people used *bone ash* as a source of phosphorus, created by roasting the bones of animals to liberate contained phosphorus. In the 19th century, people turned to *guano*, or bird and bat excrement, as the principal source of phosphorus for fertilizer. They obtained guano from small ocean islands with large bird populations. Figure 9.97 shows a typical island with white guano deposits. Similar deposits are found on many ocean islands around the world, where tens of thousands to millions of years of bird excrement has collected. In some places, layers of guano are up to tens of meters thick.

Today, instead of coming from bird dung, most phosphorus comes from *phosphorite* – which is what is being mined in the photo below in Figure 9.98 – a phosphate-rich chemical sedimentary rock that forms in several different marine environments. The most common depositional environments are in shallow, near-shore marine settings, including beaches, intertidal zones, and estuaries. The mine in this figure is in Togo, West Africa.

Figure 9.99 shows the Bou Craa phosphorite mine in the interior of Western Sahara (a disputed territory south of Morocco). A 60-mile long conveyor belt carries ore to a shipping port on the Atlantic Coast. Morocco and Western Sahara contain 70% of the world's known phosphate deposits today, but China is the number one producer. Some smaller, but still significant production occurs in other countries. In the United States, we sometimes mine phosphorite in Florida, Idaho, North Carolina, and Utah.

9.98 Phosphate mining in Togo, West Africa

9.99 Phosphate is shipped nearly 60 miles via a covered conveyer belt from the mine in the Western Sahara to the coast where it is transported for use as fertilizer around the world.

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10 Crystal Morphology and Symmetry

10.1 Spectacular blue barite crystals up to 50 mm tall. From the Huanuco Department, Peru.

10 Crystal Morphology and

Symmetry

KEY CONCEPTS

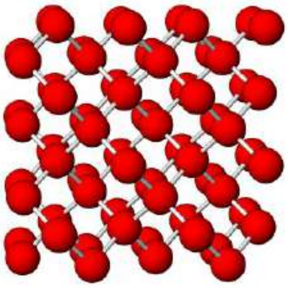
- The symmetry of a crystal is the geometrical relationship between its faces and edges.
- Crystal symmetry is a reflection of internal atomic symmetry.
- If a crystal has symmetry, the symmetry is common to all of its properties.
- By studying crystal symmetry, we can make inferences about internal atomic order.
- Crystals may have any of an infinite number of shapes, but the number of possible symmetries is limited.
- Crystal symmetry is the basis for dividing crystals into different groups and classes.

10.1 Symmetry

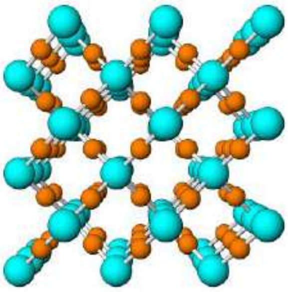
10.1.1 Introduction

The external shape of a crystal reflects its internal atomic arrangement. Of most importance is a crystal's symmetry. As defined by the ancient Greek philosopher Aristotle, *symmetry* refers to the relationship between parts of an entity. Zoltai and Stout (1984) give an excellent practical definition of symmetry as it applies to crystals: "Symmetry is the order in arrangement and orientation of atoms in minerals, and the order in the consequent distribution of mineral properties."

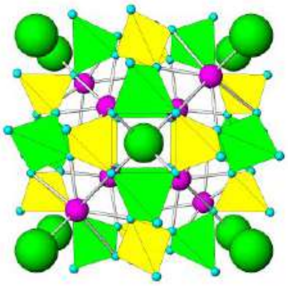
Figure 7.54 (Chapter 7) showed the atomic arrangement in halite. Halite, like all minerals, is built of fundamental building blocks called *unit cells*. In halite crystals, the unit cells have a cubic shape. Fluorite, too (Figure 7.55, Chapter 7) has a cubic unit cell. Figures 10.2, 10.3, 10.4, and 10.5, below, show other minerals with an overall cubic arrangement of their atoms. Diamond's atomic arrangement is quite simple because it only contains carbon. Cuprite is a bit more complicated because copper and oxygen atoms alternate. Sodalite and garnet are even more complicated. But, all these minerals have cubic unit cells. The unit cells have what is called *cubic symmetry*.



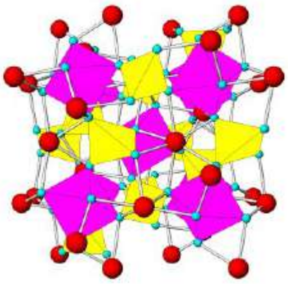
10.2 Diamond, C



10.3 Figure 10.3 Cuprite, Cu_2O

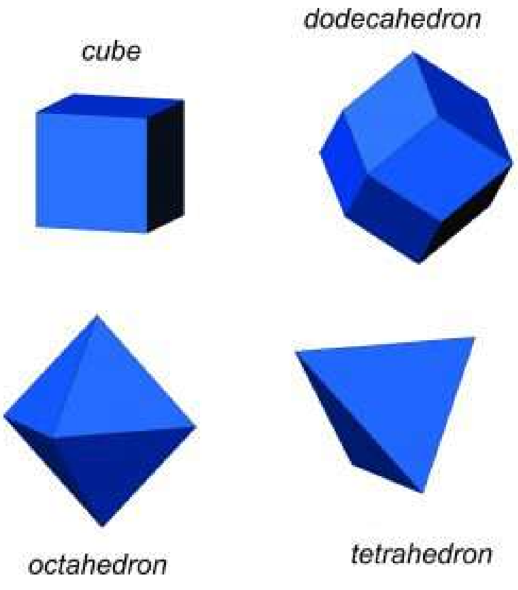


10.4 Sodalite, $Na_4(Si_3Al_3)O_{12}Cl$



10.5 Garnet, $Fe_3Al_2Si_3O_{12}$

Unit cells may have any of six fundamental shapes with different symmetries. For example, some unit cells have the shape of a shoe box instead of being cubes. Minerals with a cubic unit cell may form cubic crystals because atoms within them are arranged in a cubic pattern with identical structure in three perpendicular directions. So crystals with six identical faces (a cube) are possible. Minerals with shoe-box shaped unit cells cannot form cubic crystals. In the next chapter we will look closer at the possible unit cell shapes and the crystals they may form.



10.6 Some crystal shapes

Although the relationship between a cubic arrangement of atoms and a cube-shaped crystal may seem clear, things are not always so simple. Euhedral halite crystals are generally cubes. And, cuprite crystals (Figure 10.3) may be cubes, too, but they are also sometimes octahedra. Notice that octahedra are equivalent to cubes with their corners removed. The atomic arrangement in an octahedral crystal is the same in three perpendicular directions, just like the arrangement in a cubic crystal.

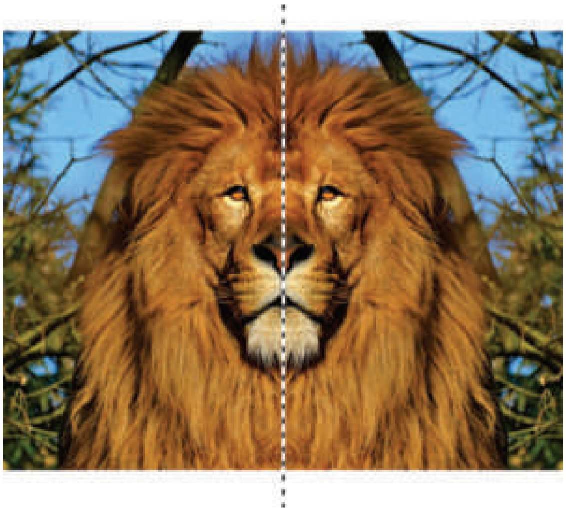
Sodalite (Figure 10.4) and garnet (Figure 10.5) typically form rhombic dodecahedral crystals. (There are different kinds of dodecahedra but for brevity, when we refer to a dodecahedron in the rest of this chapter we are talking about a rhombic dodecahedron.) And, diamond (Figure 10.2) crystals may be octahedra, dodecahedra, cubes, and tetrahedra. Figure 10.6 shows those possible crystal shapes.

So, we see that if the atomic arrangement has cubic symmetry, a crystal may or may not have the same symmetry. But, we can turn this around. If a crystal shows some kind of symmetry, the atoms within it must have at least that much symmetry. They may have more. For example, as we will see later in this chapter, minerals that form dodecahedral, octahedral or tetrahedral crystals have cubic atomic arrangements within them, even though the crystals are not cubes. Thus, the external symmetry of a crystal tells us about the atomic arrangement within. In this chapter, the focus is on crystal symmetry. In the following chapter we will look more closely at the atomic arrangements implied by that symmetry.

10.1.2 Identifying Symmetry

Looking for symmetry in natural materials can be complicated. Although atomic arrangements may be symmetrical, many things control crystal growth, so crystal shapes may not reflect their internal order. Sometimes few or no crystal faces may form. Sometimes several different crystals become intergrown. Sometimes crystals contain structural imperfections. Some crystals have *pseudosymmetry*, which means they appear to have certain symmetry but, if you could look closer or make precise measurements, you would find that they do not. And, other crystals may be too small to see clearly. An experienced eye and an active imagination are often necessary to see the symmetry of natural mineral crystals.

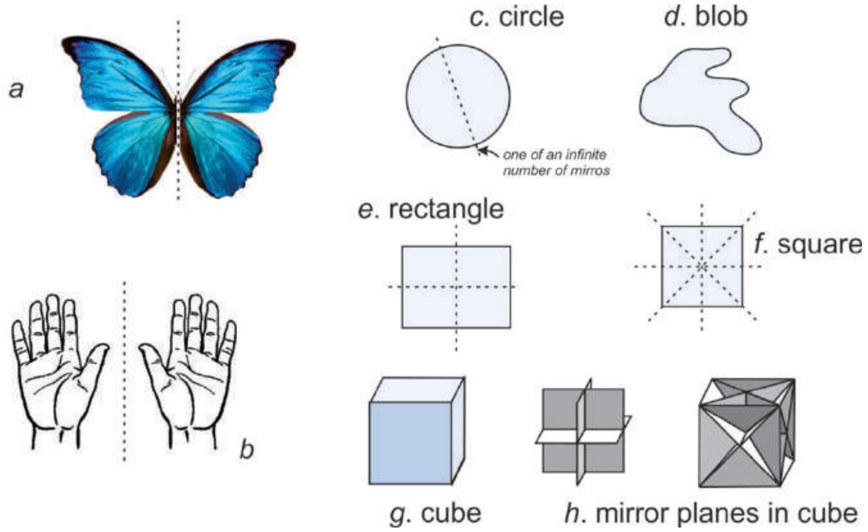
10.1.3 Mirror Planes



10.7 Lions have symmetrical faces

Most animals, including humans and lions (Figure 10.7), appear symmetrical: an imaginary mirror down their center relates the appearance of their right side to their left side. We call such symmetry *reflection*, and we call the plane of the imaginary mirror the *mirror plane*. In shorthand notation, we use the letter *m* to designate a mirror of symmetry. Reflection is the symmetry *operation*, and the mirror plane is the symmetry *operator*. Reflection often relates identical faces on a crystal. Figure 10.8*a* shows a butterfly that has the same symmetry as a lion.

A face, or any object, on one side of a mirror has an equivalent at an equal distance on the other side of the mirror. The two faces or objects are the same perpendicular distance from the mirror and have opposite *handedness*, like your two hands shown in Figure 10.8*b* (one has the thumb on the left side and the other has the thumb on the right side).



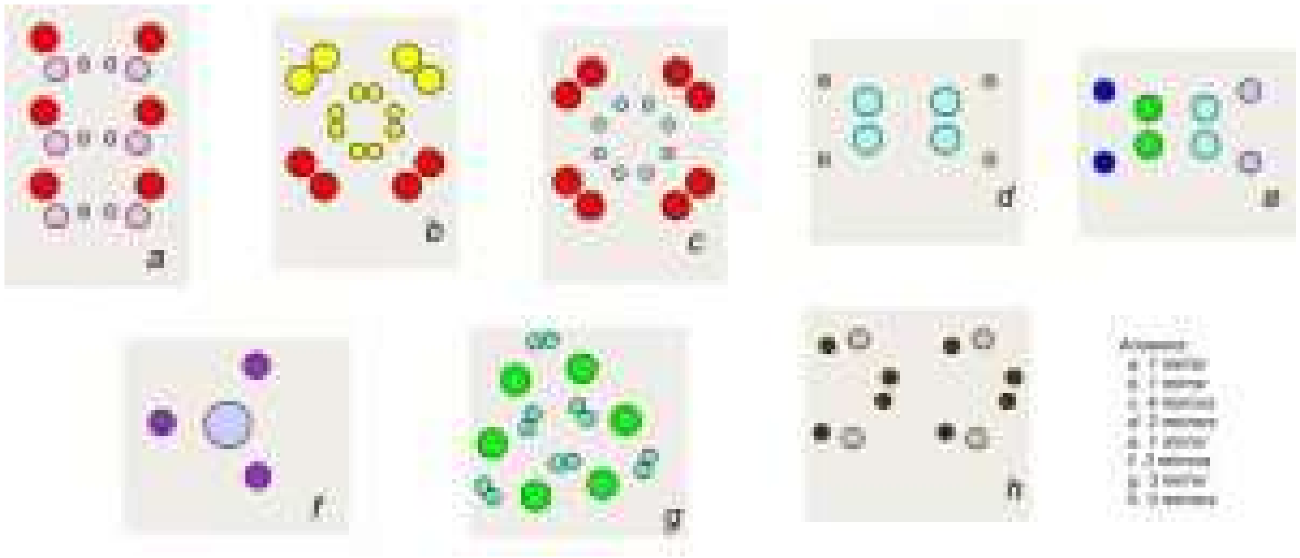
10.8 Mirror planes of symmetry

Two-dimensional drawings may have many mirror planes or no mirror planes. A circle (Figure 10.8*c*), for example, contains an infinite number of mirror planes; any line drawn through the center of the circle is a mirror of symmetry. Irregular blobs (Figure 10.8*d*), on the other hand, have no mirror planes. A rectangle (Figure 10.8*e*) contains two mirror planes, while squares (Figure 10.8*f*) have four. Box 10-1 contains more examples of mirror planes in 2D.

Three-dimensional objects, too, may have zero to many mirror planes. A cube (Figure 10.8*g*) has nine mirrors. Three are parallel to pairs of opposite faces; six intersect opposite faces along their diagonals (Figure 10.8*h*). Thus, a cube has more symmetry than a human, a lion, or a butterfly. (A perfect sphere has an infinite number of mirror planes, but, as we will see later, crystals cannot have more mirror planes than a cube.)

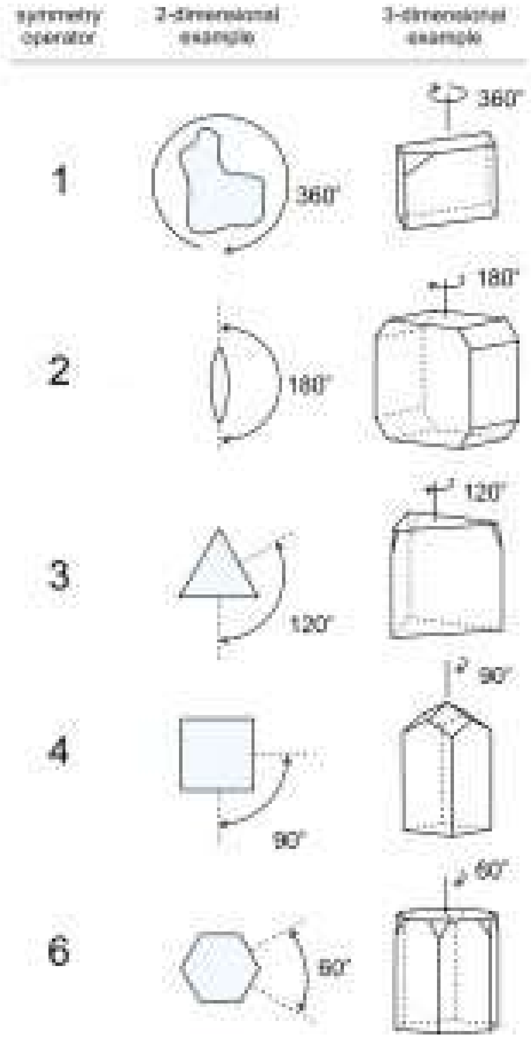
● Box 10-1 Mirror Planes in 2D

The drawings below show colorful patterns. Most of them contain mirror planes. How many mirror planes do you see in each pattern?



10.9 Some patterns that may contain mirror planes

10.1.4 Rotational Symmetry



10.10 Rotational symmetry

Reflection by a mirror is one of several types of symmetry operations. A second common type of symmetry in crystals, called *rotational symmetry*, is symmetry with respect to a line called a *rotation axis*. In two dimensions, a lens shape appears unchanged when rotated 180° (symmetry operator 2 in Figure 10.10). We say it has *2-fold symmetry* because two repeats of the rotation operation return it to its original position. A 2-fold rotation axis is perpendicular to the plane of the page.

Figure 10.10 also shows other rotational symmetry operators. Equilateral triangles have 3-fold rotational symmetry. Rotate an equilateral triangle 120° and it appears the same. Squares have 4-fold rotational symmetry (rotation of 90°), and hexagons have 6-fold rotational symmetry (rotation of 60°). Box 10-2 contains more examples of rotation axes in 2D.

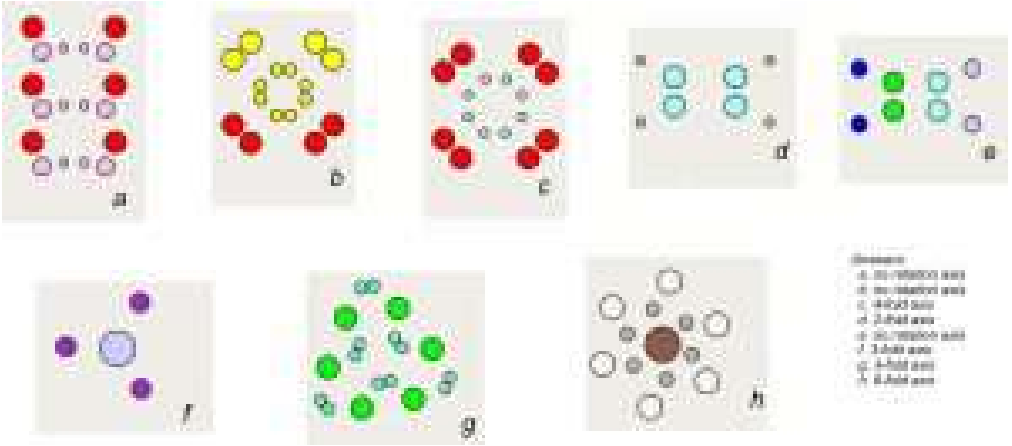
The right-hand column in Figure 10.10 shows three-dimensional shapes – they might be crystals – with the different kinds of rotational symmetry. Many of them also contain mirror planes of symmetry. Thus we see that crystals may have more than one kind of symmetry.

All objects have 1-fold rotational symmetry because they remain unchanged after rotation of 360°. But for completeness we have included 1-fold symmetry in Figure 10.10. Although we can draw shapes that have 5-fold symmetry, or greater than 6-fold symmetry, minerals never possess such symmetry. We will discuss why in the following chapter. Some natural materials, including plants and animals such as a starfish (having 5 legs), display apparent symmetries not possible for minerals.

We call all the rotation axes we have just discussed *proper rotation axes*, to contrast them with *rotoinversion axes*, which we will discuss later. In shorthand notation, we symbolize proper rotation axes using the numbers 1, 2, 3, 4, or 6, corresponding to rotations of 360°, 180°, 120°, 90°, and 60°, respectively. Sometimes in drawings, we use a small lens shape, a triangle, a square, or a hexagon instead of numbers to label these axes.

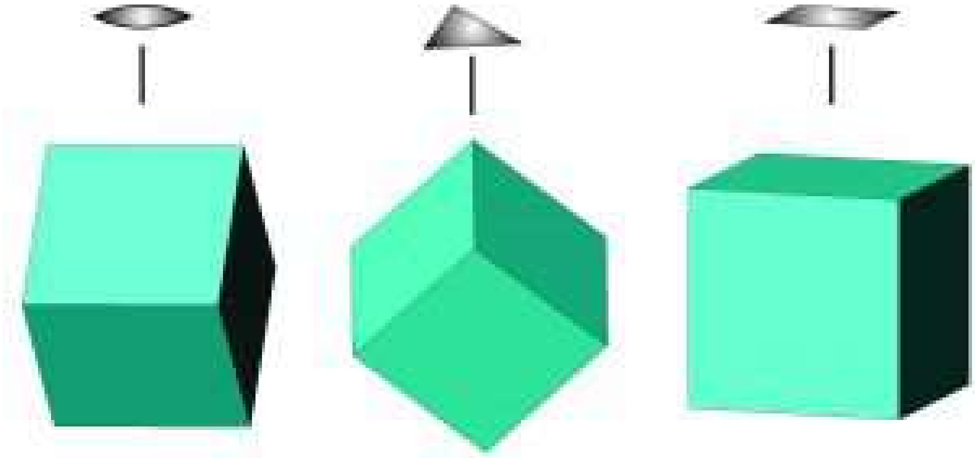
● Box 10-2 Rotation Axes in 2D

The drawings below show colorful patterns. Most are the same patterns you saw in the previous box. They all have 1-fold rotational symmetry. What other kinds of rotation axis (2-fold, 3-fold, 4-fold, or 6-fold) do you see in each drawing? (Some contain none.)



10.11 Some examples that may contain rotation axes

Above, we noted that cubes have nine mirror planes. Cubes also have 2-fold, 3-fold, and 4-fold rotational symmetry, shown in Figure 10.12. When rotated 180° about an edge diagonal, a cube appears unchanged. When rotated 120° about a main diagonal, or when rotated 90° about a line perpendicular to a face, a cube does not change. Thus, we see that different rotation axes can combine in crystals. Cubes, with all their mirror planes and rotation axes, have the most symmetry possible for a crystal.



10.12 Rotational axes of a cube

10.13 Apophyllite on stilbite and calcite

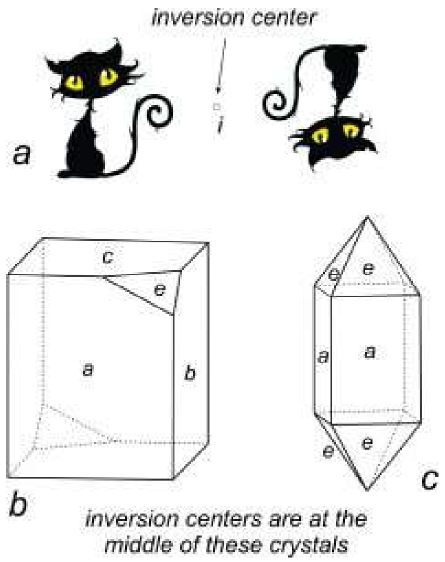
10.14 Apatite crystal from Bahia State, Brazil. 7 cm tall

Many minerals grow as *prisms*, crystals having a set of identical faces parallel to one direction. Typically, prismatic crystals are elongated in one direction. Figure 10.13 shows a green prismatic crystal of apophyllite, a zeolite. The crystal has four vertical faces and a square cross section. It also has sloping *terminating faces* at the top and bottom ends. Figure 10.14 shows a hexagonal prism of apatite. The prism has six sides and terminating faces on its top.

Prism faces are, in principle, identical in shape and size, although accidents of growth often lead to minor differences. Some minerals have multiple, nonidentical faces, all parallel to a common line. We call the collection of faces a *zone* and the common line the *zone axis*. Zones, present in most crystals, sometimes correspond to axes of symmetry. The apophyllite and apatite crystals in the above photos are examples of minerals that contain zones.

Anhedral crystals exhibit no external symmetry, while euhedral crystals may exhibit a lot. But rotational symmetry, even if present, may be hard to see. For example, the 3-fold axes of symmetry in a cube are difficult to see without turning the cube in your hand. Problems may be even more complicated in natural crystals because of growth imperfections in crystal faces, or the presence of many differently shaped crystal faces.

10.1.5 Inversion Centers

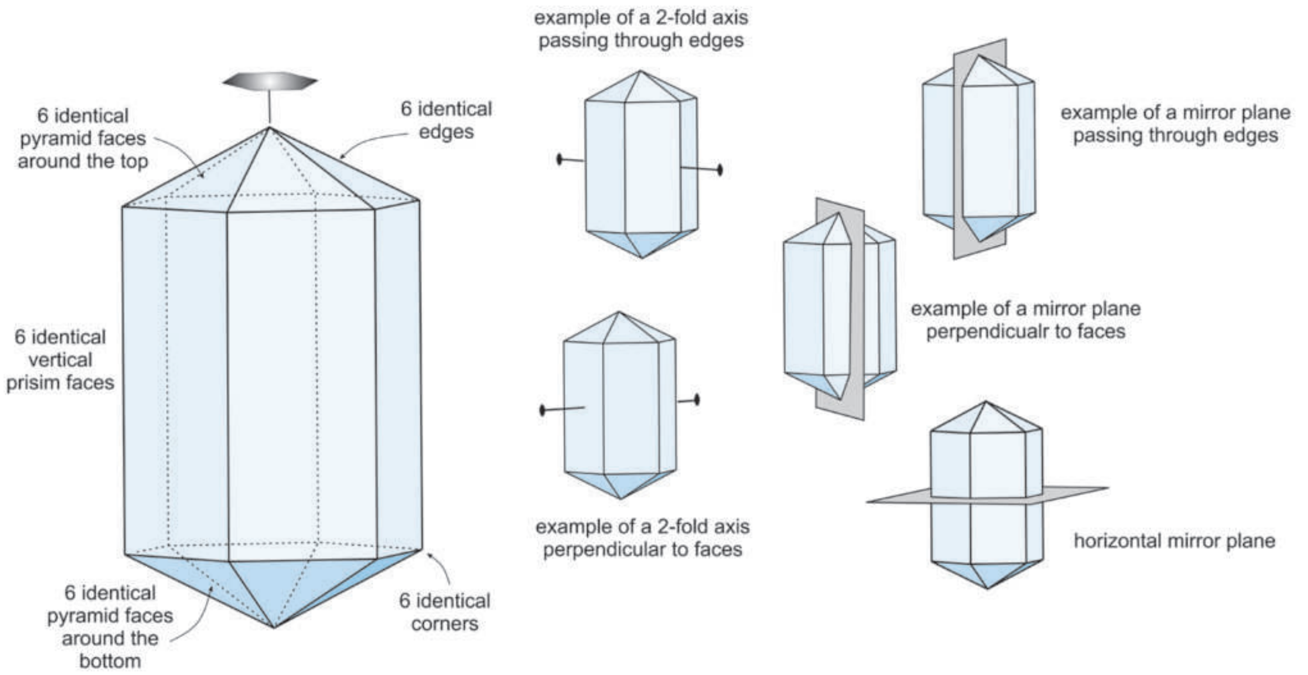


10.15 Inversion centers

Inversion, a third type of symmetry, is symmetry with respect to a point. We call the point the *inversion center* and often designate it with the lowercase letter *i*. As with mirror planes, inversion relates identical faces on a crystal. But, while mirror planes “reflect” faces and change their “handedness,” inversion centers invert them. Inversion produces faces related in the same way that a lens may yield an upside-down and backward image. In two dimensions, inversion centers give the same results as 2-fold axes of symmetry. For example, in Figure 10.15*a*, a cat has been inverted. The cat could have been rotated 180° and the result would have been the same.

In three dimensions, inversion symmetry is different from rotation. The crystal in Figure 10.15*b* has an inversion center and no other symmetry. It contains four different shaped faces (*a, b, c,* and *e*); each of them has an inverted matching face on the back and left sides of the crystal. No mirrors or rotation axes of symmetry are present. The crystal in Figure 10.15*c* contains an inversion center, but other symmetry is present, too. 90° rotation relates the four *a*-faces. Inversion and rotation relate the eight *e*-faces. Additionally, many mirror planes are present. Small letters on crystal faces, such as those seen in these two crystal drawings, are commonly used to distinguish faces of different shapes and to show those related by symmetry. Conventions, not worth discussing here, dictate which letters are used for different kinds of faces.

10.1.6 Symmetry Operates on Everything



10.16 A hexagonal prism terminated by pyramid faces

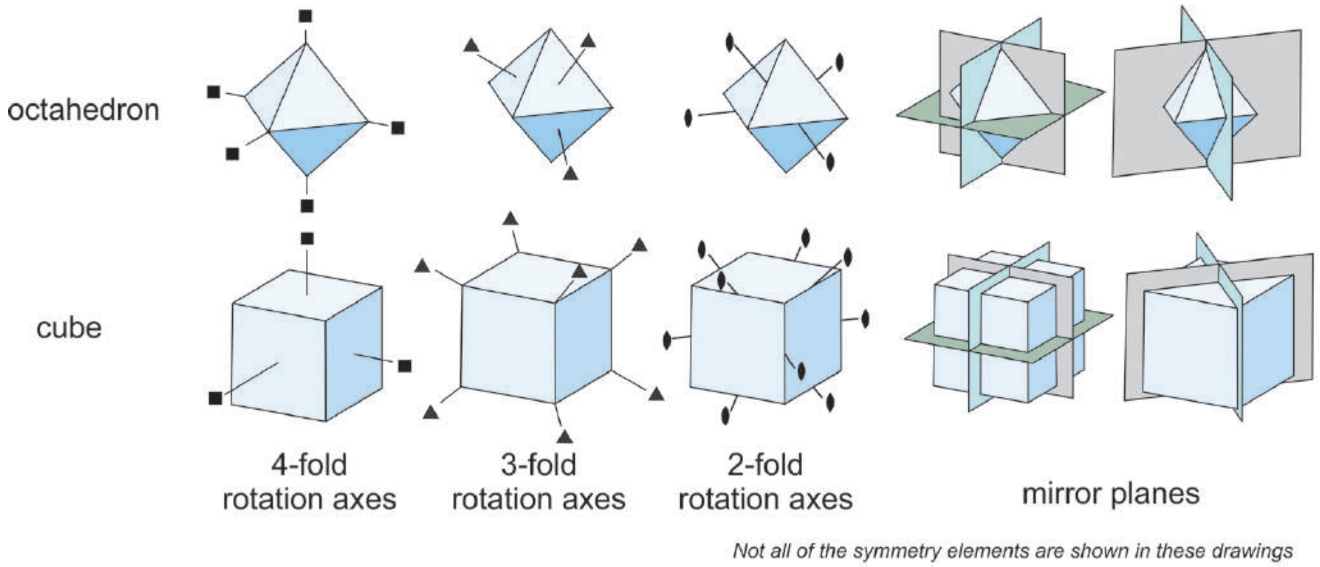
The crystal shown above in Figure 10.16 has a vertical 6-fold axis of symmetry. This means that it has six identical prism faces and six identical pyramid faces on both the top and on bottom. It also has six identical edges around the prism faces and around the pyramid faces.

The crystal has six 2-fold rotation axes that pass through edges, and six other 2-fold axes that are perpendicular to the prism faces. The small insets in Figure 10.16 show one example of each, but five others are identical. Six vertical mirror planes pass through the edges of prism faces, and six other mirrors are perpendicular to the prism faces. The figure shows examples of each. The crystal also has a single horizontal mirror plane through its equator. And, it has an inversion center. So, symmetry operates on symmetry – there are six of everything (except the horizontal mirror because it is perpendicular to the 6-fold axis).

This crystal must also have six directions of identical atomic structure and, therefore, six directions with the same hardness, reflectivity, optical properties, and so on. The 6-fold rotation axis affects everything in a crystal, including faces, edges, corners, other symmetry elements, physical properties, optical properties, and atomic arrangement.

10.1.7 Symmetry Is a Property

Mineralogists often speak of a crystal's *symmetry elements* – the different kinds of symmetry a crystal has – in quantitative terms. We can count mirror planes, rotation axes, and inversion centers. If objects have only a few symmetry elements, we say they have *low symmetry*. Those that display many have *high symmetry*. In addition, we say that objects with 6-fold rotation axes have higher symmetry than those with 4-fold, 3-fold, or 2-fold axes, and so on. References to high and low symmetry are necessarily vague because symmetry manifests itself in many different ways.



10.17 Symmetry in an octahedron and a cube

Cubes have the most symmetry possible for crystals: three 4-

fold axes, four 3-fold axes, six 2-fold axes, nine mirror planes, and an inversion center. All this symmetry is shown in Figure 10.17. But, octahedra have the same symmetry (also shown in Figure 10.17). Consider the three 4-fold rotation axes. In a cube they are perpendicular to faces. In an octahedron, they come out at the corners. But, in both, these axes are at 90° to each other. And the four 3-fold axes exit the cube at the corners, but exit the octahedron in the centers of the faces. The 2-fold axes come out of the centers of edges in both crystals. The right side of the figure shows only some of mirror planes because showing them all is too complicated. If you look closely, you will see that the ones shown have identical orientations in both crystals.

A cube has 12 edges, 8 corners and 6 faces. An octahedron has 12 edges, 8 faces and 6 corners. It is as if the faces and corners have switched places. And, both crystals have exactly the same symmetry. Cube faces are at 90° to each other; octahedron faces are at about 55° to each other, but the mirror planes, rotation axes, and the inversion center are identical for both.

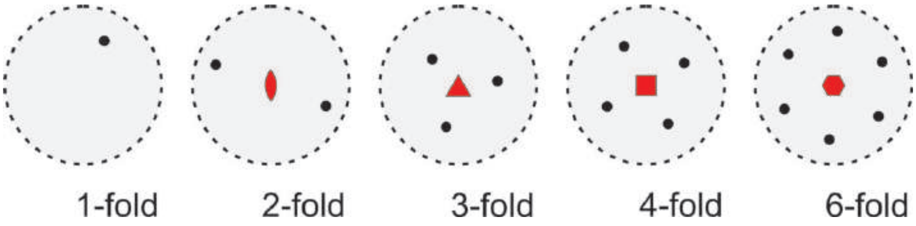
Comparison of the cube and octahedron emphasizes that symmetry is not a physical characteristic. It is a property that objects may possess. With an object in hand, a mineralogist can discuss its symmetry, but a description of an object's symmetry does not unambiguously reveal its appearance. Many objects have mirror planes, yet their overall shapes are quite different. While symmetry does not determine appearance, it does include all aspects of a crystal.

10.2 Stereo Diagrams

10.2.1 Symmetry on Stereo Diagrams

A convenient way to look at the symmetry of a crystal is to use a *stereographic projection*, also called a *stereo diagram*. Stereo diagrams allow us to depict three-dimensional symmetry in a two-dimensional diagram. Although stereo diagrams depict mirror planes, inversion centers, and rotational symmetry, and their relationships to crystal faces, stereo diagrams do not show the shape of faces. The diagrams only show symmetry.

10.2.1.1 Rotation Axes

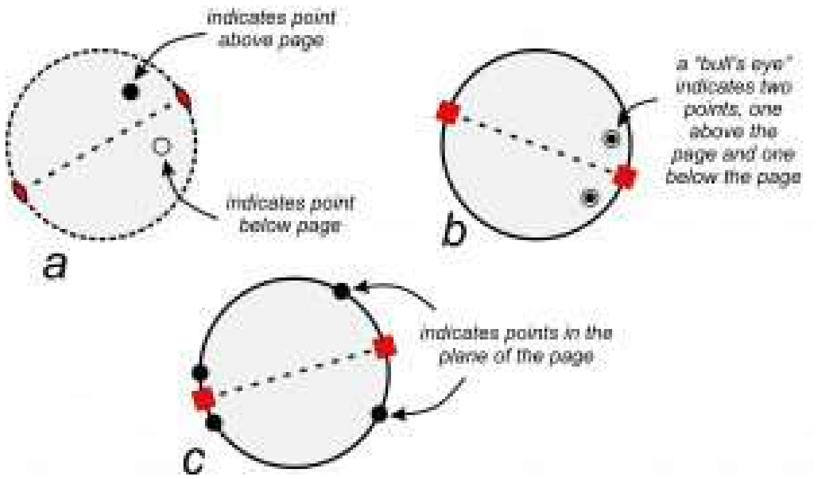


10.18 Proper rotation axes

Stereo diagrams can be quantitative and very complex. In this text, considering their qualitative aspects is sufficient. Figure 10.18 shows stereo diagrams depicting 1-fold, 2-fold, 3-fold, 4-fold, and 6-fold rotation axes perpendicular to the page. The geometric symbols (in red) at the center of the diagrams show the kind of rotation axes. In the five drawings, the rotation axis has operated on a single black dot, producing 0, 1, 2, 3, or 5 other dots by rotation of 360°, 180°, 120°, 90°, and 60° around the center of the diagram.

10.19 Crystals containing proper rotation axes

Figure 10.19 shows examples of crystals that have proper rotation axes. In drawings of this sort, it is often necessary to depict crystals with several differently shaped faces to limit symmetry and make the symmetry clear (as is done in this figure). It is easy to make drawings that have more symmetry than wanted. For example, if the top pyramid faces were not present, the crystals with 2-, 3-, 4-, and 6-fold symmetry would also contain vertical mirrors.



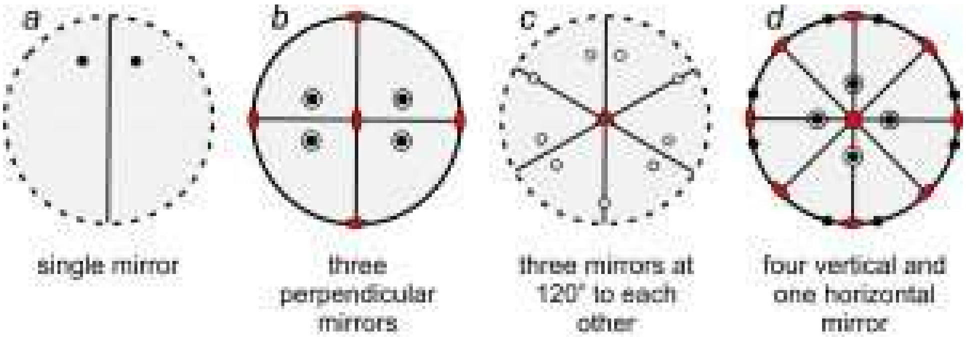
10.20 Rotation axes in the plane of the page

The diagrams in Figure 10.18 show symmetry, and repetition of points, in the plane of the page quite nicely. However, symmetry operations also work in three dimensions. To accommodate the third dimension, we need a way to show points below and above the page. By convention, solid dots represent points above the plane of the page, and circles represent points below the plane of the page (Figure 10.20*a*). A *bull's-eye* symbol, formed by a small circle around a dot, shows a point above the page that is directly above one below the page. Figure 10.20*b* shows two examples. Points within the plane of the page (around the equator of the crystal) always plot as solid dots on the outside circle of the stereo diagram (Figure 10.20*c*).

Figure 10.20*a* and *b* show a 2-fold and 4-fold axis of symmetry lying in (parallel to) the plane of the page. They operate on points above the page to produce points below. For the 2-fold axis, a black dot (above the page) becomes an open circle (below the page) after a rotation of 180° around the axis that lies in the plane of the page. The two symbols are not on top of each other. For the 4-fold axis (10.20*b*), 90° rotations around the axis (that is in the plane of the page) produce four equivalent points. The two points below the page are directly beneath the two points above, and so are shown as bull’s-eyes.

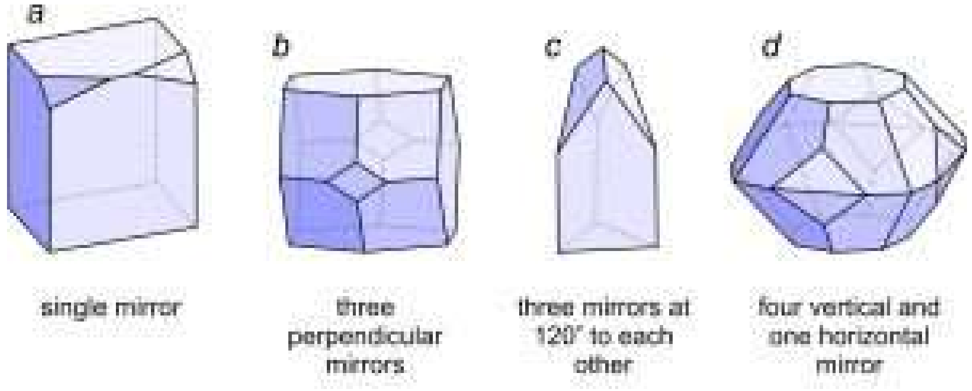
10.2.1.2 Mirror Planes

In Figure 10.20*a*, the outside circle is a dashed line. In the other two diagrams it is solid. Why the difference? A solid outside circle indicates that a horizontal mirror plane reflects points above the page to below the page (shown by the bull’s-eye symbol). In contrast, a dashed circle means there is no reflection and no mirror plane parallel to the page. In Figure 10.20*c*, the points are on the outside and, thus, within the plane of the page, and so cannot reflect up or down. In such cases, the circle could be solid or dashed but is generally shown solid.



10.21 Stereo diagrams with mirror planes

So, mirrors may lie in the plane of the page. They may also have other orientations. For example, the four stereo diagrams in Figure 10.21 include mirror planes that are perpendicular to the page. They appear as straight lines that pass through the centers of the diagrams. Diagram *a* contains a single vertical mirror and two points related by reflection. Diagram *b* contains three mirrors at 90° to each other – one in the plane of the page and two vertical. It has a total of eight points – four above the page and four below. Diagram *c* contains three vertical mirrors at 120° to each other, with nine points (below the page) related by those mirrors. Diagram *d* has a horizontal mirror in the plane of the page and four other vertical mirrors. It contains sixteen points related by the symmetry. Note also that three of the diagrams contain rotation axes (symbols in red) besides mirrors. We will talk in detail about how symmetry elements combine later in this chapter.



single mirror

three perpendicular mirrors

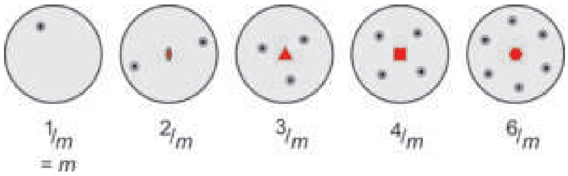
three mirrors at 120° to each other

four vertical and one horizontal mirror

10.22 Crystals with mirror planes

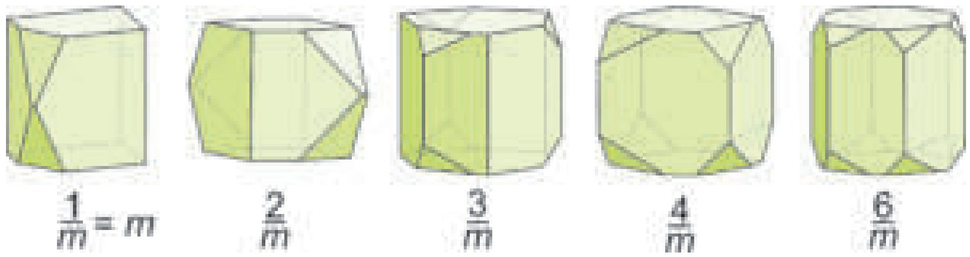
Figure 10.22 shows crystals with symmetries that match the four stereo diagrams in Figure 10.21. Crystal *a* has only a single mirror plane of symmetry. The right side reflects to the left side. Crystal *b* has three perpendicular mirror planes and three 2-fold axes. Crystal *c* has three mirrors that intersect at 120° this requires that a 3-fold axis be present. Crystal *d* has four vertical and one horizontal mirror. It also contains four horizontal 2-fold axes and a vertical 4-fold axis.

10.2.1.3 Rotation Axes with Perpendicular Mirror Planes



10.23 Rotation axes perpendicular to mirror planes

Many crystals have rotation axes that are perpendicular to mirror planes. Crystallographers use shorthand symbols to describe such combinations. We represent them by the symbols $^1/_m$, $^2/_m$, $^3/_m$, $^4/_m$, and $^6/_m$. Figure 10.23 shows stereo diagrams for each. In these drawings, the mirror is horizontal and the rotation axis is vertical (perpendicular to the page). Note that the outer circles are solid in all these diagrams, because points above the page are reflected to below the page. The symbol $^1/_m$ is somewhat redundant because the 1-fold rotation axis changes nothing. So, this symmetry is commonly just signified by *m*.



10.24 Crystals with rotation axes and perpendicular mirror planes

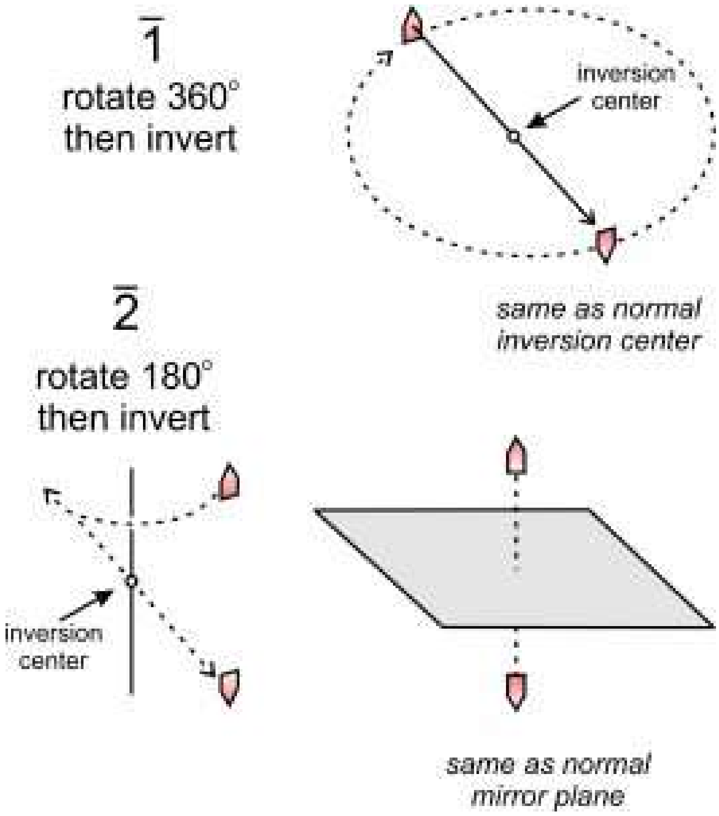
The crystal drawings in Figure 10.24 show crystals with symmetry equivalent to what we saw in Figure 10.23. In all drawings, the top faces reflect to the bottom. Note that if these crystals did not have smallish triangular faces, they would appear to have symmetry that included vertical mirror planes. They would look like simple prisms. These crystals reinforce the idea that multiple faces with different shapes are sometimes needed to depict complex symmetry.

10.2.1.4 Rotoinversion Axes

In the discussions above, we talked about reflection, rotation, and inversion operations. *Rotoinversion* is a fourth, and an important, kind of symmetry operation. Rotoinversion, a combination of rotation and inversion, is a symmetry operation sometimes distinct from the others. The symbols $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$, represent rotoinversion axes. They are articulated as "bar-1," "bar-2," etc.

In a rotoinversion operation, we apply rotation and inversion sequentially. Just as with proper rotation axes, the angle of rotation is 360° for a 1-fold rotoinversion axis, 180° for a 2-fold rotoinversion axis, 120° for a 3-fold rotoinversion axis, etc. (table below.) The difference is that for rotoinversion, rotation of a point is followed by inverting it through the center of a diagram.

rotoinversion axis	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{6}$
rotoinversion operation	rotate 360° and invert	rotate 180° and invert	rotate 120° and invert	rotate 90° and invert	rotate 60° and invert

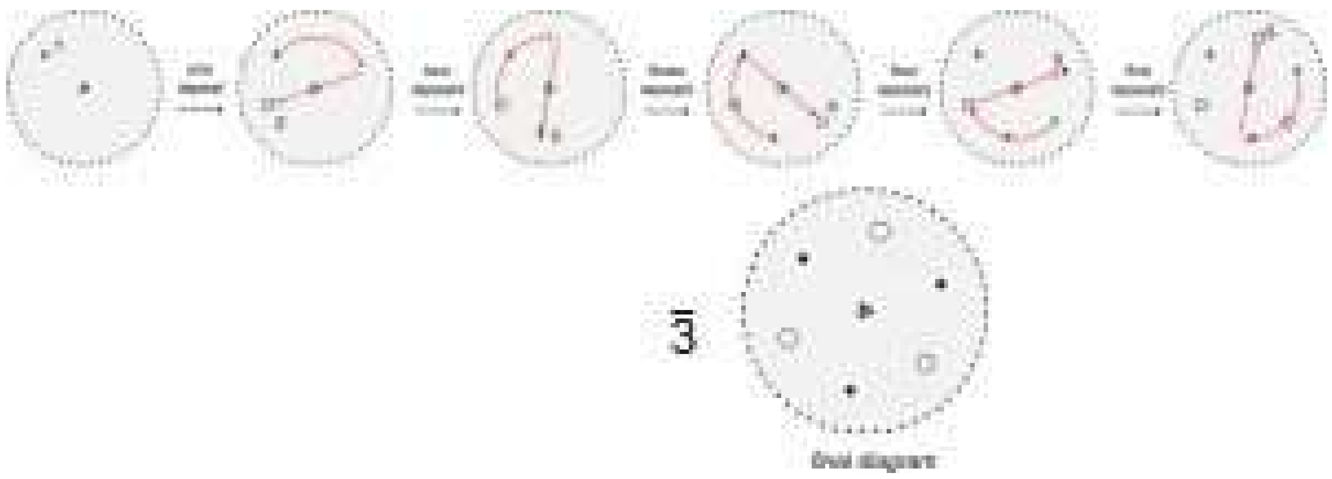


10.25 $\bar{1}$ and $\bar{2}$ rotoinversion operations

Figure 10.25 shows $\bar{1}$ and $\bar{2}$ rotoinversion operations applied to a single house-shaped motif. The $\bar{1}$ operation involves 360° rotation followed by inversion. This is the same as a normal inversion center.

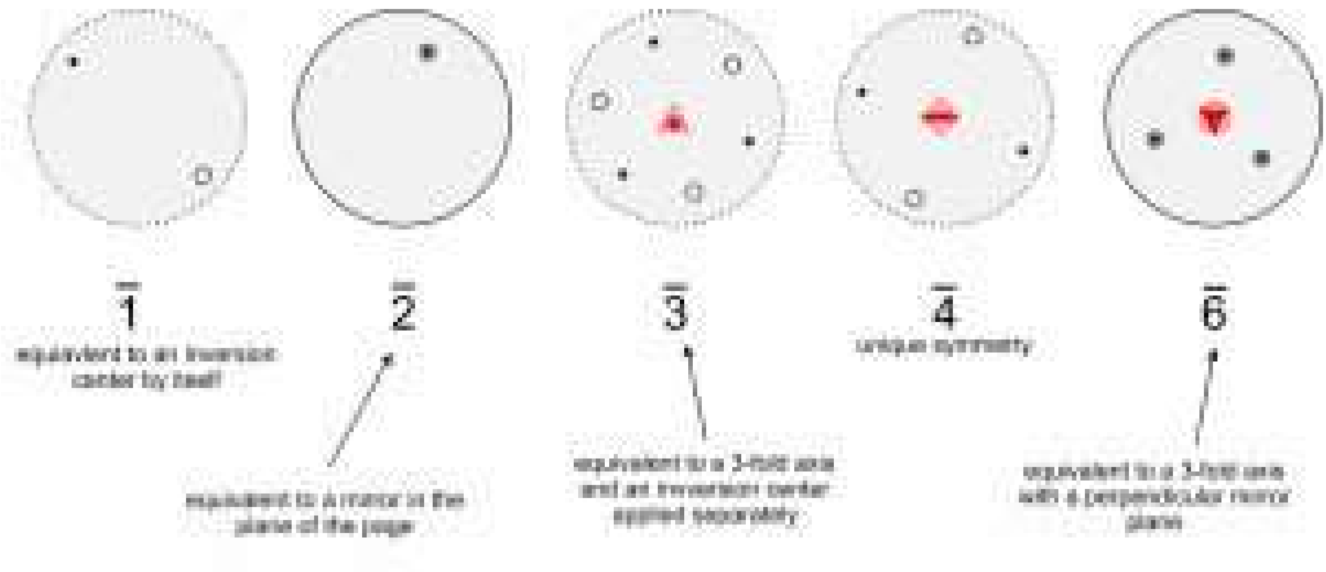
The $\bar{2}$ operation involves 180° rotation followed by inversion. This is the same as reflection by a mirror plane. We include $\bar{1}$ and $\bar{2}$ operations in our list for completeness but recognize that they are redundant.

$\bar{3}$ rotoinversion, however, is not so trivial. For example, in Figure 10.26 (below), we apply a $\bar{3}$ axis to solid point 1 (above the page). Rotation of 120° and inversion produces an open point (point 2, below the page) after one repeat. Point 2 is then rotated 120° and inverted to produce point 3, and so forth. After five repeats, we have produced points 2, 3, 4, 5, and 6, and we are done because a sixth repeat gets us back to the original point. A $\bar{3}$ axis relates six points in total, shown in the large stereo diagram in the Figure. Examination of this diagram reveals that a $\bar{3}$ axis is the same as a 3-fold axis and an inversion center operating independently. Three of the points are above the page and three below. Those above are not directly above those below – they are offset by a rotation of 60°.

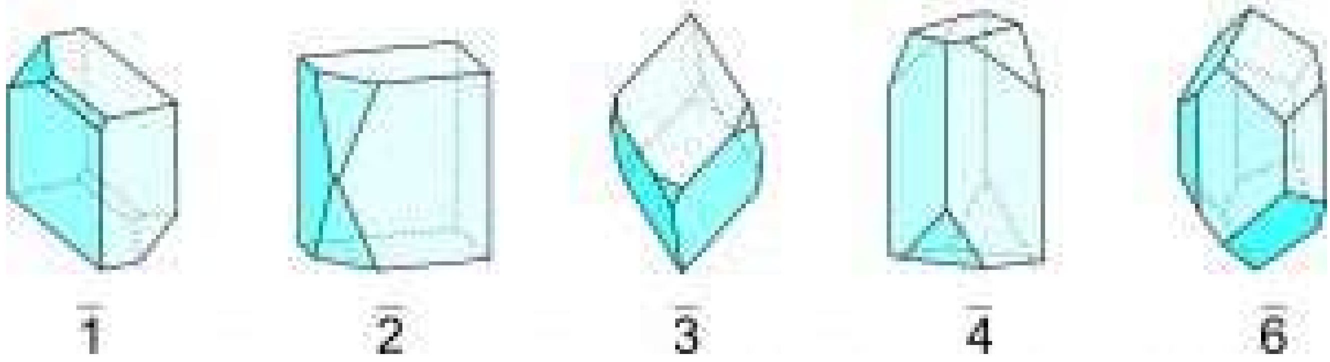


10.26 A 3-fold rotoinversion axis and a crystal with $\bar{3}$ symmetry

Figure 10.27, below, shows stereo diagrams for the different rotoinversion axes. $\overline{2}$, $\overline{4}$, and $\overline{6}$ are not equivalent to rotation and inversion operating separately, nor are they equivalent to proper 2-fold, 4-fold, or 6-fold rotation axes. But a $\overline{2}$ axis is equivalent to *m*; a $\overline{3}$ axis is equivalent to a 3-fold axis and an inversion center applied separately. A $\overline{6}$ axis is equivalent to a vertical 3-fold axis with a perpendicular mirror (in the plane of the page); it is equivalent to $^3/_m$. Note that $\overline{4}$ rotoinversion is the only rotoinversion operation completely distinct from other symmetry operations. Although it is called a *rotoinversion* axis, crystals with $\overline{4}$ symmetry have neither a 4-fold rotation axis nor an inversion center.



10.27 Rotoinversion axes



10.28 Crystals with rotoinversion symmetry

Figure 10.28 shows drawings of crystals with rotoinversion symmetry; they correspond to the stereo diagrams in Figure 10.27. Rotoinversion symmetry is often difficult to pick out in crystals and is more obvious in stereo diagrams.

Crystallographers rarely talk about $\overline{1}$ or $\overline{2}$ symmetry because it is simpler to talk about an inversion center or a mirror plane. References to $\overline{3}$, $\overline{4}$, and $\overline{6}$ are, however, normal, although we could describe two of them in other ways. The stereo diagrams in Figure 10.27 include (in red) the common symbols for $\overline{3}$, $\overline{4}$, and $\overline{6}$ at their centers.

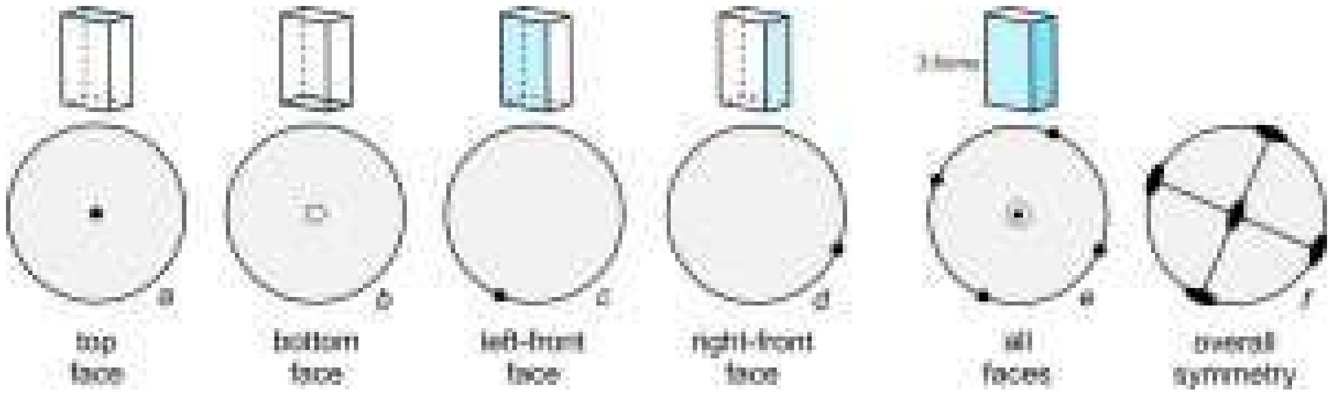
10.3 From Points to Crystal Faces and Forms

In the preceding discussion, we talked about generic points and symmetry on stereo diagrams. And, we looked at some crystals with different symmetries. Now we will return to crystals and make the connection between crystal faces and stereo diagrams.

Crystallographers use the term *form* to describe a set of identical crystal faces related by symmetry. Use of this term is unfortunate, because most of us think of form as meaning *shape*. Further confusion arises because a single crystal may contain multiple *forms*, and a single form may have as many as 48 faces. Additionally, two crystals with identical forms may appear different if the forms are of different sizes. Nonetheless, the term *form* is firmly established in crystallography and unlikely to disappear. Crystallographers use various approaches to name forms, but A. F. Rogers’s system, published in 1935, is commonly used in the United States (Box 10-3).

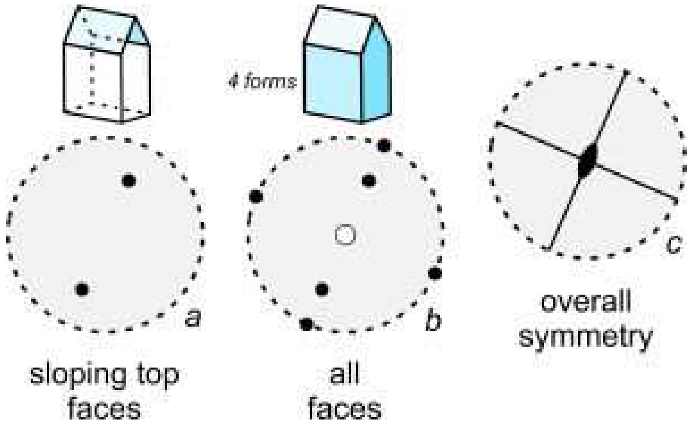
Consider a crystal shaped like a shoe box (Figure 10.29). It contains three pairs of identical faces (opposite sides of the crystal). So, the crystal contains three forms. Figure 10.29

shows how orientations of the horizontal and vertical crystal faces may be shown on a stereo diagram. We depict the horizontal faces on the top and bottom of a crystal as solid and open dots, respectively, in the middle of the circle (drawings *a* and *b*).



10.29 Plotting horizontal and vertical faces on a stereo diagram

Vertical faces always plot as dots on the outside of the circle (drawings *c* and *d*) and are situated to show the aspect of the face (the direction the face is pointing). This crystal contains four vertical faces at 90° to each other, and the crystal is oriented at an arbitrary angle. Drawing *e* shows all six of the faces on one diagram. The bull’s-eye at the center represents the top and bottom faces, and the dots on the circle represent the four vertical faces. Drawing *f* shows the overall symmetry. This crystal contains three perpendicular mirror planes and three perpendicular 2-fold axes.

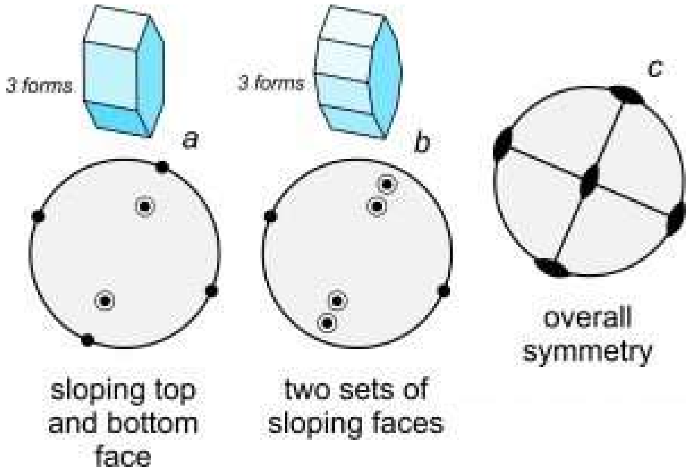


10.30 Plotting sloping faces on a

A stereo diagram

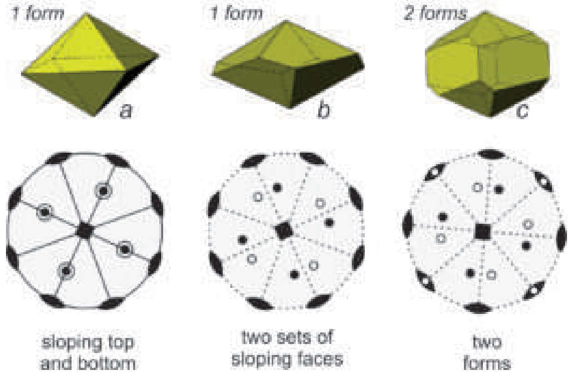
Many crystals contain sloping faces. If so, they plot as dots (or circles) that are somewhere between the center and the outside of a stereo diagram. And, we orient them to show their aspect. The house-shaped crystal seen in Figure 10.30 contains four forms – the same three that are in the shoe box we just saw plus a form composed of the two identical sloping faces on top. Black dots in drawing *a* show the sloping top faces. All faces are depicted in drawing *b*. Note that the bottom face is the only one that is an open circle. It is the only face below the plane of the page. The overall symmetry of this crystal (drawing *c*) is less than the symmetry of the shoe box described above. This crystal contains only two mirrors and a single 2-fold axis.

Earlier in this chapter, we introduced the idea of zones in crystals. In Figure 10.30*b*, five of the dots/circles representing faces are on a line (that is nearly vertical in the drawing). This means the faces are all parallel to a single horizontal direction; it means that together they form a zone.



10.31 Faces with different slopes

A crystal face that is almost, but not quite, horizontal will plot as a point near the center of a stereo diagram. A face that is almost vertical will plot close to the circle on the outside. And, faces with slopes of around 45° will plot halfway between the center and the outside. So, the distance a point is from the centers describes the slope of the face. Figure 10.31 shows an example. Crystal *a*, containing three forms, has sloping faces on both the top and bottom of the crystal. Because the top faces are above the bottom faces, they appear as (two) bull's-eyes within the circle. Crystal *b* (also three forms) contains two sets of sloping faces on the top and bottom, so the drawing contains four bull's-eyes. The symbols closest to the outside of the circle represent the four faces that are almost vertical. The bull's-eyes representing all the sloping faces indicate a zone; all faces in the zone are parallel to a single horizontal line. Drawing *c* shows the overall symmetry of both crystals; they contain three 2-fold axes and three mirrors. Although the two crystals in Figure 10.31 have a different number of faces, their symmetries are the same.

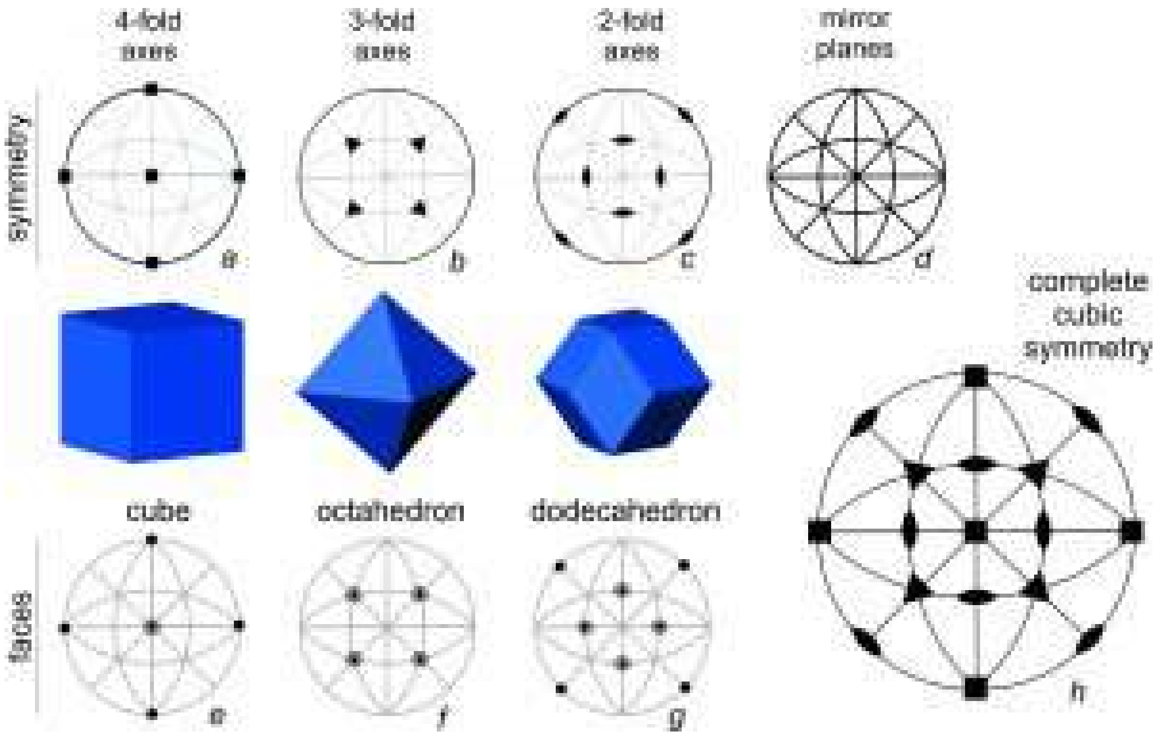


10.32 Examples of crystals and stereo diagrams

Figure 10.32 shows three more examples of crystals and stereo diagrams for each. Crystal *a* has a lot of symmetry – a 4-fold axis, four 2-fold axes and five mirror planes (four vertical and one horizontal). Crystal *b* also has a 4-fold axis and four 2-fold axes but contains no mirrors. Crystal *c* has the same symmetry as crystal *b* but contains four additional vertical prism faces. Unlike the previous figures, the stereo diagrams in Figure 10.32 show symmetry elements and face orientations (dots/circles) in the same diagram. This is standard practice but sometimes leads to a cluttered and confusing drawing, especially if points representing faces fall on top of symmetry elements.

When creating stereo diagrams, we orient a crystal so that rotation axes are vertical or horizontal (in the plane of the page or perpendicular to the page) if we can. This is what we did in Figure 10.32 and previous figures. Because mirror planes are generally parallel or perpendicular to rotation axes, mirrors too are horizontal or vertical most of the time.

If only looking at a stereo diagram, and not a crystal, we can rotate the diagram so that symmetry elements are mostly vertical or horizontal on the page. That means, for example, that if there is only one mirror plane present, we usually align it vertically and it appears as a vertical line in the diagram. But, if we wish to see side faces on a crystal, we usually rotate the crystal some arbitrary angle or the faces will not be visible. Suppose for example we view a cube perpendicular to one of its faces. We will only see a single square face – which is not very revealing. When we look at a cube from an oblique angle, we can see three faces and get a much better idea of its overall shape.



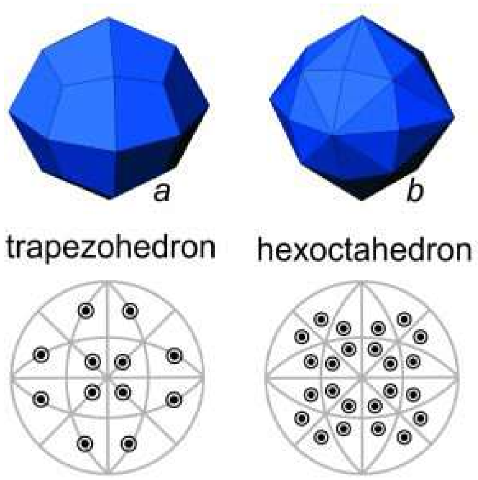
10.33 Special forms with cubic symmetry

Earlier in this chapter, we observed that a cube and an octahedron have the same symmetry. It is worthwhile to revisit that idea using stereo diagrams. Consider the drawings of a cube, octahedron, and dodecahedron above in Figure 10.33. They have identical symmetry that includes 4-fold, 3-fold, and 2-fold rotation axes and many mirrors. We call this symmetry *cubic symmetry*. The large stereo diagram in drawing *h* shows all the elements of cubic symmetry.

In Figure 10.33, stereo diagram *a* above the cube shows the orientation of the 4-fold axes; they are perpendicular to the cube faces. Diagram *b* above the octahedron shows the orientation of the 3-fold axes; they are perpendicular to the octahedron faces. And, diagram *c* above the dodecahedron shows the orientation of the 2-fold axes are; they are perpendicular to the dodecahedron faces. Diagram *d* shows the orientations of the mirror planes; there is one perpendicular to each of the 4-fold and 2-fold rotation axes. The solid outer circle shows the horizontal mirror that goes through the center of each crystal. The four straight lines that intersect at the center of the diagram show vertical mirrors that bisect the crystal faces or that coincide with face edges. The four arc-shaped curves, halfway between the vertical and horizontal straight lines and the outer circle, show inclined mirrors.

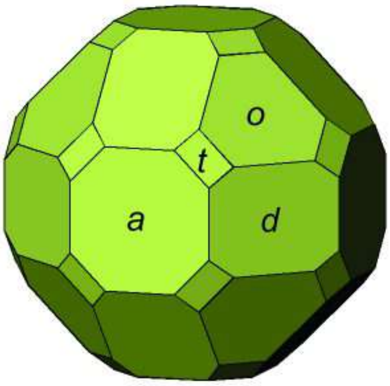
10.3.1 Special Forms and General Forms

Diagrams *e*, *f*, and *g* in Figure 10.33 show stereo diagrams with points corresponding to the faces on a cube, octahedron, and dodecahedron. Cubes, octahedra and dodecahedra are *special forms*, and the points on the stereo diagram are called *special points* because the faces/points coincide with symmetry elements. (For example, cube faces are perpendicular to 4-fold rotation axes.)



10.34 Trapezohedron and hexoctahedron

Besides the cube, octahedron and dodecahedron, other special forms have cubic symmetry. For example, Figure 10.34*a* shows a trapezohedron. As seen in the diagram beneath the crystal drawing, trapezohedron faces lie on (are perpendicular to) mirror planes. So, a trapezohedron is also a special form. The hexoctahedron in Figure 10.34*b*, however is the *general form* that has cubic symmetry. It has the maximum number of faces for minerals with cubic symmetry (48) and the faces are neither parallel nor perpendicular to any symmetry elements (mirrors or rotation axes). No matter what the symmetry, the general form always has more faces than any special form.

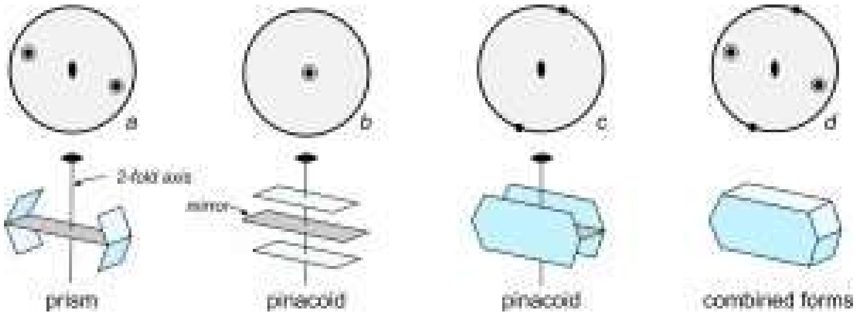


10.35 A crystal containing cube (a), octahedron (o), dodecahedron (d), and trapezohedron (t) faces.

The examples of cubic crystals just seen (in Figures 10.33 and 10.34) contain a single form. But, cubic crystals commonly contain multiple forms. The crystal in Figure 10.35 is an example. It contains four forms: cube, octahedron, dodecahedron, and trapezohedron. This crystal contains four different shaped faces, one corresponding to each form; they are labeled with different letters. In all, the crystal has 38 faces. Yet, the symmetry of this crystal is the same as the crystals seen in the previous two figures.

10.3.2 Open Forms and Closed Forms

Figure 10.36 shows another example of form combinations. The figure contains four stereo diagrams depicting points related by $^2/_m$ symmetry (a 2-fold axis with a perpendicular mirror). Drawings beneath each diagram show the same symmetry using crystal faces. The four faces of the prism (10.36*a*) are the general form; they are neither parallel nor perpendicular to the 2-fold axis or mirror plane. This form does not enclose space and so we call it an *open form*. (In contrast, the cubic forms we saw previously are all *closed forms* – they enclose a volume of space.) Because crystals cannot be open sided, additional crystal faces must terminate open forms. So, crystals with only one form must, of necessity, have a closed form.



10.36 Combining forms

10.37 Twinned orthoclase crystals

Diagrams 10.36*b* and *c* show *pinacoids.* Pinacoids, which are pairs of parallel faces, are open forms. The pinacoids are special forms because the faces are perpendicular (10.36*b*) or parallel (10.36*c*) to the 2-fold axis. The pinacoids include two faces compared with the general form’s four. A combination of the general form and the two pinacoids produces a crystal with $^{2}/_{m}$ symmetry (Figure 10.36*d)*. Crystals with $^{2}/_{m}$ symmetry always contain at least three forms. Compare this drawing with the shapes of the twinned feldspar crystals in Figure 10.37.

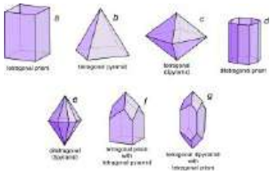
● Box 10-3 The Most Important Form Names

The table below lists the most commonly used form names. They are based on geometric shape or symmetry, but some of the names are unique to crystallography. Mineralogists group crystals into crystal systems based on common symmetry elements. We discuss the systems in detail later in this chapter. Most of the forms occur in more than one system, but the ones at the bottom of the table are exclusive to the cubic system. Figure 10.47 (later in this chapter) contains drawings of some of the cubic forms.

The Most Common Form Names	
Open Forms	
pedions	single face
pinacoids	two parallel faces
prisms	3, 4, 6, 8, or 12 faces parallel to a common line
pyramids	3, 4, 6, 8, or 12 faces that intersect at a common point
domes	two nonparallel faces related by a mirror
sphenoids	two nonparallel faces related by a 2-fold axis
Closed Forms	
scalenohedrons	8 or 12 scalene triangle faces
trapezohedrons	6, 8, or 12 trapezoid faces
disphenoids	four nonequilateral triangular faces
dipyramids	two 3-, 4-, 6-, 8-, or 12-sided pyramids
rhombohedrons	six rhomb-shaped faces
cubic forms	
tetrahedrons	four equilateral triangular faces
cubes (hexoctahedrons)	six square faces
octahedrons	eight equilateral triangular faces
dodecahedrons	12 rhomb-shaped faces
pyritohedrons	12 irregular 5 sided faces
tetartoids	12 five-sided faces
diploids and gyroids	24 five-sided faces

In form names, the suffix –*hedron* means *face*. Prefixes describe the shape of faces: *scaleno*– (scalene triangle), *rhombo*– (rhomb shaped), and *trapezo*– (trapezoid shaped).

We use descriptive modifiers to make the basic names more specific. For example, prisms may be hexagonal-, tetragonal-, orthorhombic- or monoclinic-prisms (having six, four, four, and two faces, respectively). Thus, the modifiers *hexagonal*, *tetragonal*, and *orthorhombic* identify the number of faces. For example, Figure 10.38*a* (below) shows a tetragonal (four faces) prism.



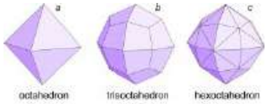
10.38 Crystals in the tetragonal system

We use these same modifiers for pyramids. For example, a hexagonal pyramid has six sides, while a tetragonal pyramid has only four (Figure 10.38*b*). An orthorhombic pyramid has four sides but they are of two different shapes.

We can add a further modifying prefix to the word *pyramid*. The prefix *di*– indicates that there are two equivalent pyramids related by a mirror plane. Figure 10.38*c* is a tetragonal dipyramid.

The prefixes *di-*, *tris-*, *tetra-*, and *hex*– describe a doubling, tripling, and so on, of faces. If each of the four sides on a tetragonal prism is split down the middle to produce two faces we get a ditetragonal prism (Figure 10.38*d*). And, if each face on a tetragonal pyramid is split into two, we get a ditetragonal pyramid (Figure 10.38*e*). These different forms can combine in a single crystal; Figures 10.38*f* and *g* show some combinations.

Similarly, if each face on an octahedron (Figure 10.39*a*) is replaced by three faces, the result is a trisoctahedron (Figure 10.39*b*). If each face on an octahedron is replaced by six faces, the result is a hexoctahedron (Figure 10.39*c*).



10.39 Variations on an octahedron

10.4 Combinations of Symmetry Elements: Point Groups

symmetry operators

i

$m = \bar{2} = {}^{1}/_{m}$

1

2

3

4

6

$\bar{3}$

$\bar{4}$

$\bar{6} = {}^{3}/_{m}$

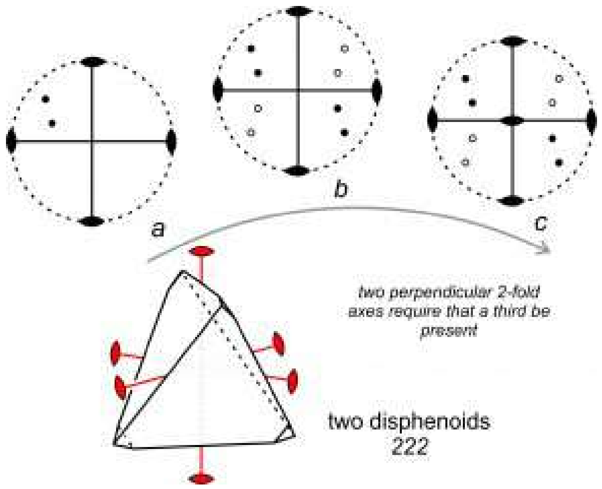
${}^{2}/_{m}$

${}^{4}/_{m}$

${}^{6}/_{m}$

Because some symmetry operators are redundant, we do not need them all to describe the symmetry of crystals. By convention, crystallographers use the 13 operators listed on the left in the table seen here. In mathematical terms, these 13 are *sufficient* to describe symmetry in any crystal.

These symmetry operators can combine, so more than one can be present in a crystal. But, the number of possible combinations is limited for two reasons. First, some combinations lead to other symmetry. Second, some combinations are contradictory and thus impossible.

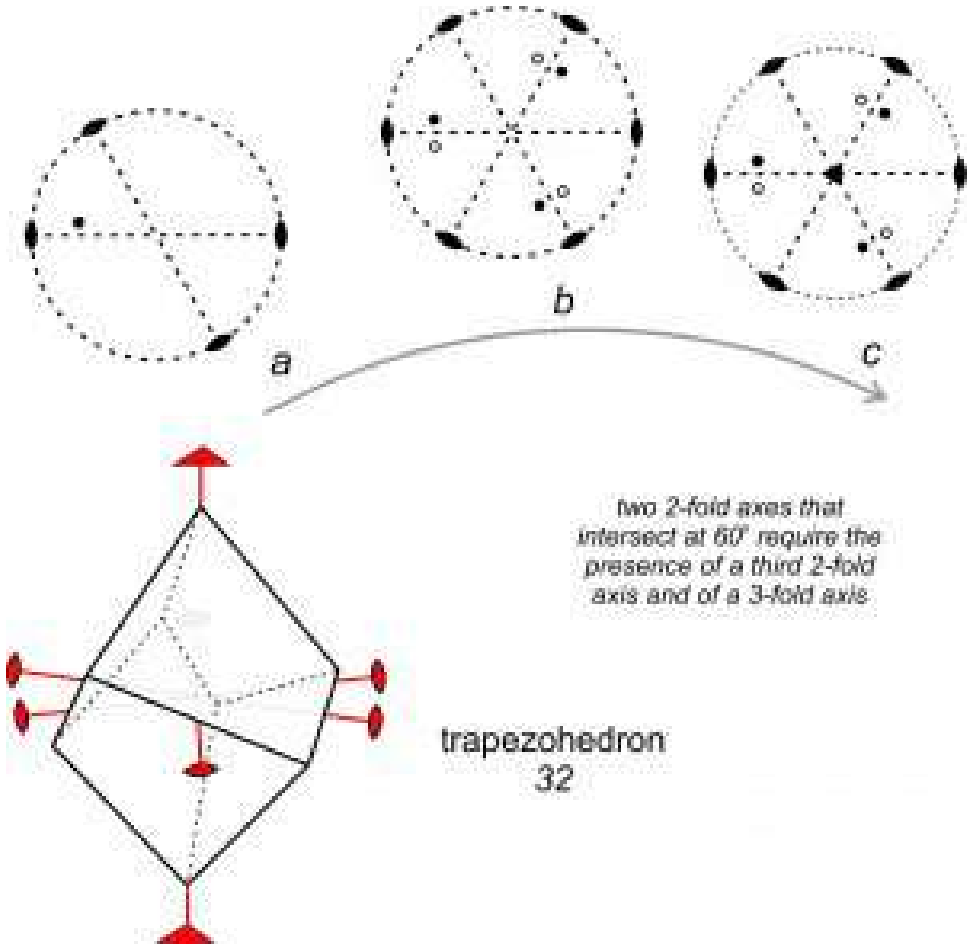


10.40 Three 2-fold axes

Consider, for example, a crystal that has two 2-fold axes of symmetry that intersect at 90° , as depicted in Figure 10.40. If we start with dots representing two faces (diagram *a*), application of the symmetry operators produces six more dots/faces (diagram *b*). Four of the faces are above the page and four below. Diagram *b* reveals that a third 2-fold axis is perpendicular to the original two, shown by a lens shape at the center of diagram *c*. Thus, we see that all objects that have two perpendicular 2-fold axes of symmetry must have a third 2-fold axis. It does not matter which two 2-fold axes we choose initially; the third must be there. Figure 10.40 reinforces what we concluded earlier – that symmetry operators operate on each other.

The symmetry depicted in Figure 10.40 consists of three mutually perpendicular 2-fold axes. We use the shorthand notation *222* to describe this symmetry. The drawing in the bottom of Figure 10.40 is only one of many possible crystal shapes that have *222* symmetry. The three 2-fold axes (shown in red) pass through the centers of edges of the crystal. Four faces related by *222* symmetry make up a *disphenoid*. The crystal depicted contains two forms; both are disphenoids. The four faces of one form are, however, quite small and just show at the corners of the crystal.

We call distinct combinations of symmetry, such as 222, *point groups*. So, the crystal in Figure 10.40 belongs to point group 222. Figure 10.36 showed a crystal that belonged to a different point group, $^{2}/_{m}$. Point groups describe symmetry around a point in the center of a crystal, and thus they relate the points in a stereo diagram to each other. The word group is used because we may treat the principles of symmetry using mathematical group theory. The terms *operator* and *operation* also derive from group theory. In group theory, the 13 operators listed in the table above form a *basis*, which means we need no other operators to describe all possible manifestations of symmetry. Box 10-4 describes the Hermann-Mauguin symbols we use to describe different symmetries and point groups.

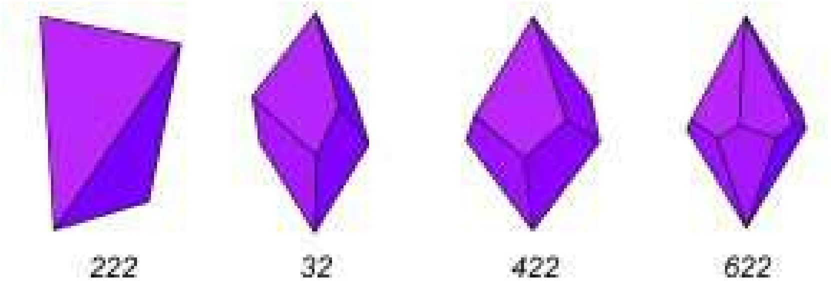


two 2-fold axes that intersect at 60° require the presence of a third 2-fold axis and of a 3-fold axis

10.41 2-fold axes intersecting at 60°

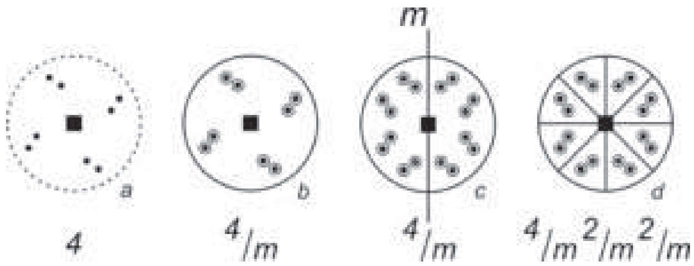
Figure 10.41 shows another example of symmetry operators acting on each other. Two 2-fold axes intersect at 60° (diagram *a*). Starting with one point and applying the symmetry operators, we soon generate five more equivalent points (diagram *b*). Examination of the resulting pattern shows that a third 2-fold axis lies at 60° to the first two. Additionally, a 3-fold axis (shown by a triangle at the center of the diagram) is perpendicular to the two folds (diagram *c*). Another way of looking at the symmetry in Figure 10.41 is to notice that the 3-fold rotation axis acts on the 2-fold axes. It requires that if one 2-fold axis of symmetry is present, two others must be present as well, and that the three are related by angles of 120°. The point group for this symmetry is designated 32. The drawing in the bottom of Figure 10.41 shows a crystal that has 32 symmetry. It is a *trapezohedron*, named after the shapes of its faces.

In Figure 10.40 we showed that two perpendicular 2-fold axes required the presence of a third mutually perpendicular one. In Figure 10.41, we showed that if two 2-fold axes intersect at 60°, another 2-fold and a 3-fold will also be present. Similarly, if we start with a 4-fold axis and one perpendicular 2-fold, we will find other 2-folds perpendicular to the 4-fold and at 45° to each other. If we start with a 6-fold axis and a perpendicular 2-fold, we will find six 2-fold axes in all.



10.42 Crystals belonging to point groups 222, 32, 422, and 622

Figure 10.42 shows drawings of crystals belonging to point groups *222*, *32*, *422*, and *622*. Note that mirror planes are absent in all four cases. The top and bottom of the crystals do not mirror each other, and the crystal faces do not have mirror planes down their centers or edges (or else an *m* would be included in the symbol for the point group). The four examples point out that symmetry operators cannot combine in random ways. The presence of two rotation axes requires a third and perhaps more. We can also show that a combination of a rotation axes and a mirror, at angles other than 0° or 90° to each other, requires other rotation axes to be present. Seeing symmetry on the complicated crystal drawings in Figure 10.42 is difficult. (That’s why we have stereo diagrams!) A better way to examine symmetry of crystals is to study models in the laboratory.

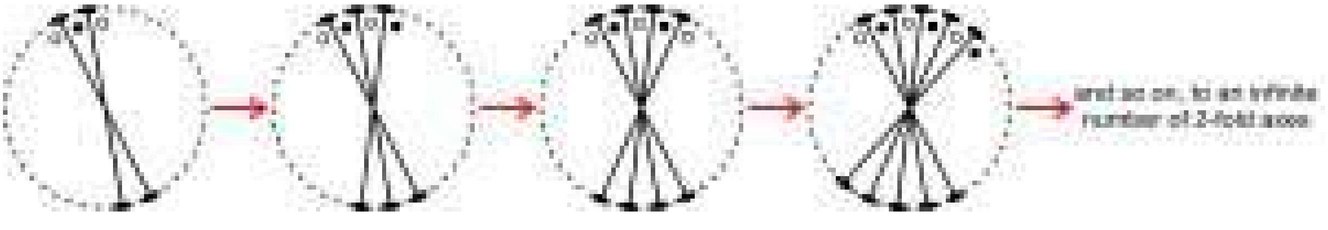


10.43 4/m2/m2/m symmetry

Before leaving this discussion about the way symmetry combines to produce other symmetry, let’s consider one more example. Figure 10.43*a* shows points related by a 4-fold rotation axis. We can add a horizontal mirror (shown by the solid outer circle) to produce the points shown in diagram *b*. Adding a vertical mirror produces diagram *c*. And, in diagram *c*, we see that this is equivalent to symmetry that includes a 4-fold axis and two different kinds of 2-fold axes (shown in diagram *d*). All the rotation axes are perpendicular to mirror planes. This is point group $^4/_m{}^2/_m{}^2/_m$.

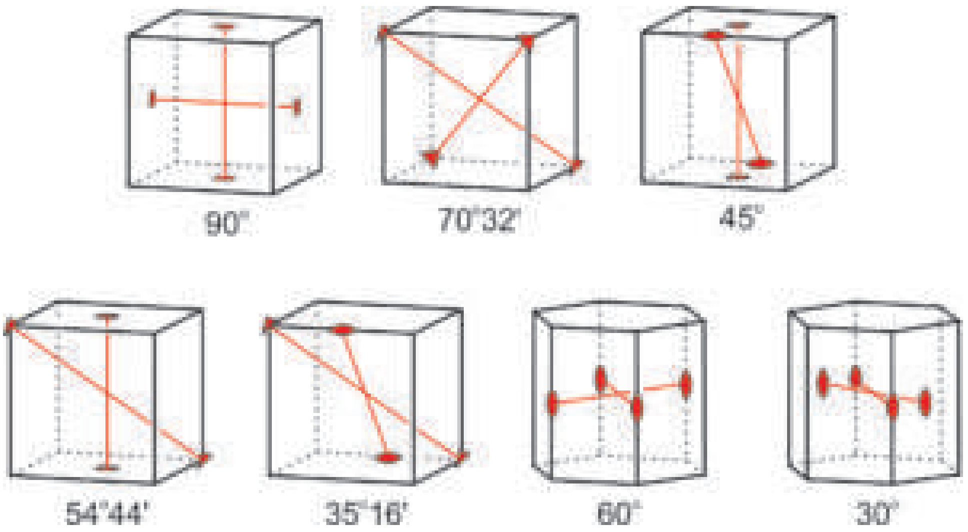
10.4.1 Special Angles and General Angles

Angles such as 30°, 45°, 60°, 90°, or 120° are called special angles. They all divide evenly into 360°. We call nonspecial angles *general angles*. In the examples in Figure 10.43, and others considered previously, we started with rotation axes and mirror planes that intersected at special angles. Suppose we start with axes or mirrors that intersect at general angles. What will be the result?



10.44 Infinite symmetry is not possible

The first diagram in Figure 10.44 shows two intersecting 2-fold axes and three points related by them. The angle between the axes is small and does not divide evenly into 360°. It is a general angle. We may apply the 2-fold axes to each other to generate more 2-fold axes and points, moving around the diagram in a stepwise manner as shown. We could do this forever, continuing around the circle indefinitely, because the new axes and points we generate will never coincide with others already present. When we continue this operation all the way around the circle, we will not end back where we started. So, the number of 2-fold axes becomes infinite, and an infinite-fold axis of symmetry must be perpendicular to the plane of the page. This is equivalent to the symmetry of a circle. Since crystals consist of a discrete number of faces (and atomic arrangements consist of a discrete number of atoms), we know that infinite symmetry is not possible. We may therefore conclude that if crystals have two 2-fold axes, they must intersect at a special angle so that they are finite in number.



10.45 Possible intersection angles for rotation axes

The preceding discussion suggests that rotation axes only combine in a limited number of ways. In fact, angles between rotation axes are limited to the seven depicted in Figure 10.45. We have already seen examples of each. These drawings are of a cube and a hexagonal prism, but angles between rotation axes in crystals of other shapes are limited to the same seven values. The possible angles between rotation axes are all special angles. If we carried out the exercise, we would find that in crystals with both rotation axes and mirror planes, the angles between the rotation axes and the mirror planes are limited to only a few special angles as well. Otherwise, we have infinite symmetry. In most crystals the angles are 0° (the rotation axis lies within the plane of the mirror) or 90° (the rotation axis is perpendicular to the mirror).

● Box 10-4 Hermann-Mauguin Symbols to Designate Point Groups

The symbols used in this book are based on notations developed by C. H. Hermann and C. V. Mauguin in the early 1900s. They have been used by most crystallographers since about 1930. One, two, or three symbols describe a point group; they combine in different ways for different systems.

crystal system	possible first symbol	possible second symbol	possible third symbol	example of a point group
cubic hexagonal tetragonal orthorhombic monoclinic triclinic	$4, {}^{4}/_{m}, \bar{4}, 2, {}^{2}/_{m}$ $6, {}^{6}/_{m}, \bar{6}, 3, \bar{3}$ $4, {}^{4}/_{m}, \bar{4}$ $222, mm2, {}^{2}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ $2, {}^{2}/_{m}, m$ $1, \bar{1}$	$3, \bar{3}$ $2, {}^{2}/_{m}, m$ $2, {}^{2}/_{m}, m$ $2, {}^{2}/_{m}, m$	$2, {}^{2}/_{m}, m$ $2, {}^{2}/_{m}, m$ $2, {}^{2}/_{m}, m$ $2, {}^{2}/_{m}$	$\bar{4}3m$ ${}^{6}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ 422 $mm2$ ${}^{2}/_{m}$ $\bar{1}$

Numbers in the symbols refer to rotation axes of symmetry; a bar over a number indicates a rotoinversion axis. Mirrors, designated by *m*, are perpendicular to an axis if they appear as a denominator (for example, ${}^{4}/_{m}$), and parallel to an axis otherwise. When articulating the symbols, they are pronounced just as if they were typographical characters. ${}^{4}/_{m}\bar{3}2/m$, for example, is read “four over em, bar three, two over em.”

For cubic point groups, the first symbol describes three mutually perpendicular principal symmetry axes, oriented perpendicular to cube faces (if cube faces are present). The second describes four axes oriented at angles of 54°44′ to the principal axes. They correspond to the *body diagonals* of a cube, a diagonal from a corner through the center to the opposite corner. The third symbol, if present, describes six 2-fold axes or mirror planes oriented at angles of 45° to the principal axes. They correspond to *edge diagonals* of a cube, diagonals from the center of edges through the center of the cube to the opposite edge.

For hexagonal point groups, the first symbol describes the single principal axis. The second, if present, describes three secondary rotation axes oriented at 120° to each other and perpendicular to the principal axis, or three mirror planes oriented at 120° to each other and parallel to the principal axis. The third symbol, if present, represents mirror planes or 2-fold axes oriented between the secondary axes.

For tetragonal point groups, the first symbol represents the principal axis. The second, if present, represents two secondary axes perpendicular to each other and to the principal axis, or two mirror planes oriented at 90° to each other and parallel to the principal axis. The third represents axes or mirror planes between the secondary axes.

Only three orthorhombic point groups are possible. Point group 222 has three mutually perpendicular 2-fold axes. Point group *mm*2 has one 2-fold axis with two mutually perpendicular mirror planes parallel to it. Point group ${}^{2}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ has three perpendicular 2-fold axes with mirror planes perpendicular to each.

For monoclinic point groups, only one symmetry element is included in the Hermann-Mauguin symbols because the only possible symmetries are a 2-fold axis, a mirror, or a 2-fold axis with a mirror perpendicular to it. Similarly, for triclinic crystals, the only possible point groups are 1 and $\bar{1}$.

10.5 Point Groups and Crystal

Systems

The 32 Point Groups

system	point group	general form
cubic	$^{4}/_{m}\bar{3}\,^{2}/_{m}$	hexoctahedron
	432	gyroid
	$\bar{4}3m$	hextetrahedron
	$^{2}/_{m}\bar{3}$	diploid
	23	tetartoid
hexagonal	$^{6}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	dihexagonal dipyramid
	622	hexagonal trapezohedron
	$6mm$	dihexagonal pyramid
	$\bar{6}m2$	ditrigonal dipyramid
	$^{6}/_{m}$	hexagonal dipyramid
	6	hexagonal pyramid
	$\bar{6}$	trigonal dipyramid
rhombohedral	$\bar{3}2m$	hexagonal scalenohedron
	32	trigonal trapezohedron
	$3m$	ditrigonal pyramid
	$\bar{3}$	rhombohedron
	3	trigonal pyramid
tetragonal	$^{4}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	ditetragonal dipyramid
	422	tetragonal trapezohedron
	$4mm$	ditetragonal pyramid
	$\bar{4}2m$	tetragonal scalenohedron
	$^{4}/_{m}$	tetragonal dipyramid
	4	tetragonal pyramid
	$\bar{4}$	tetragonal disphenoid
orthorhombic	$^{2}/_{m}\,^{2}/_{m}\,^{2}/_{m}$	rhombic dipyramid
	222	rhombic disphenoid
	$mm2$	rhombic pyramid

monoclinic	$2/m$ 2 m	monoclinic prism sphenoid dome
triclinic	$\bar{1}$ 1	pinacoid pedion

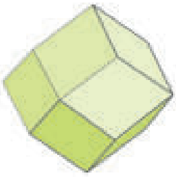
For the reasons discussed above, symmetry operators can combine in a surprisingly small number of ways. Only 32 combinations are possible; they represent the only combination of symmetry elements that crystals, or arrangements of atoms, can have. This leads to the division of crystals into 32 distinct point groups, also sometimes called the 32 *crystal classes*, each having their own distinct symmetry. They are listed in the table here.

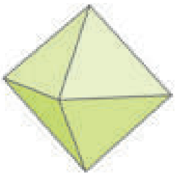
Although the expression *point group* refers only to symmetry, and *crystal class* refers specifically to the symmetry of a crystal, the semantic difference is subtle and the two phrases are often used interchangeably by mineralogists. We could make drawings of crystal shapes with all 32 possible symmetries, but some of them are not represented by any known minerals.

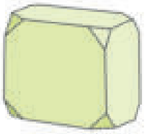
The column on the right in the table lists the names of the general forms for each point group. Sometimes crystallographers use these form names as names for the crystal classes. Some of the general forms, indicated by blue text, are open forms that must combine with other forms to make a crystal, like the forms we saw in Figure 10.36.

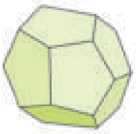
Each of the 32 classes belongs to one of the seven *crystal systems* (*cubic*, *hexagonal*, *rhombohedral*, *orthorhombic*, *tetragonal*, *monoclinic*, and *triclinic*, listed in the table) based on common symmetry elements. These common symmetries reflect the shapes of the crystal's unit cells (discussed at the beginning of this chapter and greatly expanded upon in the next chapter). In some references, the hexagonal and rhombohedral systems are considered divisions within a larger system instead of being separate. We are not doing that in this book because doing so adds complication and is not useful. Figure 10.46 shows representative drawings for common minerals that belong to each system.

Cubic

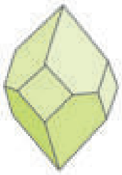

garnet

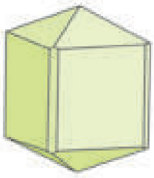

spinel

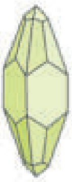

halite

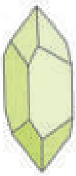

pyrite

Tetragonal

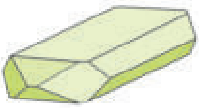

apophyllite

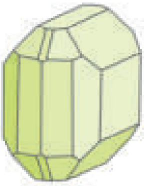

rutile

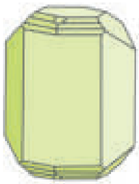

zircon

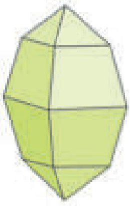

wulfenite

Orthorhombic

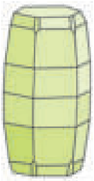

barite

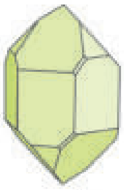

olivine


topaz

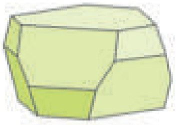

sulfur

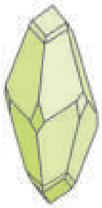
Hexagonal


corundum

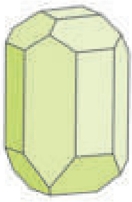

quartz

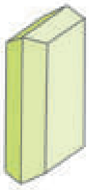
Rhombohedral

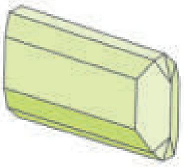

ilmenite

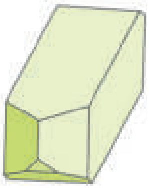

calcite

Monoclinic

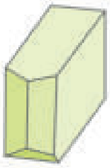

diopside


gypsum


epidote


orthoclase

Triclinic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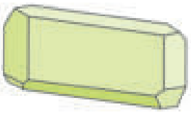
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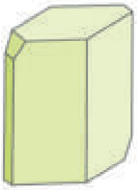
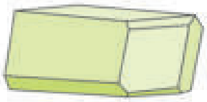

kyanite


rhodonite

10.46 Examples of mineral crystals in different systems

For further discussion of the similarities and differences of crystals belonging to different crystal, check out the video linked below:

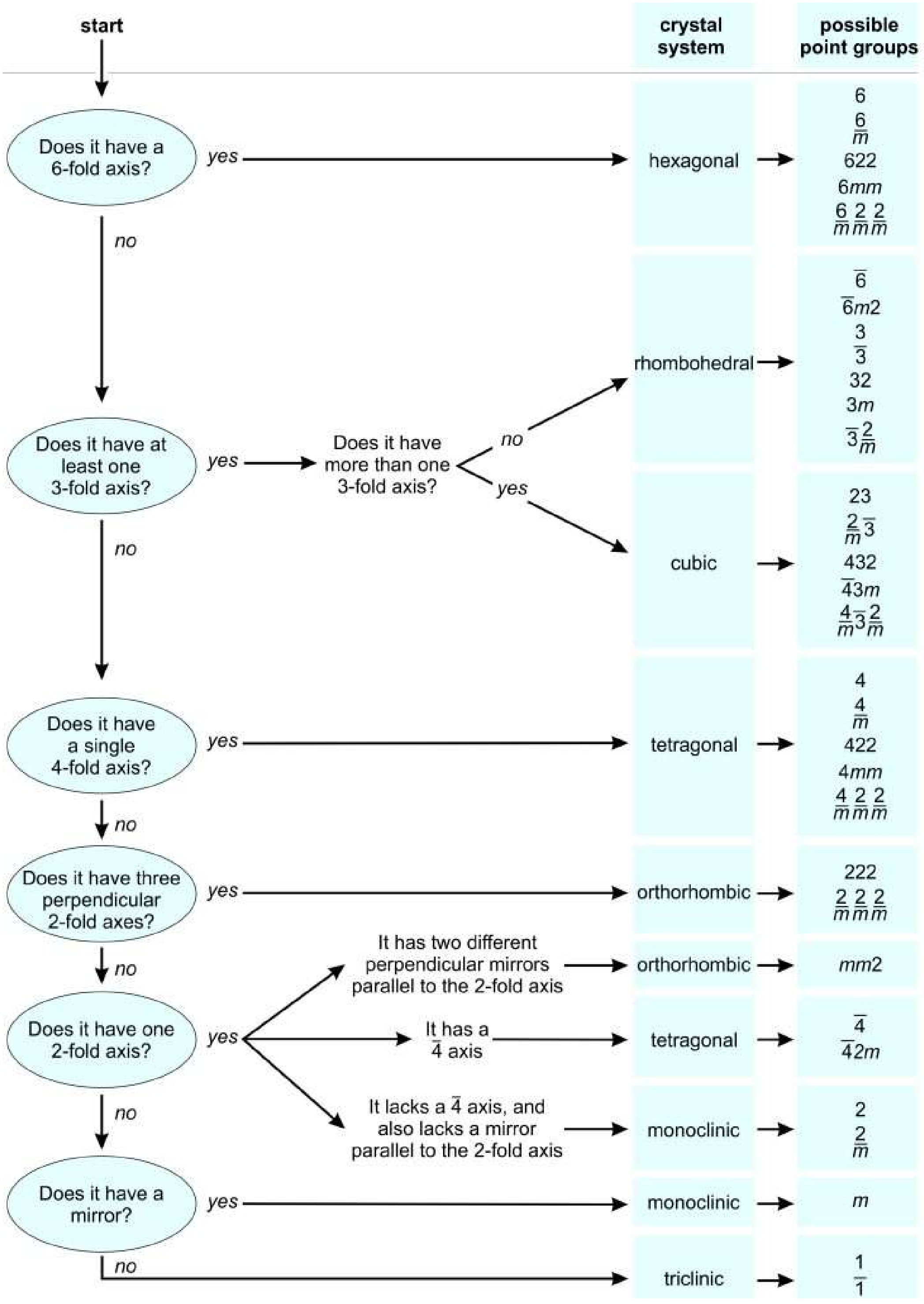
▶ Video 10-1: A closer look at different crystal systems (6 minutes)

Box 10-5 contains a flow chart that can be used to determine the crystal system and point group of many well-formed crystals. But, sometimes determining the point group and system of a crystal, especially for imperfect crystals, is quite difficult or impossible. Overall, it is much easier to see symmetry in crystals with high symmetry (*e.g.*, cubic or hexagonal crystals) than in crystals with lesser symmetry. Distinguishing monoclinic from triclinic crystals, for example, can be very difficult. Yet, crystals that belong to a given system share characteristics, so we can sometimes identify the crystal system quite quickly (especially for crystals with lots of symmetry). For example, as seen in Figure 10.46:

- cubic crystals tend to be equant (equidimensional)
- multiple perpendicular faces are common in cubic, tetragonal and orthorhombic crystals
- hexagonal and tetragonal crystals may contain prism faces parallel to a long dimension
- hexagonal crystals may contain prism faces that intersect at 120°
- rhombohedral crystals typically show 3-fold symmetry
- monoclinic crystals are commonly tabular (thin in one dimension)
- orthorhombic crystals often have an overall shoe-box shape

Minerals belong to all seven crystal systems. About 10% of the common minerals are cubic, 10% are tetragonal, 10% are triclinic, 20% are hexagonal or rhombohedral; the remainder are 25% orthorhombic and 25% monoclinic. Within each system, different point groups have different amounts of symmetry. Most natural crystals fall into the point group with the highest symmetry in each system. Few belong to the point groups of lowest symmetry.

● Box 10-5 Flow Chart for Determining Crystal System and Point Group



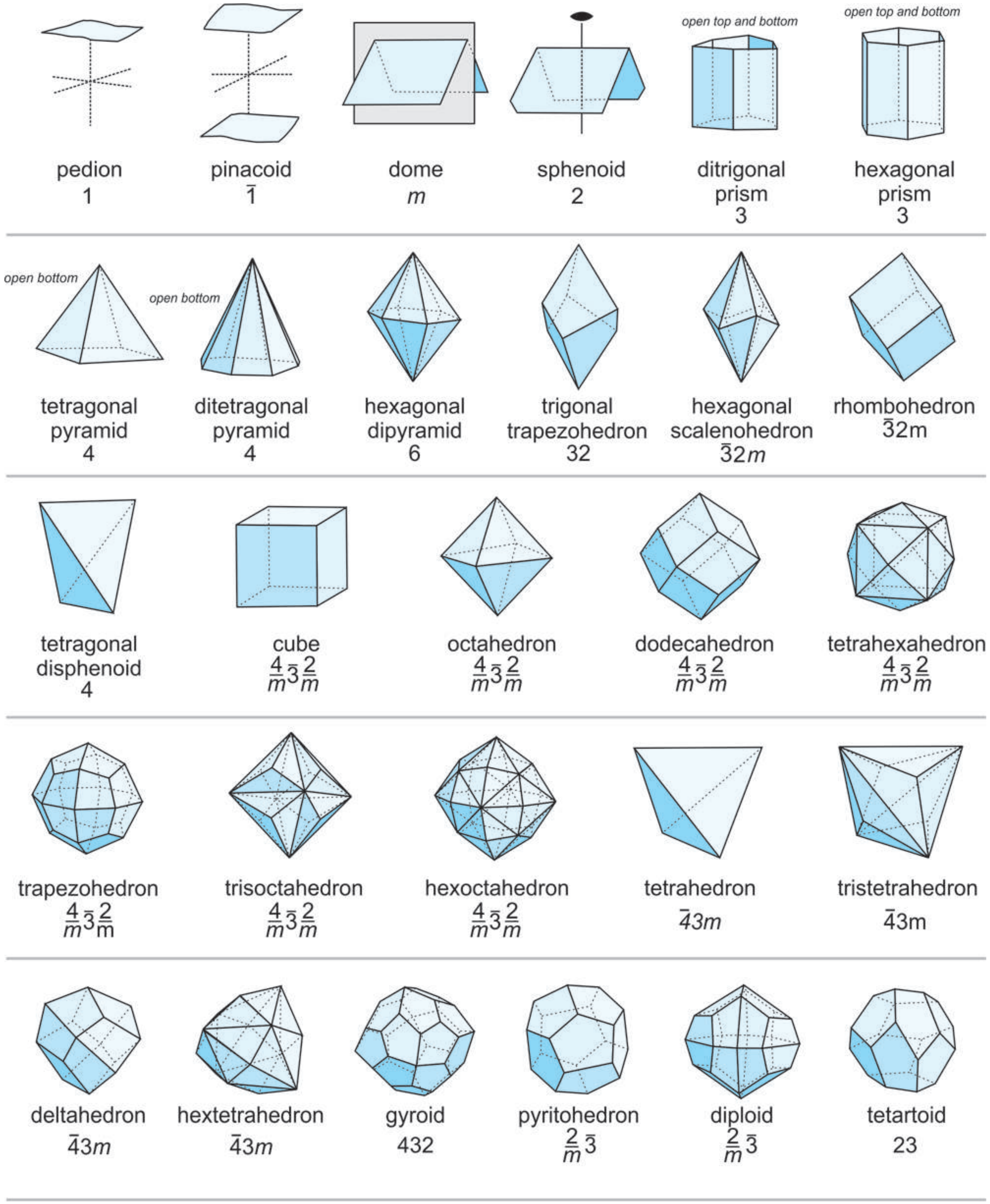
10.5.1 Forms and Point Groups

Most mineral crystals contain more than one form, leading to a large but limited number of possible combinations. The number is limited because the shape and symmetry of crystal faces depend on a crystal’s point group which, in turn depends on the atomic arrangement within the crystal. For example, if the atoms within a crystal are not arranged in hexagonal patterns, forms may not have hexagonal symmetry. Similarly, a crystal may not develop a cubic form unless atoms are in a cubic arrangement. Thus, certain forms never coexist in crystals, while others are often found together. Because the forms present in particular crystals depend on atomic arrangements, they are generally consistent for a given mineral. Uncertainty arises, however, because some minerals can have crystals with several different combinations of forms, and it is not always clear why one develops instead of another.

The number of possible forms is limited. On the basis of the relative positions of their faces and possible symmetries, only 48 can be distinguished. Figure 10.47, below, shows 28 examples. Symmetry is listed for each, but many of the forms can occur in crystals of more than one point group because they can be both general forms and special forms. For example, a tetragonal pyramid is the general form for crystals with symmetry 4. It is a special form for crystals with symmetry $4mm$. A rhombohedron is the general form for point group $\bar{3}$, but is a special form in point groups 32 and $\bar{3}$. And, cube faces may be present in crystals with symmetry of any of the cubic point groups (23, 432, $^{2}/_{m}\bar{3}$, $\bar{4}3m$, or $^{4}/_{m}\bar{3}\,^{2}/_{m}$). The table below Figure 10.47 lists the possible forms in each of the 32 point groups.

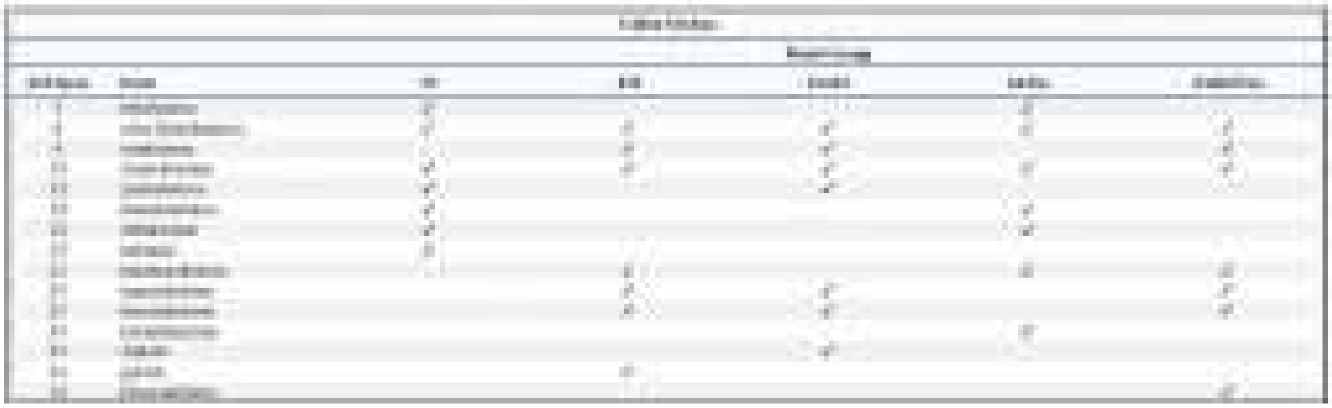
We should emphasize that although only 48 possible forms exist, they can have an infinite number of sizes and shapes. A disphenoid, a form consisting of four faces, may be tall and skinny or short and wide. Nevertheless, it is still a disphenoid. And Figures 10.36 and 10.37 show a crystal that contains two different pinacoids with different shaped faces.

Forms retain their names, even if truncated by other forms. Consider the complex crystal in Figure 10.35. It contains four forms: cube, octahedron, trapezohedron, and dodecahedron. The faces corresponding to the forms do not have the same shape as they would if they were the only form in the crystal. And, in many other figures (*e.g.*, Figures 10.28, 10.32, 10.38), pyramids and prisms truncate each other.



10.47 28 of the possible 48 forms

Possible Forms in Different Point Groups



10.5.2 Characteristics of Crystals Belonging to the Different Crystal Systems

10.5.2.1 Cubic System

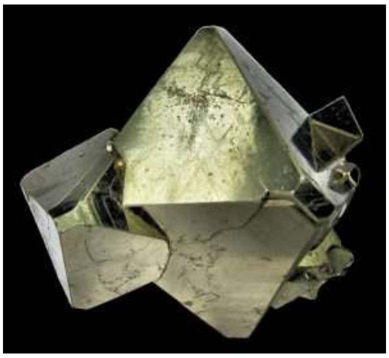
The cubic system is also called the *isometric system*. Crystals have high symmetry, all having four 3-fold or four $\bar{3}$ axes. Some have three 4-fold axes as well, and some have 2-fold axes or mirror planes. Cubes and octahedra are examples of forms belonging to the cubic system, but other forms belong to the cubic system, too. We saw some special forms (cube, octahedron, dodecahedron, and trapezohedron) and the general form, a hexoctahedron, earlier in this chapter.

The three photos below are crystals belonging to the cubic system. Figure 10.48 shows a dodecahedral garnet. It has symmetry $^{4}/_{m}\bar{3}^{2}/_{m}$; a dodcahedron is a special form in that point group. Figure 10.49 shows a pyrite crystal with 5-sided faces. The form is called a *pyritohedron*. Pyrite has symmetry $^{2}/_{m}\bar{3}$, and the pyritohedron is the general form in the $^{2}/_{m}\bar{3}$ point group. Figure 10.50 shows pyrite octahedra. Some small cube faces are present, too. Like the dodecahedral garnet, these crystals have symmetry $^{4}/_{m}\bar{3}^{2}/_{m}$. And like the dodecahedron, octahedra and cubes are special forms in the class.

Crystals of the cubic system may have many different and complex shapes, but all tend to be *equant*, meaning they are approximately equidimensional. Often the crystals contain only one or two forms.

10.48 Pyrope (garnet) ($Mg_3Al_2Si_3O_{12}$) crystal with dodecahedral faces

10.49 Pyrite (FeS_2) pyritohedron. 3.2 cm across.



10.50 Pyrite (FeS_2) octahedra with small cubic faces.

We saw other examples of minerals whose crystals belong to the cubic system in earlier chapters:

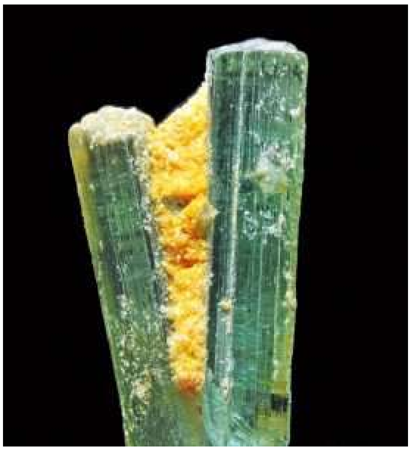
- pyrite in Figure 3.3 (Chapter 3)
- halite in Figure 3.2 (Chapter 3)
- garnet in Figure 3.6 (Chapter 3)
- fluorite in Figure 3.69 (Chapter 3), Figure 4.37 (Chapter 4)
- galena in Figure 9.34 (Chapter 9)

10.5.2.2 Hexagonal and Rhombohedral Systems

Hexagonal crystals have a single 6-fold, or $\bar{6}$ axis. Rhombohedral crystals contain a single 3-fold or $\bar{3}$ axis. Crystals with more than one 3-fold or $\bar{3}$ axis belong to the cubic system. No crystals have more than one 6-fold or $\bar{6}$ axis. Crystals in either system may also have 2-fold axes and mirror planes. Because they have one direction that is different from others, hexagonal crystals are often prisms of three or six sides terminated by pyramid faces. Other forms, including scalenohedron and rhombohedron, are also common in both the hexagonal and rhombohedral systems.

Figure 10.51 shows a crystal of hanksite, a rare sodium-potassium evaporite mineral that has symmetry $^{6}/_{m}$. The hexagonal symmetry is reminiscent of apatite crystals. Figure 10.52 shows prismatic tourmaline crystals. They have symmetry $3m$. Figure 10.53 shows one large, and several small, calcite scalenohedra. Calcite has symmetry $\bar{3}2m$, but calcite crystals have many common forms and come in many shapes.

10.51 Hanksite (Na-Ca sulfate carbonate) from Searles Lake, California



10.52 Greenish tourmaline (complex boron-containing ring silicate) crystals from Paraiba, Brazil

10.53 Calcite ($CaCO_3$) scalenohedra (grey) with fine grained tarnished chalcopyrite ($CuFeS_2$). The specimen is 12.5 cm wide.

We saw other examples of minerals whose crystals belong to the hexagonal or rhombohedral systems in earlier chapters:

- quartz in Figure 1.8 (Chapter 1)
- beryl in Figure 1.12 (Chapter 1), Figure 4.1 (Chapter 4), Figure 6.89 (Chapter 6), Figure 9.60 (Chapter 9)
- tourmaline in Figure 4.13 (Chapter 4) and 6.22 (Chapter 6)
- calcite in Figure 3.1 (Chapter 3)
- molybdenite in Figure 3.40 (Chapter 3)
- graphite in Figure 3.78 (Chapter 3)
- ilmenite in Figure 9.55 (Chapter 9)
- chabazite in Figure 7.56 (Chapter 7)

Note that micas and other sheet silicate minerals sometimes appear to be hexagonal. For example, look at the biotite crystals in Figure 6.62, the lepidolite in Figure 6.66, and the clinochlore in Figure 6.69. In two dimensions they appear hexagonal, but if you could see the third dimension clearly it would be apparent that they are not. Most sheet silicates are monoclinic. Tourmaline, too, often appears hexagonal but a close look reveals that the crystal cross sections are 6-sided but are not true hexagons.

10.5.2.3 Tetragonal System

All tetragonal crystals have one 4-fold or one $\bar{4}$ axis of symmetry; crystals that have more than one 4-fold or $\bar{4}$ axis must belong to the cubic system. Tetragonal crystals may also have 2-fold axes and mirror planes. As with the crystals in the hexagonal system, tetragonal crystals are often combinations of prisms with other forms. Figure 10.54 shows a green apophyllite crystal with prominent tetragonal prism and tetragonal pyramid faces. Compare this with the other photo of apophyllite earlier in this chapter (Figure 10.13). The apophyllite in Figure 10.54 is on top of stilbite. Apophyllite (which is a sheet silicate) usually occurs with zeolites such as stilbite (which is a monoclinic framework silicate). We find these minerals most commonly as secondary minerals in vugs and pockets in basalt.

Figure 10.55 show tetragonal vesuvianite crystals with both prism and pyramid faces. Both apophyllite and vesuvianite have symmetry $^{4}/_{m}\,^{2}/_{m}\,^{2}/_{m}$. Figure 10.56 shows another tetragonal mineral, wulfenite, forming thin square orange crystals. Wulfenite crystals have symmetry $^{4}/_{m}$.

10.54 Green apophyllite (K-Na-Ca sheet silicate) on top of stilbite (Na-Ca zeolite), from Bombay, India. The specimen is about 16 cm tall.

10.55 Vesuvianite (complex Ca-Mg-Fe silicate). The specimen is 4.4 cm wide.

10.56 Orange wulfenite ($PbMoO_4$) on top of calcite. Los Lamentos Mine, Mexico.

10.5.2.4 Orthorhombic System

Crystals in the orthorhombic system have either three perpendicular 2-fold axes, two perpendicular mirror planes paralleling a 2-fold axis, or three perpendicular $2/m$ axes. A shoebox shape is an excellent example, but many shapes and forms are possible. The sulfur crystal shown in Figure 10.57, the topaz in Figure 10.58, and the barite in Figure 10.59 all have symmetry $2/m2/m2/m$. The crystal with disphenoids in Figure 10.40, earlier in this chapter, is also orthorhombic and belongs to point group 222. Sometimes orthorhombic crystals may be rather equant but they are often quite tabular, like the barite crystals seen in Figure 4.4 (Chapter 4) and in Figure 10.59, here. For an especially spectacular example of barite crystals, see the opening figure in this chapter (Figure 10.1).

10.57 Sulfur (S) crystal

10.58 Topaz $Al_2SiO_4(F,OH)_2$. from the Mimoso do Sul Mine, Brazil. The crystal is 9.1 cm tall.

10.59 Orthorhombic prisms of barite ($BaSO_4$) terminated by pyramids.

10.5.2.5 Monoclinic System

A single 2-fold axis, a single mirror, or a 2-fold axis perpendicular to a mirror characterize crystals in the monoclinic system. In the simplest case, monoclinic crystals may appear as shoe boxes distorted in one direction so that two faces are not rectangles. The symmetry may be hard to see because monoclinic crystals often comprise many different forms. Figure 10.60 shows gypsum, Figure 10.61 shows a large orthoclase crystal, and Figure 10.62 shows a cluster of heulandite crystals. All these monoclinic crystals have symmetry $2/m$ but it is hard to discern in the heulandite crystals.

10.60 Clear crystal of gypsum ($CaSO_4 \cdot 2H_2O$)

10.61 A crystal of orthoclase $KAlSi_3O_8$) from the Jarilla Mountains, southern New Mexico. The crystal is 3 cm long.

10.62 Heulandite (Ca-Na zeolite) crystals from Maharashtra, India. The specimen is 7.5 cm tall.

We saw other examples of minerals whose crystals belong to the monoclinic system in earlier chapters:

- twinned gypsum Figure 4.39 (Chapter 4)
- twinned orthoclase in Figure 4.41 (Chapter 4)
- augite in Figure 6.78 (Chapter 6)

10.5.2.6 Triclinic System

Triclinic crystals have no symmetry greater than an inversion center. The photos below show three examples: albite (Figure 10.63), amblygonite (Figure 10.64), and rhodonite (Figure 10.65). The photo of albite also contains minor amounts of black tourmaline and quartz. These crystals all have symmetry $\bar{1}$, equivalent to an inversion center, and no more. It appears that the albite crystal might have a vertical mirror and so, perhaps, be monoclinic. But albite, like all plagioclase, is triclinic. In contrast with plagioclase feldspars, K-feldspar is monoclinic at high temperature (sanidine, orthoclase) and triclinic at low temperature (microcline).


10.63 Albite ($NaAlSi_3O_8$) crystal with minor tourmaline and quartz from Tuscany, Italy


10.64 Amblygonite (an Li-Al phosphate) from Minas Gerais, Brazil


10.65 Rhodonite ($MnSiO_3$) crystal from Minas Gerais, Brazil. The crystal is 5.7 cm tall.

We saw other examples of feldspar crystals in the triclinic system in earlier chapters:

- albite in Figure 6.37 (Chapter 6)
- anorthite in Figure 6.38 (Chapter 6)

●Figure Credits

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10.16 A hexagonal prism terminated by pyramid faces, Géry Parent, Wikimedia Commons
10.37 Twinned orthoclase, skywalker, Wikimedia Commons
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Video 10-1: Crystal systems, Keith Putirka, YouTube

11 Crystallography

11.1 A pink topaz crystal from Pakistan

11 – Crystallography

KEY CONCEPTS

- All crystals are made of basic building blocks called unit cells.
- Unit cells may have any of 7 fundamental shapes.
- Unit cells fit together in one of 14 ways to make crystals.
- We make inferences about unit cell shape and lattice type based on crystal habit and symmetry.
- The symmetry of an atomic structure depends on unit cell shape, the lattice, and the locations of atoms in the unit cell.
- There are 230 possible atomic-structure symmetries that can only be distinguished using X-ray techniques.
- Crystals contain one or several different kinds of crystal faces.
- We differentiate crystal faces based on their orientations with respect to a coordinate system based on unit cell edges.

11.1 Observations in the Seventeenth through Nineteenth Centuries

In 1669 Nicolaus Steno studied many quartz crystals and found angles between adjacent prism faces, termed *interfacial angles*, to be 120^o no matter how the crystals had formed. For example, Figures 11.2 to 11.5 show four varieties of quartz with nearly identical crystal shapes and angles between faces. Steno could not make precise measurements, and some of his contemporaries argued that he was overlooking subtle differences.

11.2 Citrine from Minas Gerais, Brazil

11.3 Amethyst from Veracruz, Mexico. The specimen is 5.8 cm wide.

11.4 Smoky quartz from near Roswell, New Mexico

11.5 Phantom quartz from Minas Gerais, Brazil. The photo is 7.8 cm tall.

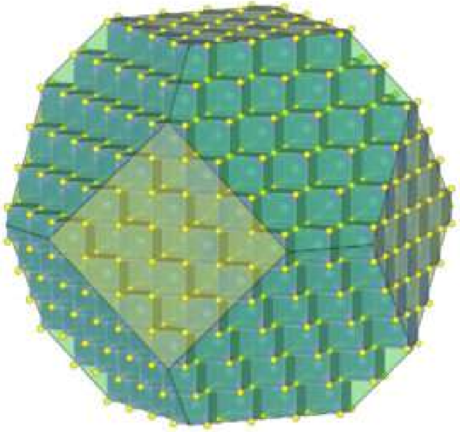
A century after Steno, in 1780, more accurate measurements became possible when Arnould Carangeot invented the *goniometer*, a protractor-like device used to measure interfacial angles on crystals. Carangeot's measurements confirmed Steno's earlier observations. Shortly after, Romé de l'Isle (1782) stated the first law of symmetry, a law called the "constancy of interfacial angles," which we commonly call *Steno's law*. This law states that:

■ *Angles between equivalent faces of crystals of the same mineral are always the same.*

Steno’s law acknowledges that the size and shape of the crystals may vary.

In 1784 René Haüy studied calcite crystals and found that they had the same shape, no matter what their size. Haüy hypothesized the existence of basic building blocks called *integral molecules* and argued that large crystals formed when many integral molecules bonded together. Haüy erroneously concluded that integral molecules formed basic units that could not be broken down further. At the same time, Jöns Jacob Berzelius and others established that the composition of a mineral does not depend on sample size. And Joseph Proust and John Dalton proved that elements combined in proportions of small rational numbers. Scientists soon combined these crystallographic and chemical observations and came to several conclusions:

- Crystals are made of small basic building blocks.
- The blocks stack together in a regular way, creating the whole crystal.
- Each block contains a small number of atoms.
- All building blocks have the same atomic composition.
- The building block has shape and symmetry that relate to the shape and symmetry of the entire crystal.



11.6 The atomic arrangement in fluorite.

Figure 11.6 is the same figure we saw in Chapter 1. It shows the arrangement of atoms and basic building blocks in a fluorite crystal. Notice that the overall crystal has a sort of cube shape, and the building blocks are also cubes. This relationship between crystal symmetry and building block symmetry is at the heart of crystallography.

Early in the 1800s, several researchers found that crystals of similar, but not identical, chemical composition could have identical shapes. W. H. Wollaston (*c.* 1809) showed that calcite ($CaCO_3$), magnesite ($MgCO_3$), rhodochrosite ($MnCO_3$), and siderite ($FeCO_3$) all commonly formed the same distinctive rhombohedron-shaped crystals (Figures 11.7, 11.8, 11.9, and 11.10).


11.7 Calcite


11.8 Magnesite from Minas Gerais, Brazil


11.9 Rhodochrosite from Colorado


11.10 Siderite from Mt. Saint Hilaire, Quebec

Those who studied sulfate compounds also found that crystals of different compositions had the same crystal shape. Both the rhombohedral carbonates and the sulfates are examples of *isomorphous series*. Wollaston and others concluded that when crystal shapes in such series are truly identical, the distribution of atoms within the crystals must be identical as well, even if the compositions are not. Minerals with identical atomic distributions are termed *isostructural* even if (unlike carbonates or sulfates) they have significantly different compositions.

Sometimes isostructural minerals form solid solutions because they can mix to form intermediate compositions. Fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4) are isostructural and form a complete solid solution; olivines can have any composition between the two end members. In contrast, halite (NaCl) and periclase (MgO) are isostructural but do not form solid solutions. Calcite, magnesite, rhodochrosite, and siderite are isostructural but their mutual solubility is limited. They form only limited solid solutions, also called *partial solid solutions*.

In 1821 Eilhard Mitscherlich, a student of Berzelius's, discovered that the same elements may combine in different atomic structures. For instance, calcite and aragonite both have composition $CaCO_3$, but they form different crystal shapes and have different physical properties. We call such minerals *polymorphs* because, although identical in composition, they have different atomic arrangements and crystal morphologies. Mineralogists have now studied several other $CaCO_3$ polymorphs, but none except vaterite occur naturally. In calcite and vaterite the basic building blocks have rhomb-shaped faces, while in aragonite the faces are rectangles.

Figure 11.11 shows calcite and siderite crystals that do not have the same shapes as those above in Figures 11.7 and 11.10. Many minerals, especially carbonate minerals have multiple common habits. Figure 11.12 shows aragonite crystals and Figure 11.13 shows vaterite crystals. Both minerals, like calcite, have composition $CaCO_3$.

11.11 White calcite with siderite from the Pyrenees. The specimen is 11 cm tall.

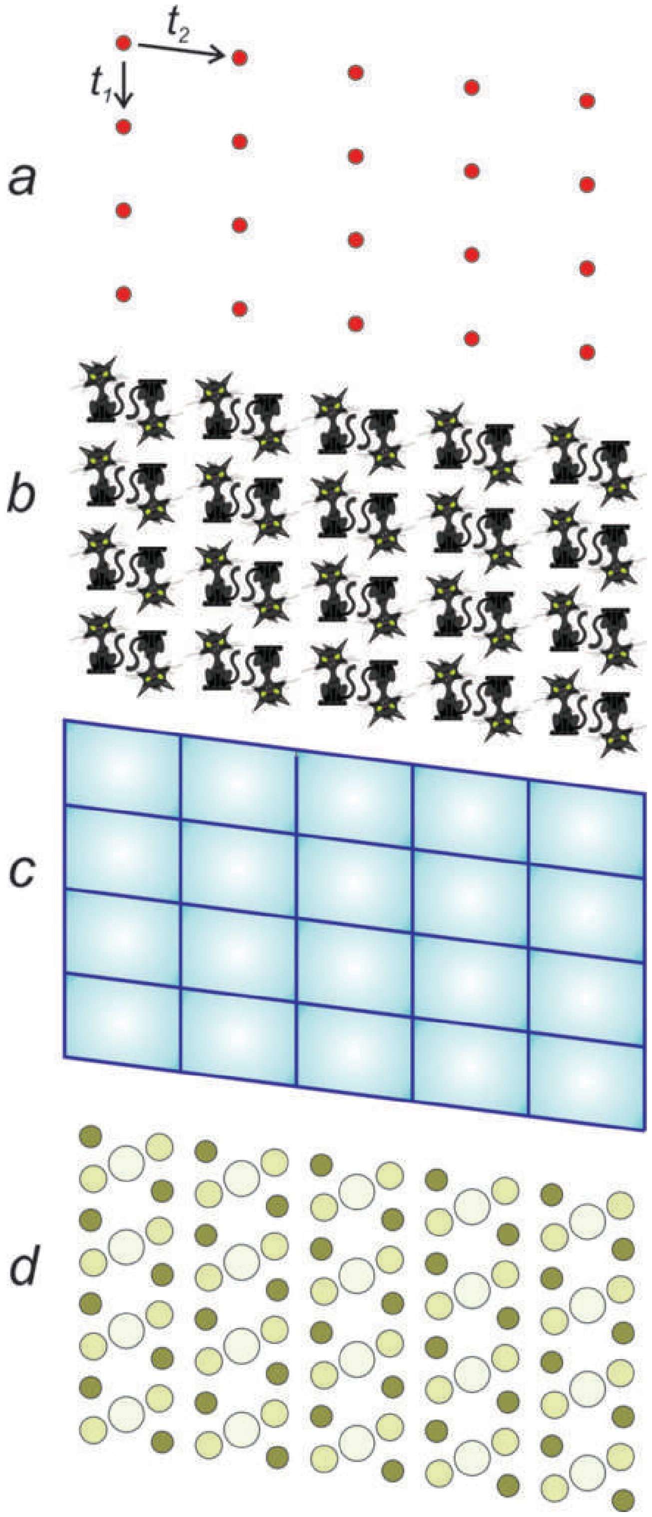
11.12 Aragonite crystals from Guadalajara, Spain

11.13 White vaterite crystals from near Naples, Italy. The sample is 7.1 cm wide.

By the early/mid 1800s it was clear that there was no direct correlation between the shapes of building blocks and crystal composition, as Haüy had originally thought. Despite flaws in some of his ideas, however, we must credit René Haüy as one of the founders of crystallography. In later years, he pioneered the application of mathematical concepts to crystal properties which established the basis for modern crystallography and crystallographers still use much of his work today. We now accept that:

- All crystals have basic building blocks called *unit cells*.
- The unit cells are arranged in a pattern described by points in a *lattice*.
- The relative proportions of elements in a unit cell are given by the chemical formula of a mineral.
- Crystals belong to one of seven crystal systems. Unit cells of distinct shape and symmetry characterize each crystal system.
- Total crystal symmetry depends on both unit cell symmetry and lattice symmetry.

11.2 Translational Symmetry



11.14 Plane lattices and translational symmetry

In the previous chapter we discussed symmetry due to rotation, reflection, and inversion. These are all types of *point symmetry*. The orderly repetition of patterns due to *translation* is another form of symmetry, called *space symmetry*. Space symmetry differs from point symmetry.

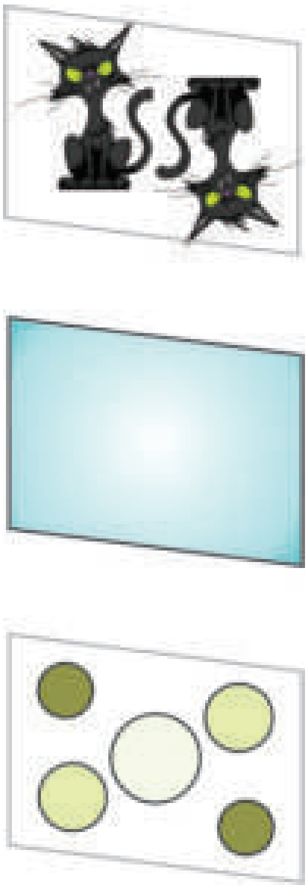
Space symmetry repeats something an infinite number of times to fill space, while point symmetry repeats something a discrete number of times and only describes symmetry localized about a central point. Point symmetry operators return a dot or a crystal face to its original position and orientation after 1, 2, 3, 4, or 6 repeats of the operation, but space symmetry operators do not. Translation goes on (almost) forever!

We often envision translational symmetry by thinking about a *lattice*, a set of an infinite number of points related by translations. In two dimensions, a lattice is called a *plane lattice*. In three dimensions, a lattice is a *space lattice*. Whether two or three dimensional, lattices are imaginary – they are not physical entities – they are patterns that we use to describe translational symmetry.

Figure 11.14a shows an example of how we depict a plane lattice. The vectors t_1 and t_2 are translation operators that generate the entire lattice from a single starting point. This drawing only shows part of the lattice; in your mind you should picture it extending infinitely in all directions.

Translational symmetry, like all symmetry, is a property that objects may have. If we have an object or a drawing, we can describe its translational symmetry. But it does not work the other way around because many different objects or drawings may have identical symmetry.

For example, Figure 11.14*b* (above) shows cats related by the same symmetry depicted in Figure 11.14*a*. Figure 11.14*c* shows parallelograms related by the same symmetry. And Figure 11.14*d* shows colored circles (that might represent atoms) related by the same symmetry.



11.15 Examples of unit cells

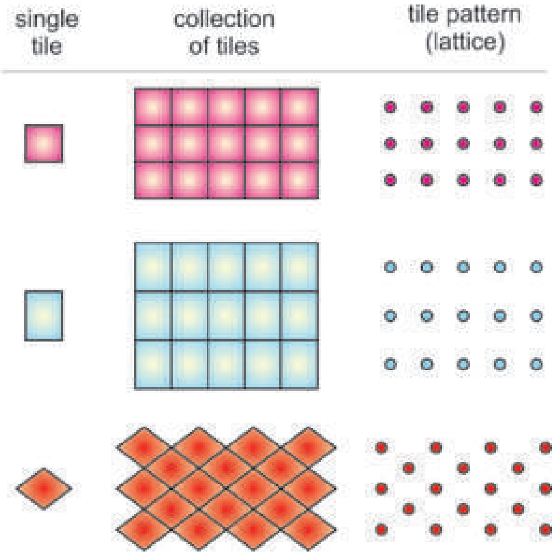
The four drawings in Figure 11.14 have more than just translational symmetry. They also contain multiple 2-fold rotation axes perpendicular to the plane of the page. And there are inversion centers, too. So we see that translational symmetry can combine with other kinds of symmetry.

Repetitive patterns are composed of motifs, which are designs that repeat, such as a flower pattern that might be on wallpaper. The term *motif* is used in an analogous way in music to refer to a sequence of notes that repeat. Interior decorators or clothing designers use the term to describe a common theme or element in their work.

A motif (whether it comprises two cats, a parallelogram, or colored circles) and empty space around it, make up *unit cells* that repeat to create an infinite pattern. The lattice describes the nature of the repetition, with each lattice point representing one motif. But lattice points do not correspond to any particular point on a motif. We could choose them at the motif's center or one of its corners and the result would be the same.

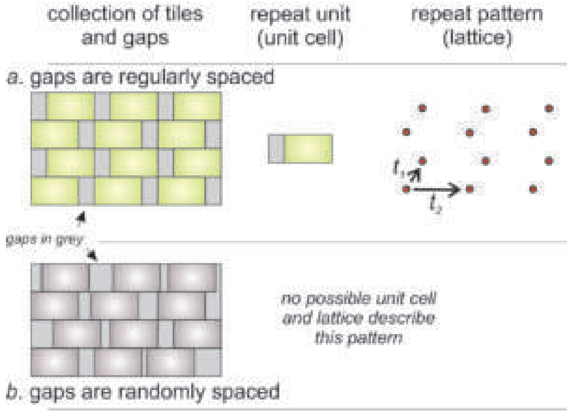
Figure 11.15 shows *unit cells* that can be used to generate the patterns seen in Figure 11.14. These unit cells are parallelograms with dimensions and angles that match the translation vectors of the lattice. Notice that each one of these unit cells has a vertical 2-fold axis of symmetry and an inversion center. This symmetry must be present to be consistent with the lattice.

11.3 Unit Cells and Lattices in Two Dimension



11.16 Some possible shapes for floor tiles

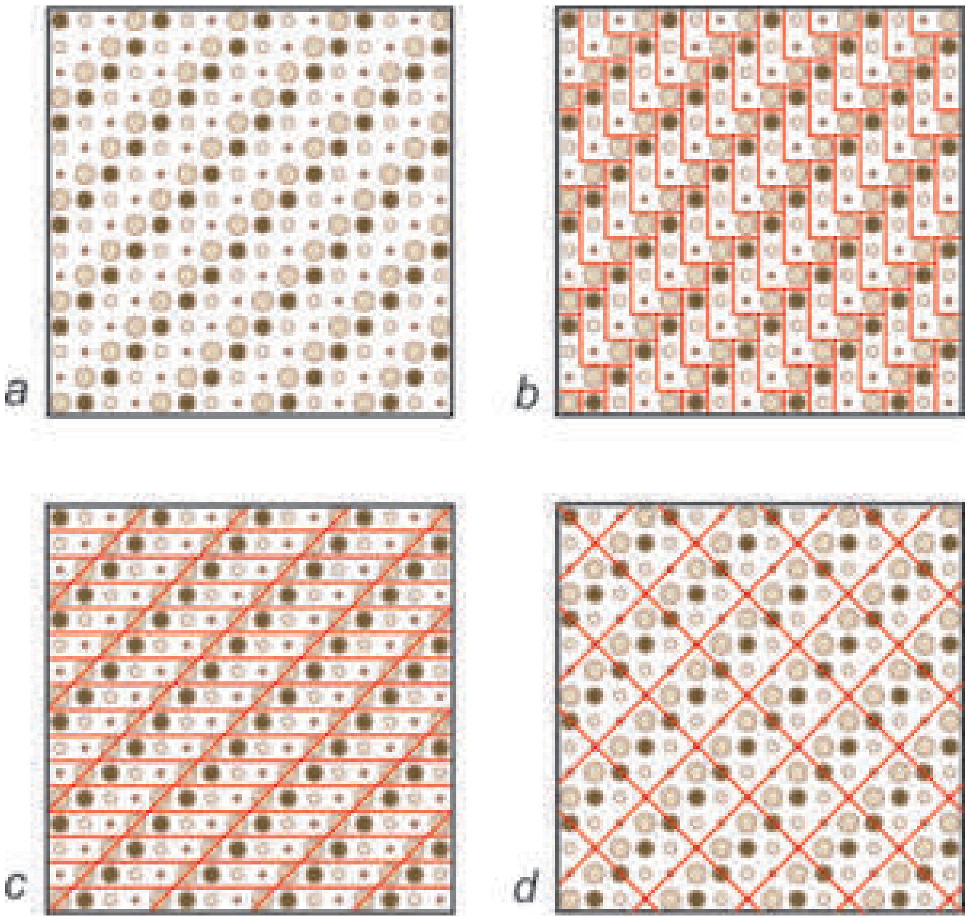
What possible shapes can unit cells have? Mineralogists begin answering this by considering only two dimensions. This is much like imagining what shapes we can use to tile a floor without leaving gaps between tiles. Figure 11.16 shows some possible tile shapes. In the right-hand column of this figure, a single dot has replaced each tile to show the plane lattice that describes how the tiles repeat. This figure does not show all possible shapes for tiles or unit cells, but as we will see later the number of possibilities is quite small.



11.17 What if there are gaps (shown in grey) between floor tiles?

What happens when gaps occur between tiles? Figure 11.17 shows the two possibilities: The gaps may be either regularly (11.17*a*) or randomly (11.17*b*) distributed. If regularly distributed, we can define a unit cell that includes the gap, as we have in drawing 11.17*a*. The two vectors, t_1 and t_2 and the lattice they create describe how the unit cell repeats to make the entire tile pattern.

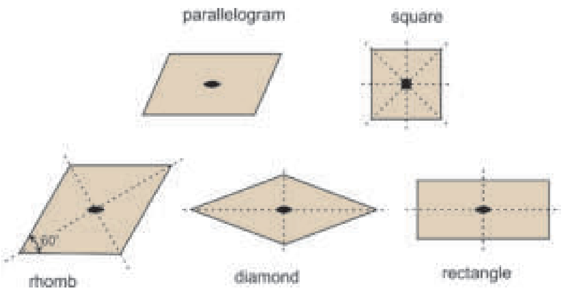
If gaps between tiles are random, the entire structure is not composed of identical building blocks that fit together in a regular way. It is not repetitive and we cannot describe it with a unit cell and a lattice. It does not, therefore, represent the symmetry of a possible crystal structure and we need not consider it further.



11.18 Floor tiles and a complex pattern

Various complex patterns can appear on tiled floors, but the tiles are usually simple shapes such as squares or rectangles. For example, suppose we wish to tile a floor in the pattern shown in Figure 11.18*a*. We could use L-shaped tiles, shown in red in Figure 11.18*b*. However, parallelogram- or square-shaped tiles would get us the same pattern (Figures 11.18*c* and *d*). Other shapes, too, would work.

We can make any repetitive two-dimensional pattern, no matter how complicated, with tiles of one of four fundamental shapes: parallelogram, rhomb (a parallelogram with sides of equal length), rectangle, and square. These shapes are relatively simple compared to more complex ones we could choose, and they reveal symmetry that is present. So, they are used by mineralogists and preferred by tile makers.



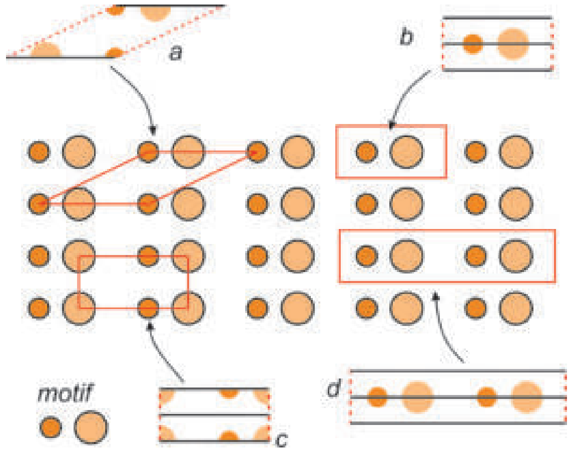
11.19 The five possible two-dimensional shapes

For reasons we will see later, we usually distinguish two types of rhombs (parallelograms with sides of equal length): those with *nonspecial angles* between sides and those with 60° and 120° angles between sides. For the rest of this chapter, we will refer to the general type of rhomb as a *diamond*, and the term *rhomb* will be reserved for shapes with only 60° and 120° angles (and sides of equal length). So, Figure 11.19 shows the five basic shapes, the only ones needed to discuss two-dimensional unit cells, and their symmetries.

We can now explain why we only considered 1-, 2-, 3-, 4-, and 6-fold rotational symmetry in the previous chapter. Two-dimensional shapes with a 5-fold axes of symmetry, for example, cannot be unit cells because they cannot fit together without gaps. We can verify this by drawing equal-sided pentagons on a piece of paper. No matter how we fit them together, space will always be left over. The same holds true for equal-sided polyhedra with seven or more faces. They cannot fit together to tile a floor. And if the shapes cannot fit together in two dimensions, they cannot fit together in three dimensions.

11.3.1 Motifs and Unit Cells

We can think of atomic arrangements as starting with one motif. The motif is then reproduced by translating (moving) it a certain distance and reproducing it. The distance of the translation is the distance between lattice points. If a dot replaces each motif, we get the lattice.



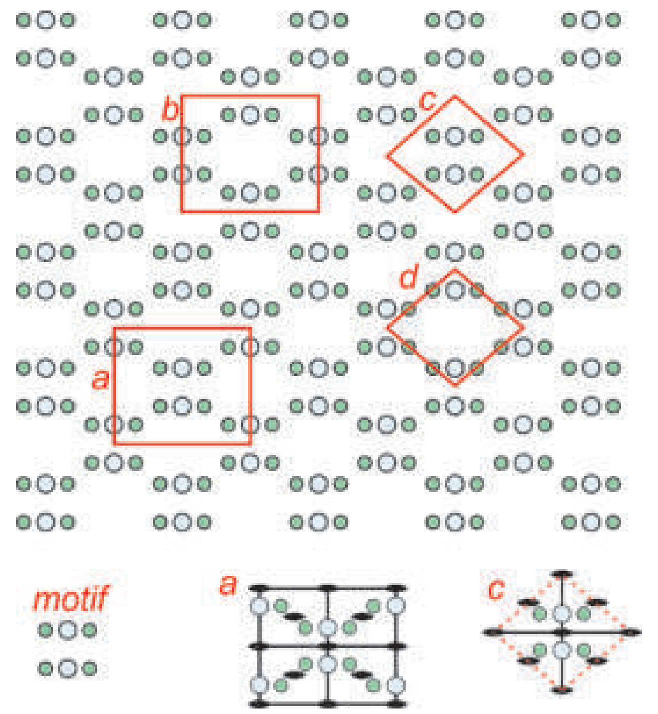
11.20 A motif with two atoms and some possible unit cells

Figure 11.20 shows a pattern made of two atoms, symbolized by different sized orange circles. The entire pattern consists of motifs composed of one of each kind of atom. The pattern contains multiple horizontal mirror planes but no other symmetry.

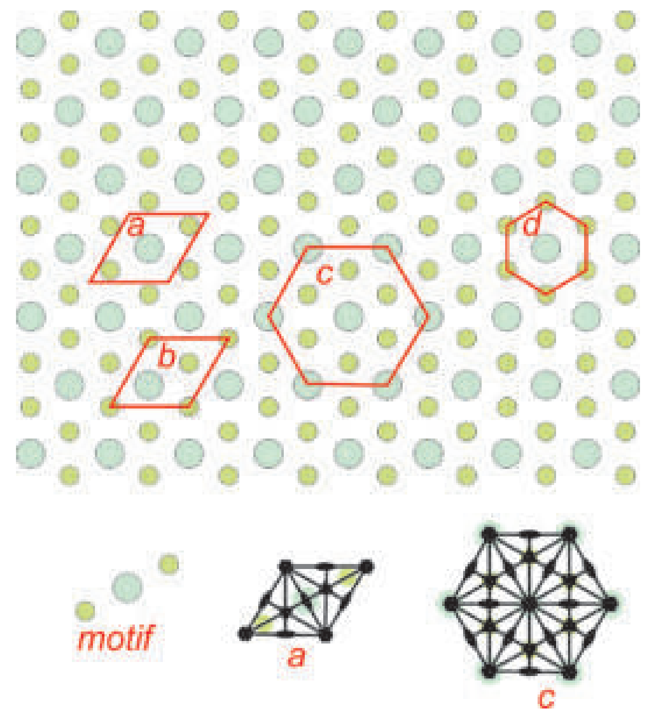
The figure shows several possible choices of unit cells (labeled *a* through *d*). In the individual unit cell drawings, solid black lines show mirror planes of symmetry.

Unit cells *a*, *b*, and *c* contain only one motif in total (one small orange circle and one larger lighter orange circle). We call them *primitive* because they are the smallest unit cell choices possible. All primitive unit cells contain exactly one motif, but atoms within a primitive unit cell may be in parts as in unit cell *c*. Add up the parts and you get one motif. We term unit cell *d* *doubly primitive* because it contains two motifs. Triply primitive unit cells contain three motifs, etc.

We can always choose a primitive unit cell for a repetitive pattern of atoms, but sometimes a primitive cell does not show symmetry clearly. By convention, we usually choose the smallest unit cell that contains the same symmetry as the entire pattern or structure. In Figure 11.20, unit cell *b* would be the choice of most crystallographers because it is simple, primitive, does not contain any partial atoms, and contains a horizontal mirror plane (which is the same symmetry as the entire pattern). Note that unit cell *a*, while also being primitive, does not have a mirror plane of symmetry within it; the other choices do.



11.21 Motifs and unit cells with orthorhombic symmetry



11.22 Motif's and unit cells with rhombohedral or hexagonal symmetry

The pattern shown in Figure 11.20 has relatively simple symmetry; the patterns in Figures 11.21 and 11.22 have more. Figure 11.21 shows an orthogonal (containing lots of 90° angles) arrangement of atoms. The repeating motif contains six atoms – four green and two larger light blue ones. The letters *a*, *b*, *c*, and *d* designate four possible choices for unit cell. Cells *c* and *d* are primitive, containing six atoms total, although some are on the edges in cell d so only half of each green atom is in the unit cell. Cells *a* and *b* are doubly primitive but they are rectangular shapes. The symmetries of two of the unit cells are shown in the bottom of the figure. Solid black lines designate mirrors and lens shapes designate 2-fold axes. Unit cell *a*, although being double primitive, is the one that best shows the symmetry elements and so would be the choice of most crystallographers.

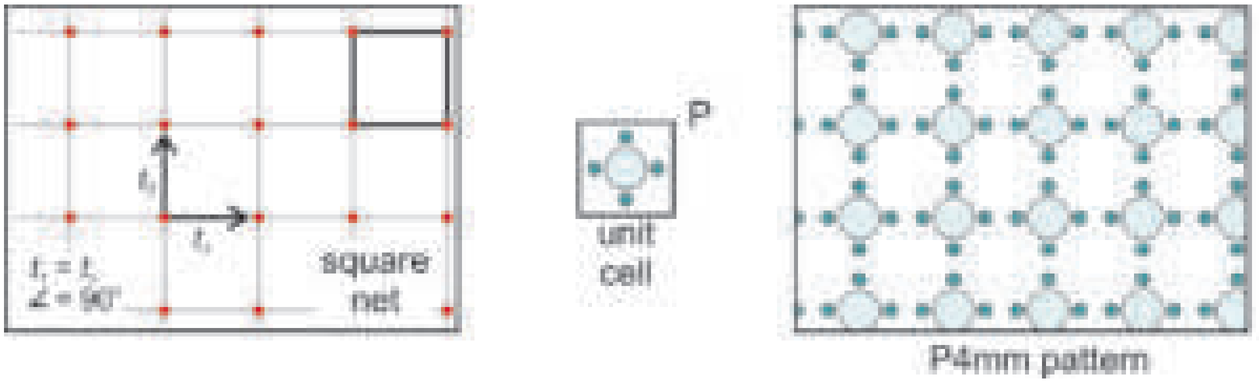
Figure 11.22 shows an overall hexagonal pattern. The motif consists of one large turquoise atom and two smaller green atoms. Four possible choices for unit cells are shown. Drawings in the bottom of the figure show symmetry of two of the potential unit cell with solid black lines as mirrors, lens shapes as 2-fold axes, and hexagons as 6-fold axes. Two of the potential unit cells are rhomb shaped and two are hexagonal. Because the overall pattern has hexagonal symmetry, unit cells *c* and *d* are preferred choices compared with the other two. Unit cell *d* is primitive, but does not include all the symmetry. (It does not have 2-fold rotation axes.). So cell *c* is the best choice. This pattern demonstrates why we treat rhombs with 60° and 120° angles at their corners as special cases – they sometimes result in hexagonal symmetry while diamonds with general angles at their corners cannot.

Although crystallographers follow standard conventions, they are often forced to make choices. If they choose primitive unit cells, each lattice point corresponds to one unit cell and one motif. If they choose nonprimitive unit cells, lattices represent the way motifs repeat, but not the way unit cells repeat because there is more than one lattice point per unit cell.

11.3.2 What are the Possible Plane Lattices?

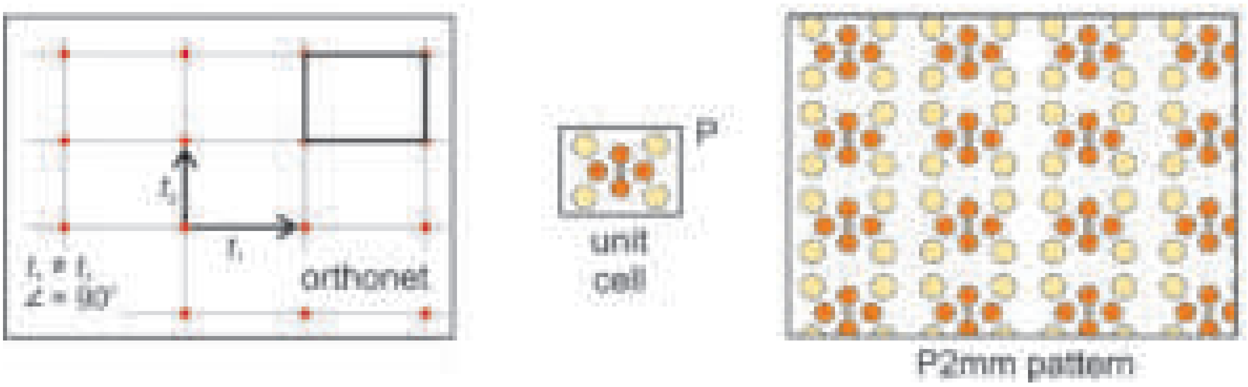
Above we looked at a number of different examples of lattices and unit cells. To get a complete list of possibilities let’s look at all the possible plane lattices. In a plane lattice, lattice points are related by two vectors describing translation. The vectors may be *orthogonal* (perpendicular to each other) or not. And they may be equal length or not.

Square Net: Let’s consider the simplest possibility – that the vectors are orthogonal and of equal length. This produces a *square net* (lattice), as shown on the left in Figure 11.23, below. If we choose a square unit cell and put a motif (five atoms) with square symmetry within it, we get the pattern seen in the drawing on the right. This pattern has the same symmetry as the lattice and of the unit cell. The symmetry includes 4-fold and 2-fold rotation axes, and mirror planes that intersect at 45° and 90°. The small P next to the unit cell reminds us that it is primitive. Because the overall atomic arrangement contains a 4-fold axis and two differently oriented mirrors, we describe its symmetry as *P4mm*.



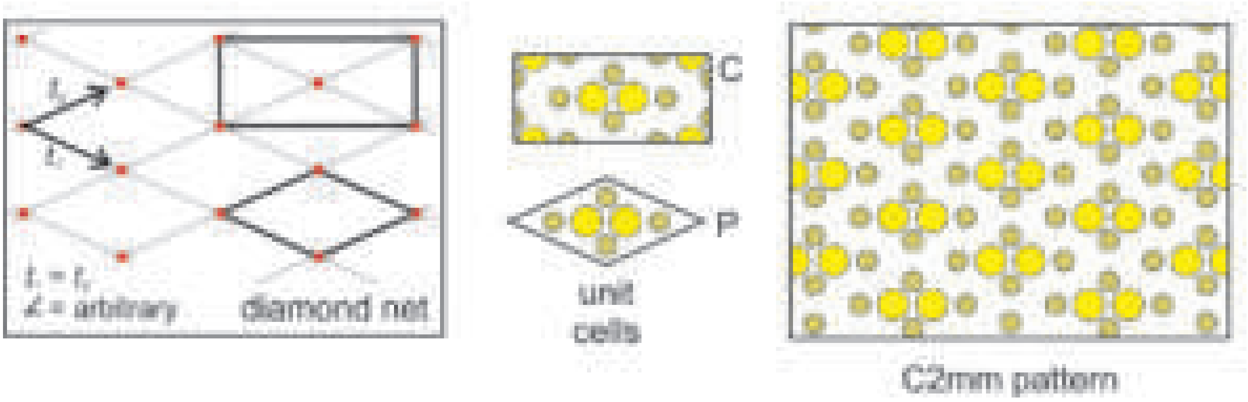
11.23 Square net and pattern

Orthonet: Suppose the two vectors relating lattice points are orthogonal but not of equal length. If so, we get an *orthonet*, equivalent to a *rectangular lattice*, as shown in Figure 11.24, below. We can choose a rectangular unit cell and add a rectangular motif that contains nine atoms. We get the pattern shown on the right in Figure 11.24. Note that the lattice, the primitive (P) unit cell, and the pattern have equivalent symmetry that includes mirror planes and 2-fold rotation axes. The overall atomic arrangement contains a 2-fold axes with horizontal and vertical mirrors; we describe its symmetry as *P2mm*.



11.24 Orthonet and pattern

Diamond Net: A third general possibility is that the vectors relating lattice points are of equal magnitude but intersect at a non-special angle. This combination produce a *diamond net* (lattice) like the one below in Figure 11.25. We can add a motif of six atoms to a diamond-shaped unit cell to get the atomic arrangement shown on the right in Figure 11.25. But, notice that we can also choose a rectangular unit cell that is doubly primitive – it has an extra lattice point at its center and contains two motifs. Either unit cell will generate the same pattern. We use the letter *P* to indicate the primitive unit cell, and the letter *C* to indicate the cell with an extra lattice point in its center. The rectangular unit cell shows the vertical and horizontal perpendicular mirror planes and the 2-fold rotation axes more clearly than the diamond shaped one. So, we describe the symmetry of the pattern as *C2mm*.

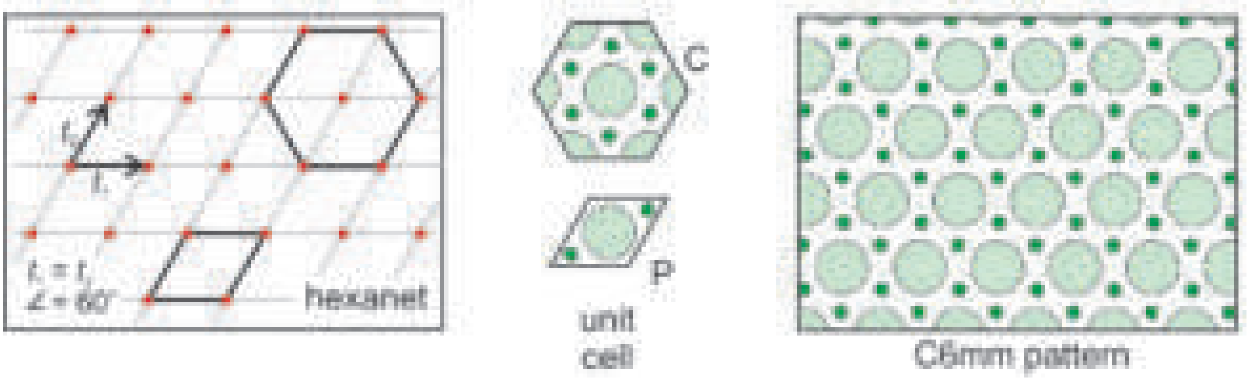


11.25 Diamond net and pattern

Clinonet: The fourth possibility is that the two translation vectors are of different lengths and are not orthogonal. This produces a *clinonet* (Figure 11.26) that corresponds to a primitive unit cell with the shape of a parallelogram. Adding a motif containing six atoms gives us the atomic arrangement on the right in Figure 11.26. There are no mirror planes here – the only symmetry is 2-fold rotation perpendicular to the page. The arrangement of atoms has symmetry *P2*.

11.26 Clinonet and pattern

Hexanet: The fifth possible net is the created by the special case when the two translation vectors are of equal magnitude and intersect at 60°. This combination gives us a *hexanet* (hexagonal lattice) like the one shown in Figure 11.27, below. As with the diamond net, we can choose either a primitive rhomb-shaped unit cell or a triply-primitive hexagonal unit cell. The lattice and the overall atomic arrangement have hexagonal symmetry, so the hexagonal unit cell (which also has hexagonal symmetry) is generally chosen. A 6-fold axis and two kinds of mirrors at different orientations characterize this pattern; the symmetry is designated *C6mm*.



11.27 Hexagonal net and pattern

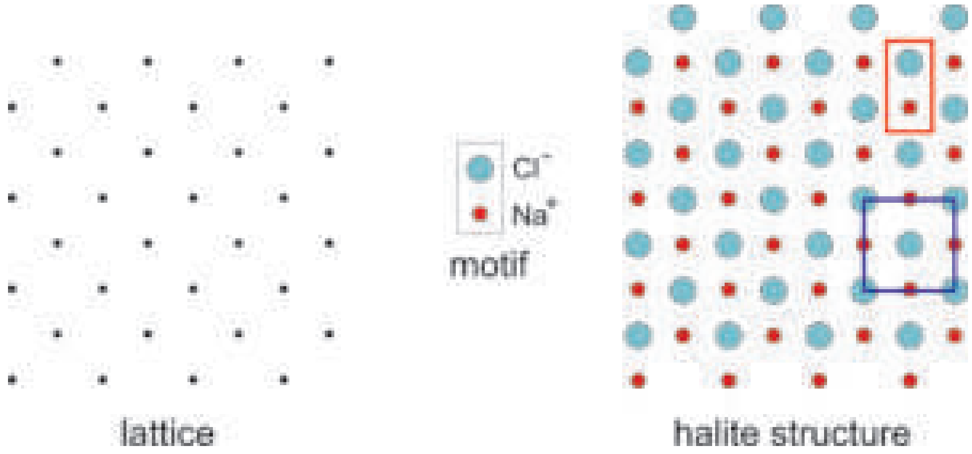
11.3.3 How May Motifs and Lattices Combine?

Above, we saw examples where the lattice, the motif, and the overall pattern had the same symmetry. This was true in Figures 11.23, 11.24, 11.25, and 11.26. But, it was not true in Figure 11.27 where the motif and a primitive unit cell consisted of 3 atoms and a mirror plane of symmetry, while the lattice and overall pattern have hexagonal symmetry. Notice that in Figure 11.27, we could choose a triply primitive unit cell that had the same symmetry as the lattice and overall pattern. Because the triply primitive cell shows the 6-fold symmetry, it is the best choice.

This leads to an important second law of crystallography:

- *If a motif has certain symmetry, the lattice must have at least that much symmetry.*

A motif with a 4-fold axis of symmetry requires a square plane lattice because it is the only plane lattice with a 4-fold axis. A motif may have less symmetry than a lattice. If a motif has a 2-fold axis of symmetry, it may be repeated according to any of the five plane lattices because they all have 2-fold axes of symmetry.

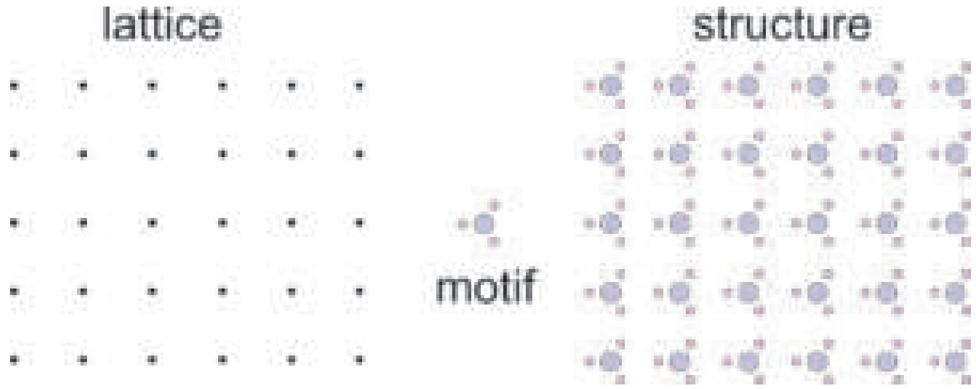


11.28 Lattice, motif, and structure of halite

Halite (NaCl) is an excellent example of a mineral in which the simplest motif has less symmetry than the lattice. Figure

11.28 shows a two-dimensional model of the atomic arrangement in halite. The lattice is on the left and the motif, consisting of a Cl$^-$ anion and an Na$^+$ cation is shown in the center of the figure.

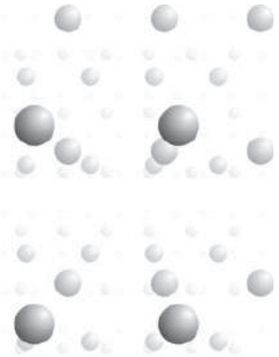
In two dimensions the lattice has square symmetry (although it is tilted to 45° in this drawing), but the motif, consisting of one Na and one Cl atom, does not. Putting a motif at every lattice point gives the atomic arrangement on the right. A primitive unit cell (P), containing two atoms (outlined in red), is rectangular and does not have square symmetry. Notice, however, that we can choose a nonprimitive unit cell containing four atoms and two motifs (outlined in blue) that has square symmetry. This would not be possible if the lattice did not have "at least as much symmetry as the motif."



11.29 An impossible combination of a lattice and a motif

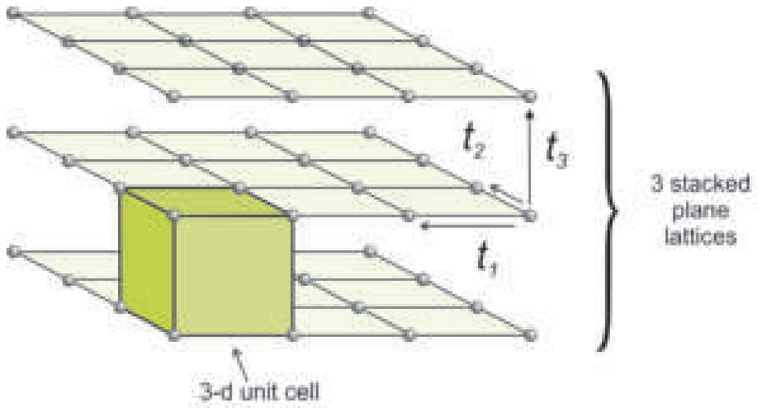
Figure 11.29 shows an impossible combination of a lattice and a motif. The lattice has 4-fold rotational symmetry, the motif has 3- fold symmetry. But the combination yields a structure that has no rotational symmetry. Looking at this figure should give you the sense that something is wrong. And, it is. If the motif really has 3-fold symmetry, it is identical in three directions 120° apart. So bonds around it should be the same in three directions 120° apart. But, they are not in the structure drawing. A motif with 3-fold symmetry requires a lattice that has at least 3-fold symmetry. There is only one and it is a hexanet. The lattice cannot be a square lattice.

11.4 Unit Cells and Lattices in Three Dimensions



11.30 An atom repeating indefinitely in space

In two dimensions, patterns are made of unit cells and lattices describe how unit cells and motifs repeat. These relationships are the same in three dimensions. Figure 11.30, for example, shows a single atom repeated an indefinite number of times and disappearing into the distance. Choose any four nearest neighbor atoms and you can connect them to get a 3D unit cell that is the basis for the entire atomic array.



11.31 Square nets and a cubic unit cell

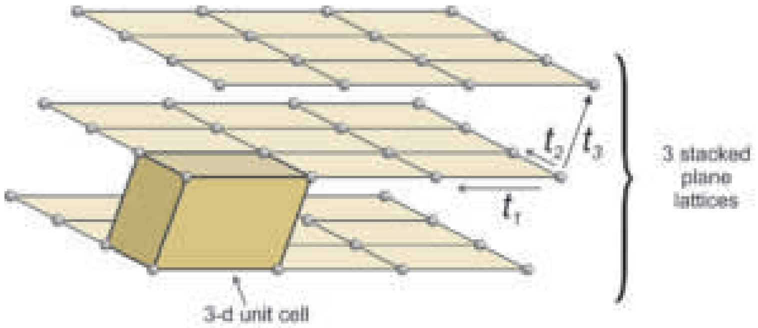
In two dimensions, two vectors describe the translation that relates lattice points. To move from two dimensions (planes) to three dimensions (space), we need only to define a third vector, t_3, that translates a plane lattice some distance where it is repeated. We continue this process many times to get a space lattice. Figure 11.31 shows an example.

We can start with any of the two-dimensional plane lattices. The third translation may be orthogonal to one or both of the first two translations, but it need not be. Its magnitude may be the same as one or both of the first two translations, or not. We can envision space lattices as identical points that repeat indefinitely in three-dimensional space.

(Note that, for convenience, in this and subsequent drawings, we are choosing unit cells with lattice points at their corners. But we could choose unit cells with lattice points at their centers or anywhere else in the cell, because lattice points are simply patterns showing how unit cells repeat. It makes no difference if the lattice point corresponds to the corner, center, or any other point in the motif.)

In Figure 11.31, we start with a square lattice, and choose a third translation vector (t_3) that is equal in magnitude and also perpendicular to the first two. The result is in an overall cubic lattice. Connecting eight nearest-neighbor lattice points gives us a *cubic unit cell*. The plane lattices had symmetry 4mm; the cubic unit cell has symmetry $^4/_m\bar{3}\,^2/_m$ (described in the previous chapter).

If we stack a square net directly above another square net, as in Figure 11.31, the 4-fold rotation axis and the mirror planes line up and we preserve all symmetry. But, suppose the third translation is not perpendicular to the first two, and each square net is slightly offset from the ones above and below it. If so, rotation axes and mirrors in the different nets will not line up. The resulting space lattice may contain no 4-fold axes and no mirrors.

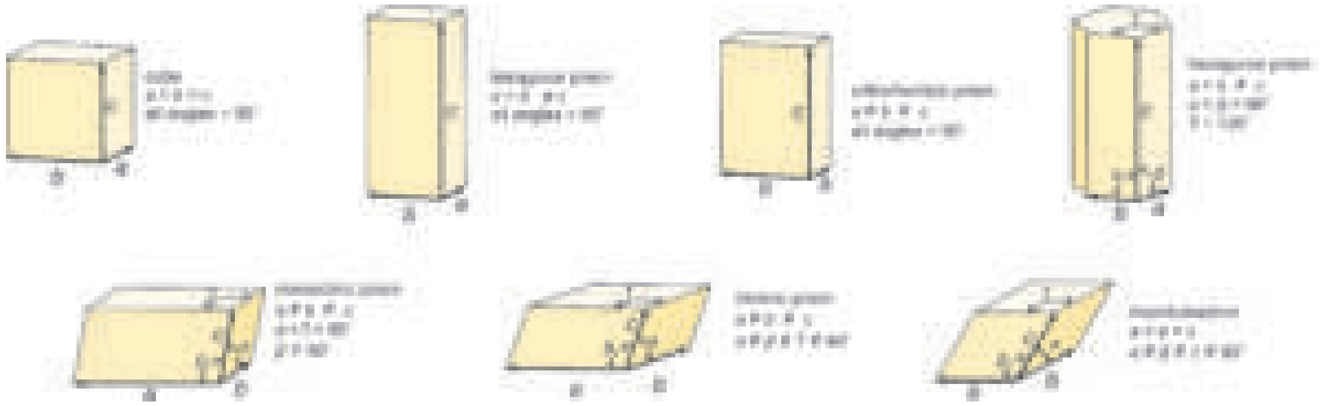


11.32 Orthonets and a monoclinic unit cell

Figure 11.32 shows an example of losing symmetry when nets are stacked with an offset. In this figure, we started with an orthonet. The third translation (t_3) is neither perpendicular to, nor of the same magnitude as, either of the other two. Each plane lattice is offset slightly to the right compared with the one below it. The result is a unit cell that has rectangular faces on four sides and parallelograms on two. It is called a *monoclinic* unit cell (because one angle at each corner is not 90°. An individual orthonet contains mirror planes and 2-fold axes perpendicular to the net. But because, in this example, the third translation was not perpendicular to the first two, those mirrors and rotation axes do not persist in the space lattice, nor in the unit cell. The orthonet has symmetry 2mm; the unit cell has symmetry $^2/_m$. The $^2/_m$ axis is perpendicular to the front parallelogram face.

If we consider all possible combinations of plane lattices and a third translation, we come up with seven fundamental unit cell shapes (Figure 11.33). Two of the unit cells, the hexagonal prism and the rhombohedron, are commonly grouped because they both derive from stacking hexanets. If we stack hexanets one above another, we preserve the 6-fold rotation axis and get a hexagonal prism. If the nets are offset, we may instead preserve a 3-fold rotation axis and get a rhombohedron.

You can think of these 3D shapes as the shapes that bricks can have if they fit together without spaces between them. We made a similar analogy to tiles when we were looking at 2D symmetry earlier in this chapter. Just like the tile shapes, more complex brick shapes are possible. But it can be shown that they are all equivalent to one of the seven below.



11.33 The seven fundamental unit cell shapes

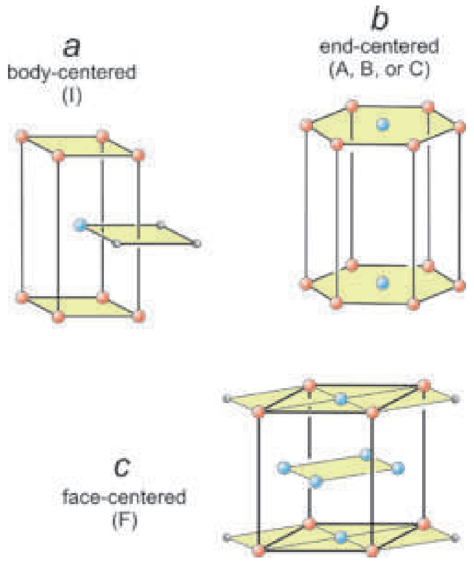
These seven unit cell shapes have unique symmetries: $^{4}/_{m}\bar{3}^{2}/_{m}$ (cube), $^{4}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ (tetragonal prism), $^{2}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ (orthorhombic prism), $^{6}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ (hexagonal prism), $^{2}/_{m}$ (monoclinic prism), $\bar{1}$ (triclinic prism), and $\bar{3}^{2}/_{m}$ (rhombohedron). Each unit cell corresponds to the one of the seven crystal systems introduced in the previous chapter: cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic, and rhombohedral. The symmetry of each unit cell seen here is the same as the symmetry of the general form in each system. A third law of crystallography is that:

- *The symmetries of the unit cells are the same as the point groups of greatest symmetry in each of the crystal systems.*

All minerals that belong to the cubic system have cubic unit cells with symmetry $^{4}/_{m}\bar{3}^{2}/_{m}$. Their crystals, however may have less symmetry. Similarly, all minerals that belong to the tetragonal system have tetragonal unit cells. Tetragonal crystals may have $^{4}/_{m}{}^{2}/_{m}{}^{2}/_{m}$ symmetry but may have less. This same kind of thinking applies to crystals in the other 5 systems, too.

We describe the shapes of unit cells with *unit cell parameters* that include a, b, and c, the length of unit cell edges, and α, β, and γ, the angels between cell edges. By convention, the angle between the a and b edges is γ (c in the Greek alphabet), the angle between a and c is β (b in the Greek alphabet), and the angle between b and c is α (a in the Greek alphabet). As seen in Figure 11.33, in cubic unit cells, a, b, and c are equal, and all angles are 90°. In tetragonal unit cells, a and b are equal and all angles are 90°. In orthorhombic unit cells, the three cell edges have different lengths, but all angles are 90°. In hexagonal unit cells, a and b have equal lengths, and the angle between a and b (γ) is 120°. In monoclinic unit cells, a, b and c are all different. α and γ are 90°, but β can have any value. (This is the general convention, but sometimes the non-90° angle is chosen as one of the other angles instead of β.) In triclinic unit cells, all cell edges are different lengths and all angles are different and not 90°. And in rhombohedral unit cells, the cell edges are all the same length, and the angles are all the same but are not 90°.

The seven distinct unit cell shapes shown above in Figure 11.33 are all that are possible. The seven are primitive – they contain one lattice point in total. But stacking plane lattices can lead to other, nonprimitive, unit cells that have one of the seven shapes we have seen. Figure 11.34 shows three examples.



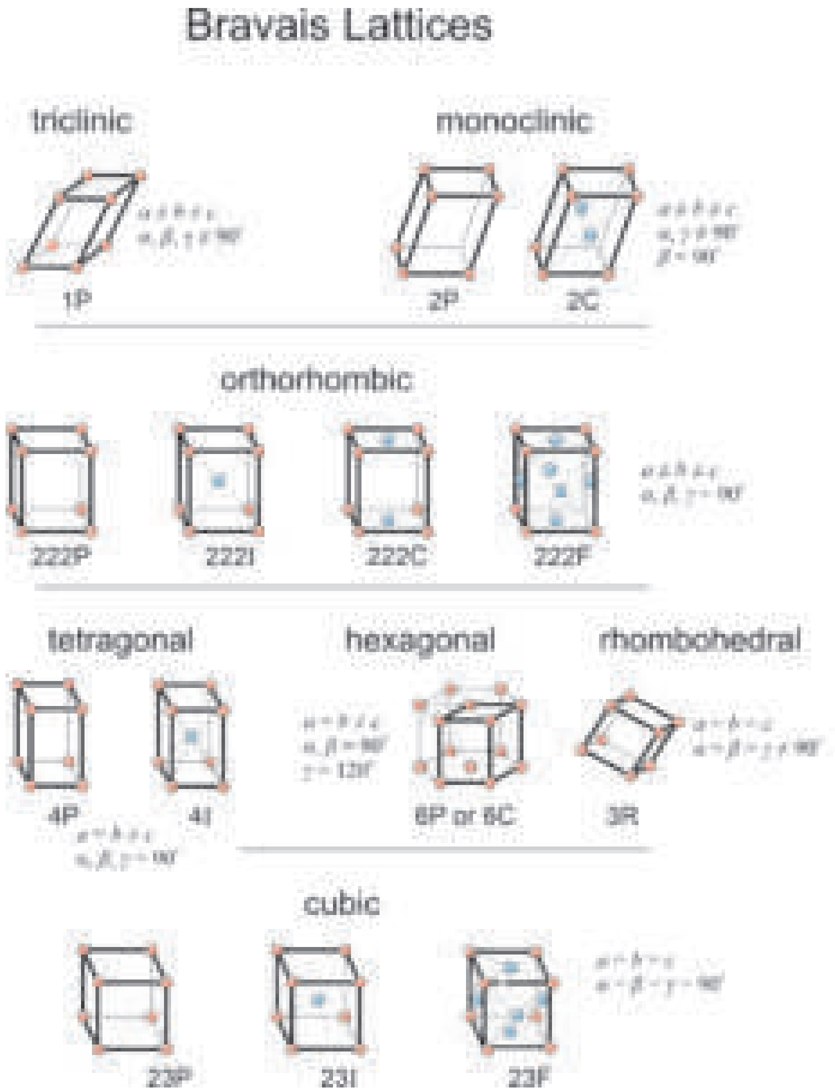
11.34 Centered 3-d lattices containing extra lattice points

In Figure 11.34*a*, square nets have been stacked so that every other net is offset. One square from each of three layers is shown. The offset layer puts an extra lattice point (blue) in the center of a tetragonal prism. This is an example of a *body-centered* unit cell, symbolized by the letter *I*.

In Figure 11.34*b*, we put a hexanet directly above another. The result is a hexagonal prism with extra lattice points (blue) in the centers of its top and bottom. This is an example of an *end-centered* unit cell, symbolized by the letters *A*, *B*, or *C*, depending on which pair of faces contain the extra lattice points.

In Figure 11.34*c*, diamond nets are stacked with the middle layer offset. This produced an orthorhombic prism that contains extra lattice points at the centers of every face. This is an example of a *face-centered* unit cell, symbolized by the letter *F*.

11.4.1 Bravais Lattices



11.35 The 14 Bravais lattices

When all possibilities have been examined, we can show that only 14 distinctly different space lattices exist. We call them the 14 *Bravais lattices*, named after Auguste Bravais, a French scientist who was the first to show that there were only 14 possibilities. The 14 Bravais lattices correspond to 14 different unit cells that may have any of seven different symmetries, depending on the crystal system.

Figure 11.35 lists the 14 Bravais lattices and shows a unit cell for each. In this figure, red lattice points are at the corners of unit cells and blue spheres are the extra points due to centering. Symbols such as 1P, 2P, 2C, 222P, etc., beneath each figure describe their symmetries and are standard labels we use for each of the 14 lattices.

Seven of the possible unit cells are primitive (P), one in each system (shown in Figure 11.33). In these unit cells, eight cells share each of the eight lattice points at the corners, so the total number of lattice points per cell is one.

The other eight Bravais lattices involve nonprimitive unit cells containing two, three, or four lattice points. Body-centered unit cells (I), for example, contain one extra lattice point at their center (Figure 11.34*a*). End-centered unit cells (C) contain extra lattice points in two opposite faces (Figure 11.34*b*). But the extra points are only half in the cell, so the total number of lattice points is 2. Face-centered unit cells (F) have lattice points in the centers of six faces (see Figure 11.34*c*). Each of the six points is half in the unit cell and half in an adjacent cell. The total number of lattice points is therefore 1 (at the corners) + 3 (in the faces) = 4.

As pointed out in the discussion of two-dimensional lattices, we sometimes make arbitrary decisions when choosing unit cells. The 14 Bravais lattices, in fact, do not represent the only 14 that we could list. For example, in the monoclinic system, the end-centered (*2F*) unit cell is equivalent to a body-centered one (*2I*) with different dimensions. Most crystallographers consider only the end-centered cell because that is the way it has been done since the time of Bravais. The important thing to realize is that no matter what unit cells and lattices we consider, only 14 are distinct. Furthermore, the 14 in Figure 11.35 are the simplest and the ones used by most crystallographers.

For a good discussion of Bravais Lattices, watch this video:
▶ Video 11-1: Bravais Lattices (6 minutes)

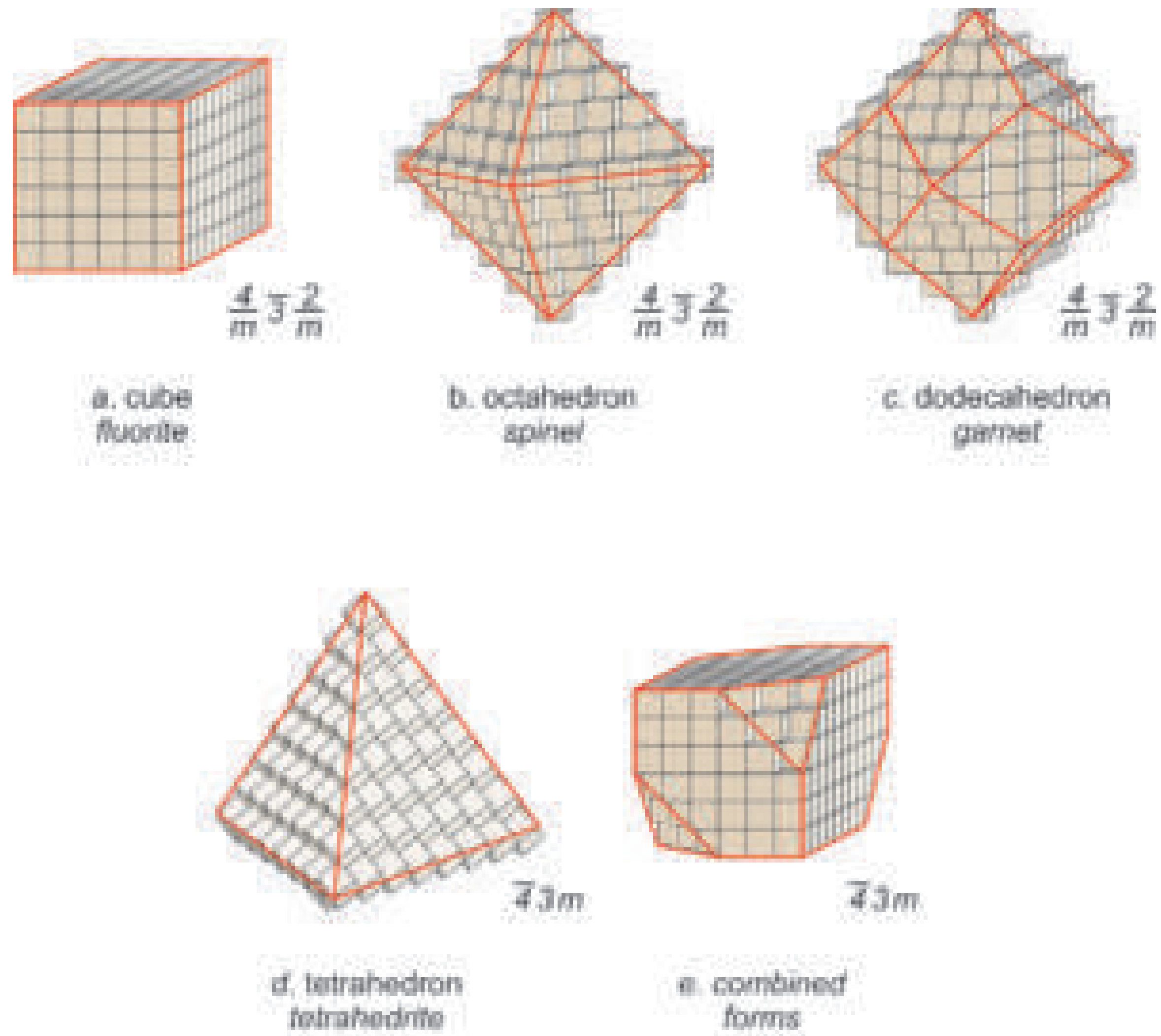
11.4.2 Unit Cell Symmetry and Crystal

Symmetry

Consider fluorite (CaF_2), spinel ($MgAl_2O_4$), the garnet almandine ($Fe_3Al_2Si_3O_{12}$), and the rare mineral tetrahedrite ($Cu_{12}As_4S_{13}$). Tetrahedrite has a primitive cubic unit cell; fluorite and spinel have face-centered cubic unit cells; almandine has a body-centered cubic unit cell. In fluorite, Ca^{2+} is found at the corners of the unit cell and at the center of each face, while F^- occupies sites completely within the unit cell (see Figure 11.6). Spinel, almandine, and tetrahedrite have more complex structures, in large part because they contain more than one cation.

Many unit cells together make up a crystal. The crystal may or may not have the same symmetry as a single unit cell. In fluorite, spinel, and almandine crystals, unit cells stack together so that all symmetry elements (rotation axes and mirror planes) are preserved. However, fluorite crystals are typically cubes, spinel crystals are typically octahedra, and almandine crystals are typically dodecahedra. Figure 11.36 shows how cubes can combine to make these shapes. Figure 11.36*e* shows an example of a crystal, made with a cubic unit cell, that contains two forms.

Figures 11.37 through 11.40 show mineral examples. We also saw a beautiful dodecahedral garnet crystal in Figure 10.48 (Chapter 10) and well formed fluorite crystals in Figures 4.3 and 4.37 (Chapter 4). The cube, octahedron, and dodecahedron are all special forms that have the same symmetry as the unit cell, $^4/_m\bar{3}^2/_m$. Tetrahedrite crystals (Figures 11.36*d* and 11.40), in contrast with the other three, do not have the same symmetry as their unit cell. Although made of cubic unit cells, the crystals lack 4-fold rotation axes. Instead, when euhedral, tetrahedrite crystals typically form pyramids that have symmetry $\bar{4}^3/_m$.



11.36 Cubic unit cells combining to make crystals

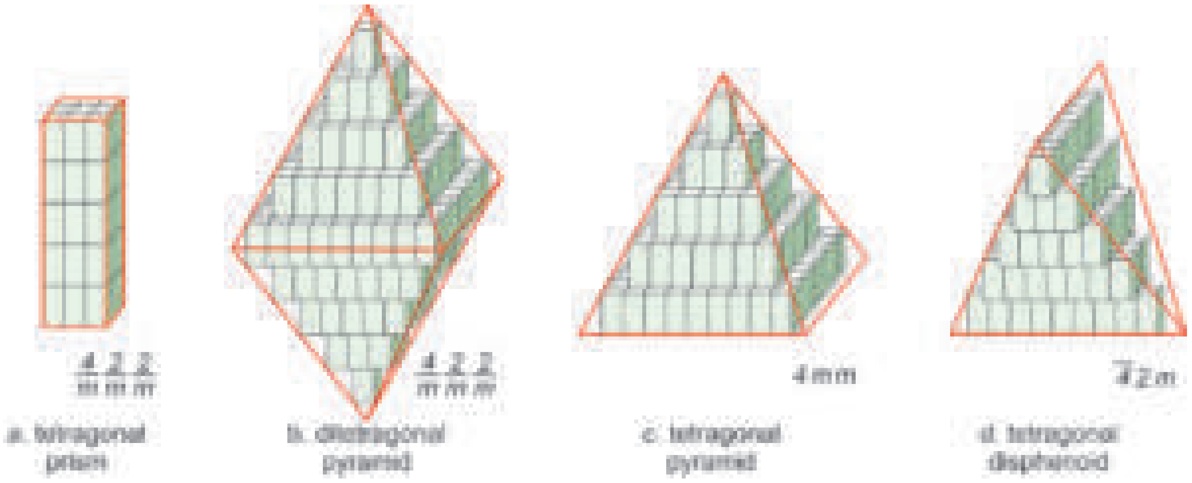
11.37 Fluorite cubes with specks of pyrite on top

11.38 Spinel octahedra in a white calcite marble

11.39 Garnet in a schist from Alaska

11.40 Tetrahedrite with minor malachite and azurite

Figure 11.41 shows how tetragonal unit cells can be stacked to produce crystals. The results include a tetragonal prism and a ditetragonal pyramid that have the same symmetry as the unit cell ($^4/_m{}^2/_m{}^2/_m$). But tetragonal unit cells can also create a pyramid (with symmetry 4mm) or a tetragonal disphenoid (with symmetry $\bar{4}2m$). Other shapes with other symmetries are possible too. Note that the crystal in Figures 11.41*b* and *d* contain a single form; the other two crystals contain two forms.



11.41 Four crystals composed of tetragonal unit cells

The preceding discussion points out a fourth important law of crystallography is:

- *If a crystal has certain symmetry, the unit cell must have at least as much symmetry.*

As a corollary to this law, because crystals consist of unit cells, the symmetry of a crystal can never be more than that of its unit cell. If a crystal has a 4-fold axis of symmetry, it must have a unit cell that includes a 4-fold axis of symmetry. A mineral that forms cubic crystals must have a cubic unit cell. If a crystal has certain symmetry, it is certain that the unit cell and crystal’s atomic structure have at least that much symmetry. They may have more, as in the case of tetrahedrite.

This fourth law is the basis for the crystal systems we introduced in the previous chapter. The symmetry of a crystal requires certain symmetry in the crystal’s unit cell. And we divide the 32 possible symmetries – the 32 point groups – into systems based on that understanding. The six crystal systems are defined by symmetry and named by their unit cell shape. And crystals in the same crystal system all have the same-shaped unit cells, even if the crystals themselves do not look the same.

If, for example, a crystal has symmetry 4, $\bar{4}$, $^{4}/_{m}$, 422, $4mm$, $\bar{4}2m$, or $^{4}/_{m}{}^{2}/_{m}{}^{2}/_{m}$, it must have a unit cell that is a tetragonal prism. If a crystal has symmetry 222, $mm2$, or mmm, it must have a unit cell that is an orthorhombic prism, and so forth. The table below summarizes these relationships. By examining a crystal's morphology, we can often determine the point group, system, and unit cell shape. Determining whether a unit cell is primitive, face-centered, body-centered, or end-centered, however, is not possible without additional information, which usually comes from X-ray diffraction studies.

Crystal Systems and Point Groups

crystal system	**unit cell shape**	**point groups**
triclinic	triclinic prism	1, $\bar{1}$
monoclinic	monoclinic prims	2, m, $^{2}/_{m}$
orthorhombic	orthorhombic prism	222, $mm2$, mmm
tetragonal	tetragonal prism	4, $\bar{4}$, $^{4}/_{m}$, 422, $4mm$, $\bar{4}2m$, $^{4}/_{m}{}^{2}/_{m}{}^{2}/_{m}$
rhombohedral	rhombohedron	3, $\bar{3}$, 32, $3m$, $\bar{3}\ m$
hexagonal	hexagonal prism	6, $\bar{6}$, $^{6}/_{m}$, 622, $6mm$, $\bar{6}2m$, $^{6}/_{m}{}^{2}/_{m}{}^{2}/_{m}$

cubic	cube	23, $^{2}/_{m}\bar{3}$, 432, $\bar{4}3m$, $^{4}/_{m}\bar{3}^{2}/_{m}$

It is important to remember that the symmetry of a crystal depends not only on the symmetry of the unit cell, but also on how the unit cells combine to make the crystal. Some minerals, such as halite and other salts, tend to develop euhedral crystals with obvious symmetry, making it easy to infer the symmetry of the unit cell. Others develop crystals with faces that are nearly identical, suggesting the presence of symmetry but leaving some uncertainty. While size and shape of faces can vary because of accidents of crystal growth, the angles between faces vary little from the ideal (Steno’s law). Consequently, crystallographers often rely on angles instead of face shapes to infer the symmetry of the unit cell. Even if a crystal is anhedral and poorly formed, its internal structure is orderly and its unit cells all have the same atomic arrangement.

11.5 Symmetry of Three Dimensional Atomic Arrangements

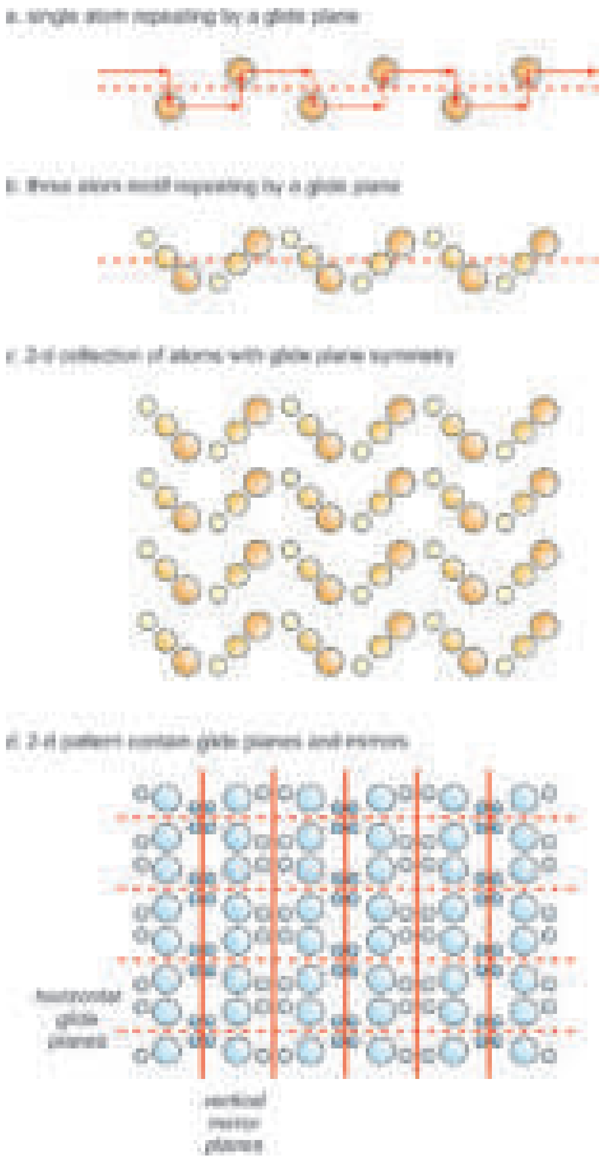
In the preceding sections, we discussed the shapes and symmetries of crystals. We now turn our attention briefly to space symmetry, the symmetry of three-dimensional atomic structures. What possible symmetry can be present? An atomic arrangement in a crystal consists of groups of atoms (an atomic motif) that repeat an infinite number of times according to one of 14 space lattices. Thus, the overall symmetry depends on both the arrangement of atoms in a motif and the lattice type.

Atomic motif symmetry may involve rotation axes, rotoinversion axes, mirror planes or inversion centers. So motifs may have symmetries equivalent to any of the 32 point groups. Consider an orthorhombic mineral, for example. Its atomic motif may have symmetry mmm, ${}^{2}/_{m}{}^{2}/_{m}{}^{2}/_{m}$, or *mm*2. Its lattice may be 222P, 222C, 222I, or 222F. That gives 12 possible combinations. If we do this calculation for all crystal systems, we come up with 61 possible symmetries for 3D atomic arrangements. But there are many more than that. Because in 3D, we find two additional symmetry operators that we have not considered previously.

11.5.1 Space Group Operators

In 3D, we assign atomic arrangements to different *space groups* that have different *space symmetries*. Each space group is characterized by a combination of one of the 14 Bravais lattices with a unit cell that has a particular symmetry. We call the different kinds of possible symmetry operators, collectively, *space group operators*. Space symmetry includes the point group symmetries that we discussed previously. And it also includes *glide planes* and *screw axes*. These two are special kinds of space group operators that involve combinations of point symmetry and translational symmetry, in much the same way that rotoinversion axes involve rotation and inversion applied simultaneously.

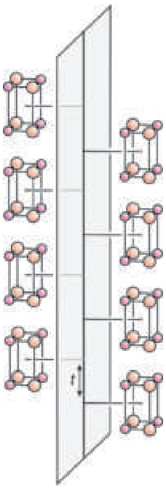
11.5.1.1 Glide Planes



11.42 Examples of glide planes

Glide planes differ from normal mirror planes because they involve translation before reflection. Figure 11.42 shows some examples. In drawing *a*, a single atom is repeated by a horizontal glide plane (dashed red line). The red arrows show how the atom repeats by translation followed by reflection. In drawing *b*, a three-atom motif repeats according to a horizontal glide plane. And in drawing *c*, we see a 2D pattern with glide plane symmetry. The pattern contains no mirrors, rotation axes, and no inversion center. Yet, it contains significant symmetry.

Space group operators and other symmetry elements combine in many ways. For example, Figure 11.42*d* shows a pattern that contains horizontal glide planes and vertical mirror planes. As we have seen previously, combination of symmetry elements often requires other symmetry to be present. The combination of a glide plane with a mirror means that this pattern contains additional (horizontal) mirror planes and 2-fold rotation axes.



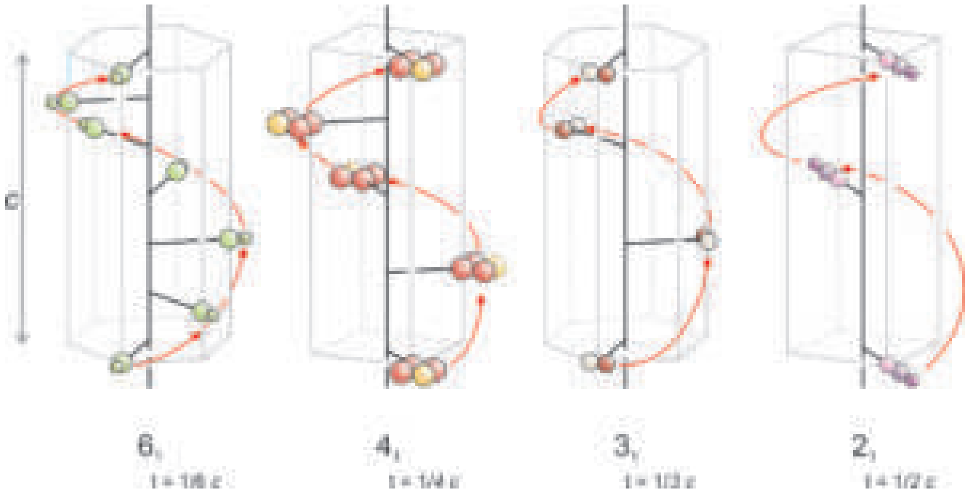
11.43 A glide plane in three dimensions

Figure 11.43 shows a glide plane in three dimensions; a motif of 8 atoms repeats by vertical translation and reflection. This figure involves a simple motif with lots of space around it. The arrangements of atoms in most minerals are generally more complicated and difficult to draw in 3D in a way that shows their symmetries clearly. In part, this is because a glide plane affects all atoms in a structure, not just the ones adjacent to the plane as seen in Figure 11.43.

Atomic arrangements may contain any of six symmetry elements involving reflection, singly or in combination. These include proper mirror planes and 5 different kinds of glide planes. Glide planes may have any of the orientations that mirror planes can have. So, they may be parallel to the *a*-, *b*-, or *c*-axis, parallel to a face diagonal, or parallel to a main (body) diagonal. For most glide planes, the magnitude of the translation (*t*) is half the unit cell dimension in the direction of translation. The direction of gliding distinguishes different glides and allows us to classify them. The table below summarizes the possibilities.

Space Symmetry Operators Involving Reflection			
operator	**type of operation**	**orientation of translation**	**translation***
m	proper mirror	none	none
a	axial glide	parallel to a	$^1/_2\ a$
b	axial glide	parallel to b	$^1/_2\ b$
c	axial glide	parallel to c	$^1/_2\ c$
n	diagonal glide	par. to a face diagonal	$^1/_2\ t$
d	diamond glide	par. to main diagonal	$^1/_4\ t$
**t* = the unit cell dimension in the direction of translation			

11.5.5.2 Screw Axes

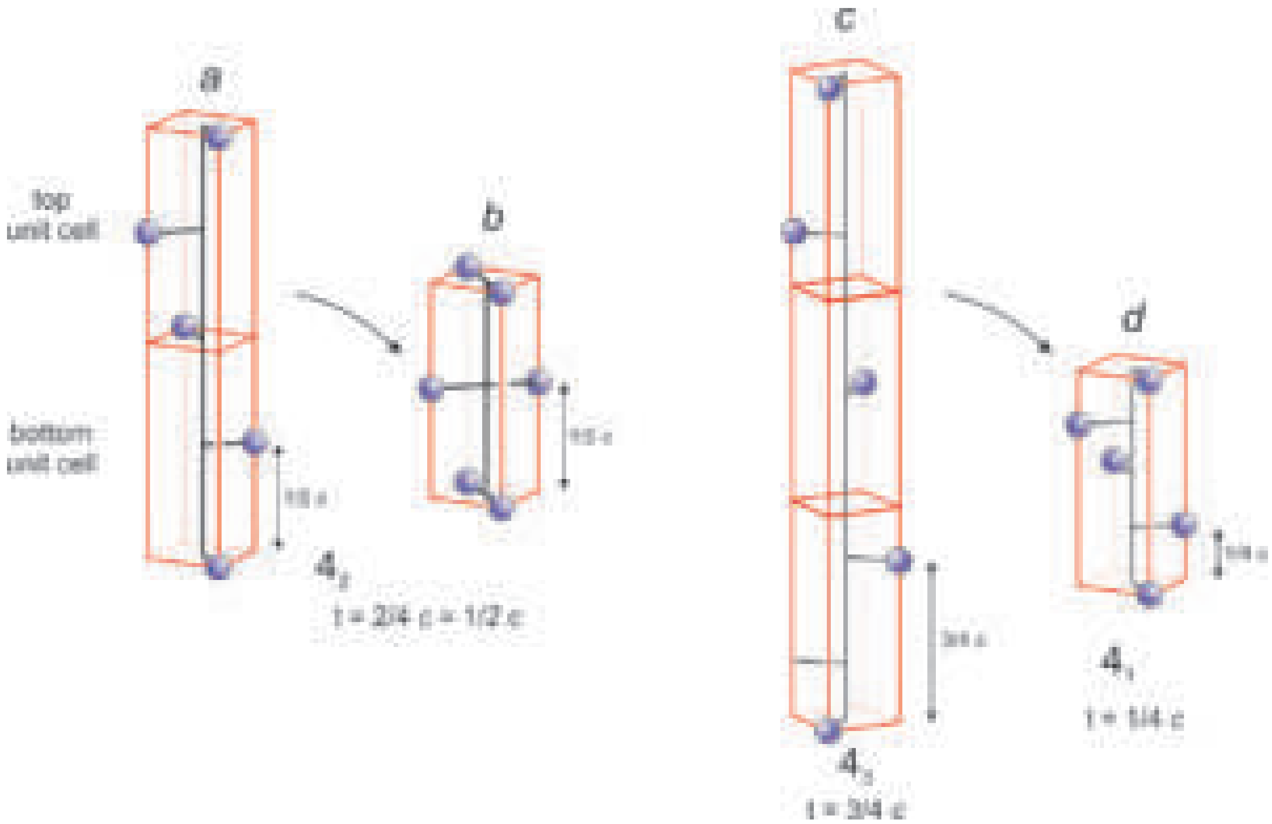


11.44 Examples of screw axes

Screw axes result from the simultaneous application of translation and rotation. We combine 2-, 3-, 4-, or 6-fold rotation operators with translation to produce these symmetry elements. Many combinations are possible. Figure 11.44 shows a few examples.

A screw axis has the appearance of a spiral staircase. We rotate a motif, translate it, and get an additional motif. As with proper rotation axes (rotation axes not involving translation), each *n*-fold screw operation involves rotation of $360^{\circ}/n$. After *n* repeats, the screw has come full circle. The translation associated with a screw axis must be a rational fraction of the unit cell dimension or the result will be an infinite number of atoms, all in different places in different unit cells.

We label screw axes using conventional symbols. In Figure 11.44, they are 6_1, 4_1, 3_1, and 2_1. In the labels, the large 6, 4, 3, or 2 signifies 6-fold, 4-fold, 3-fold, or 2-fold rotation. The subscript tells the translation distance. A 6_1 screw axis, for example, involves translation that is $^1/_6$ of the unit cell dimension in the direction of the screw axis. 4_1, 3_1, and 2_1 axes involve translations that are $^1/_4$, $^1/_3$, and $^1/_2$ the unit cell dimension. Similarly, 6_2, 6_3, 6_4, and 6_5 screw axes (not shown) would involve translations of $^2/_6$, $^3/_6$, $^4/_6$, and $^5/_6$ of the cell dimension.



11.45 Some 4-fold screw axes

Figure 11.45*a* shows application of a 4_2 operator to a single atom. The translation distance is $^{1}/_{2}$ the unit cell height, and we must go through four 90° rotations and two unit cells to get another atom that is directly above the starting atom. All unit cells must be identical, but the 4_2 operation gives a bottom and top unit cell with atoms in different places. The only way this operator can be made consistent is to add the extra atoms shown in Figure 11.45*b*. In other words, the presence of a 4_2 axis requires the presence of a 2-fold axis of symmetry.

Figure 11.45*c* shows a 4_3 axis and 11.44*d* shows a 4_1 axis. After four applications of either operator the total rotation is 360°, bringing the fourth point directly above the first. For the 4_1 axis, after four applications the total translation is equivalent to one unit cell length. But for the 4_3 axis it is three unit cell lengths because the translation is $^{3}/_{4}$ of the unit cell. The only way the 4_3 operator can be made consistent is to add the extra atoms shown in Figure 11.45*d*. Note that the 4_3 and 4_1 axes produce patterns that are mirror images of each other. The two axes are an *enantiomorphic pair*, sometimes called *right-handed* and *left-handed* screw axes.

When all combinations are considered, we get the 21 possible rotation axes (either proper rotation axes or screw axes) listed in the table below. As with proper rotational axes, some screw axes are restricted to one or a few crystal systems. For example, 3_1 and 3_2, which are an enantiomorphic pair, only exist in the rhombohedral system. Similarly, the 6_n axes only exist in the hexagonal system.

Space Symmetry Operators Involving Rotation

operator	type of operation	rotation angle	translation*

1	identity	360°	none
$\bar{1}$	inversion center	360°	none
2	proper 2-fold	180°	none
2_1	2-fold screw	180°	1/2 *t*
$\bar{2}$	mirror	180°	none
3	proper 3-fold	120°	none
3_1	3-fold screw	120°	1/3 *t*
3_2	3-fold screw	120°	1/3 *t*
$\bar{3}$	3-fold rotoinversion	120°	none
4	proper 4-fold	90°	none
4_1	4-fold screw	90°	1/4 *t*
4_2	4-fold screw	90°	2/4 = 1/2 *t*
4_3	4-fold screw	90°	3/4 *t*
$\bar{4}$	4-fold rotoinversion	90°	none
6	proper 6-fold	60°	none
6_1	6-fold screw	60°	1/6 *t*
6_2	6-fold screw	60°	2/6 = 1/3 *t*
6_3	6-fold screw	60°	3/6 = 1/2 *t*
6_4	6-fold screw	60°	4/6 = 2/3 *t*
6_5	6-fold screw	60°	5/6 *t*
$\bar{6}$	6-fold rotoinversion	60°	none

**t* = the unit cell dimension in the direction of translation

11.6 Space Groups

When we combine the space group operators in the tables above with the 14 possible space lattices, we get 230 possible space groups. See Box 11-1. They represent all possible symmetries crystal structures can have, although most of them are not represented by any known minerals. Deriving them all is not trivial, and crystallographers debated the exact number until the 1890s when several independent studies concluded that there could only be 230.

Crystallographers use several different notations for space groups; the least complicated is that used in the *International Tables for X-ray Crystallography* (ITX) (Hahn, 1983). ITX space group symbols consist of a letter indicating lattice type (*P, I, F, R, A, B,* or *C*) followed by symmetry notation similar to conventional Hermann-Mauguin symbols. An example is $\mathrm{P}4_2/_m2_1/_n2/_m$, the space group of rutile. Rutile has a primitive (*P*) tetragonal unit cell, a 4_2 screw axis perpendicular to a mirror plane, a 2_1 screw axis perpendicular to an *n* glide plane, and a proper 2-fold axis perpendicular to a mirror plane. Rutile crystals have symmetry ${}^4/_m{}^2/_m{}^2/_m$.

Or consider garnet. Garnet crystals have point group symmetry ${}^4/_m\overline{3}{}^2/_m$. Garnet’s space group is $I4_1/_a\overline{3}2/_\mathrm{d}$. This describes a body-centered unit cell, a 4_1 screw axis perpendicular to an *a* glide plane, a 3-fold rotoinversion axis, and a proper 2-fold axis perpendicular to a *d* glide plane. Rather than using an entire symbol, crystallographers often use abbreviations for space groups (and occasionally for point groups). Thus, they would say that garnet belonged to the space group *Ia*3*d*.

The translations associated with lattices, glide planes, and screw axes are very small, on the order of tenths of a nanometer, equivalent to a few angstroms. Detecting their presence by visual examination of a crystal is impossible, with or without a microscope. A crystal with symmetry ${}^4\square_m{}^2/_m{}^2/_m$ could belong to the space group $\mathrm{I}4_1/_a2/_c2/_d$, but there are also 19 other possibilities. We say that the 20 possibilities are *isogonal*, meaning that when we ignore translation they all have the same symmetry. Without detailed X-ray studies, telling one isogonal space group from another is impossible, and we are left with only the 32 distinct point groups.

For some supplementary information and a different perspective on space groups, check out the video that is linked here:

▶ Video 11-2: Space group operators and space groups (8 minutes)

● Box 11-1 Why Are There Only 230 Space Groups?

In Chapter 10 we showed that point groups may have one of 32 symmetries; in this chapter we determined that crystal structures must have one of 14 Bravais lattices. When we combine point groups with Bravais lattices, and consider all possible space group operators, we get 230 possible space groups. The 230 space groups are the only 3D symmetries that a crystal structure can have. They were tabulated in the 1890s by a Russian crystallographer, E. S. Federov; a German mathematician, Artur Schoenflies; and a British amateur, William Barlow, all working independently.

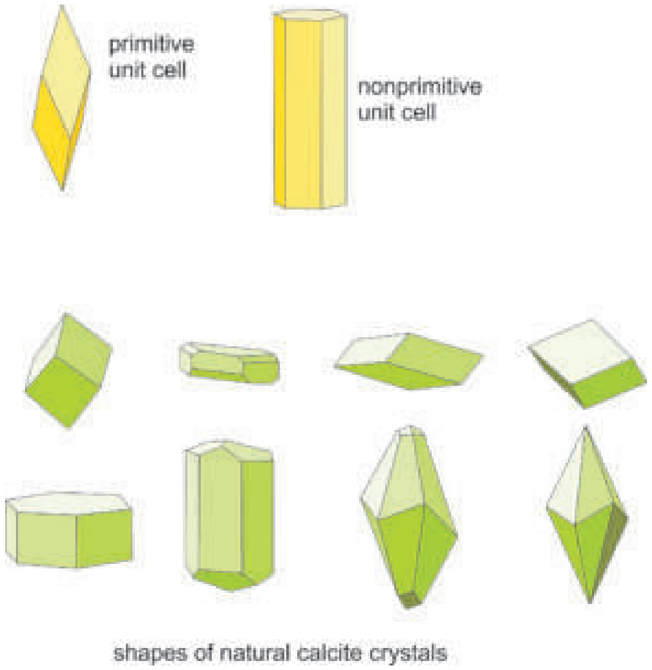
Why are there only 230 space groups? The answer is that symmetry operators, as we have already seen, can only combine in certain ways. In the discussion of point group symmetry, we concluded that mirrors and rotation axes can only combine in 32 ways. Some combinations required that other symmetry be present. Other combinations were redundant or led to infinite symmetry, which is impossible. The same is true of space group operators and Bravais lattices; only certain combinations are allowed and some combinations require other symmetry to be present.

Triclinic lattices (P1 and $P\bar{1}$) may not be combined with 2-fold axes of any sort. Similarly, 3, 3_1, and 3_2 axes are only consistent with a rhombohedral or hexagonal lattice (3R or 6P). If an atomic arrangement contains two perpendicular 4-fold axes, it must contain a third and it must contain 3-fold axes, too. And, we just showed that the presence of a 4_2 axis require that a 2-fold axis is present. There are many other constraints, too, which is why the total number of space groups is only 230.

11.7 Crystal Habit and Crystal Faces

Why do halite and garnet, both cubic minerals, have different crystal habits? It is not fully understood why crystals grow in the ways they do. Cubic unit cells may lead to cube-shaped crystals such as typical halite crystals, octahedral crystals such as spinel, dodecahedral crystals such as garnet, and many other shaped crystals. Why the differences? Crystallographers do not have complete answers, but the most important factor is the location of atoms and lattice points within a unit cell. Crystals of a particular mineral tend to have the same forms, or only a limited number of forms, no matter how they grow. Haüy and Bravais noted this and used it to infer that atomic structure controls crystal forms. In 1860 Bravais observed what we now call the *Law of Bravais*:

- *Faces on crystals tend to be parallel to planes having a high density of lattice points.*



11.46 Two choices of unit cells and some typical shapes for calcite crystals

This means that, for example, crystals with hexagonal lattices and unit cells often have faces related by hexagonal symmetry. Crystals with orthogonal unit cells (those in the cubic, orthorhombic, or tetragonal systems) tend to have faces at 90° to each other.

The relationship between lattice/unit cell symmetry and crystal habit can be seen in Figure 11.46. The figure shows two choices for calcite’s unit cell. The rhombohedron is a doubly primitive unit cell and the hexagonal equivalent contains four $CaCO_3$ motifs. The drawings below the unit cells show some common shapes for natural calcite crystals. There is noticeable resemblance between unit cell shapes, which represent the lattice symmetry, and some of the crystal shapes. Thus, Bravais’s Law works well. The photos below in Figures 11.47 – 11.52 show natural calcite crystals that match quite well the drawings in Figure 11.46.

11.47 Calcite scalenohedra

11.48 A calcite rhombohedron

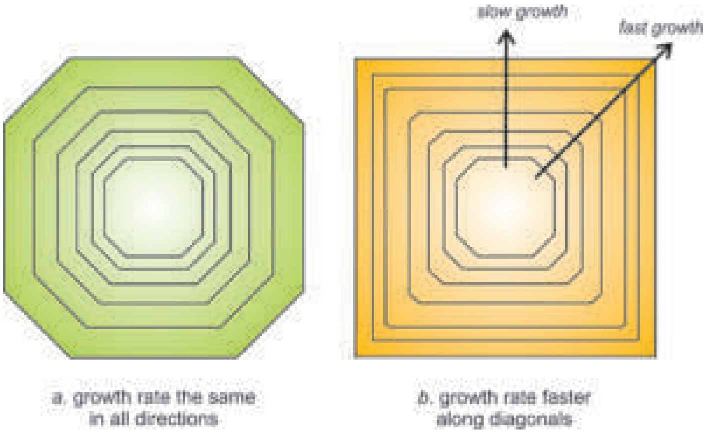
11.49 Calcite on fluorite

11.50 Calcite on galena

11.51 Calcite with orpiment

11.52 Calcite with siderite

Unfortunately, some minerals, including pyrite (FeS_2) and quartz (SiO_2), appear to violate Bravais's Law. Bravais's observations were based on considerations of the 14 Bravais lattices and their symmetries, but in the early twentieth century, P. Niggli, J. D. H. Donnay, and D. Harker realized that space group symmetries needed to be considered as well. By extending Bravais's ideas to include glide planes and screw axes, Niggli, Donnay, and Harker explained most of the biggest inconsistencies. They concluded that crystal faces form parallel to planes of highest atom density, a slight modification of the Law of Bravais.



a. growth rate the same in all directions

b. growth rate faster along diagonals

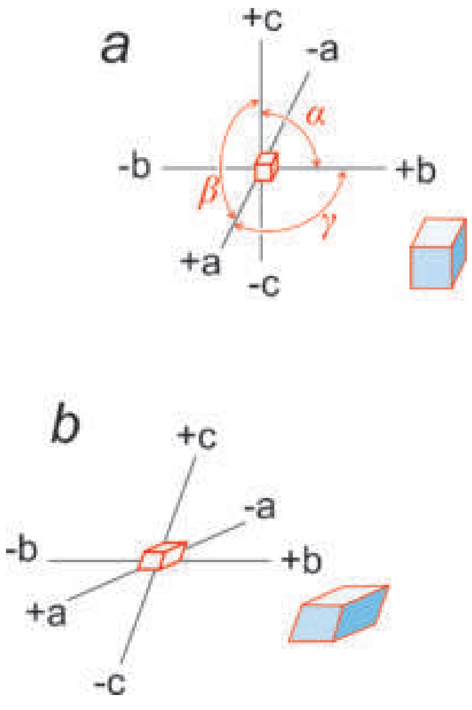
11.53 The rate at which faces grow affects crystal shape

As a crystal grows, different faces grow at different rates. Some may dominate in the early stages of crystallization while others will dominate in the later stages. The relationship, however, is the opposite of what we might expect. Faces that grow fastest are the ones that eventually disappear. Figure 11.53 shows why this occurs. If all faces on a crystal grow at the same rate, the crystal will keep the same shape as it grows (the green crystal in Figure 11.53*a*). However, this is not true if some faces grow faster than others.

In Figure 11.53*b*, the diagonal faces (oriented at 45° to horizontal) grew faster than those oriented vertically and horizontally. Eventually, the diagonal faces disappeared; they "grew themselves out." The final crystal has a different shape, and fewer faces, than when it started growing. We observe this phenomenon in many minerals; small crystals often have more faces than larger ones.

11.8 Quantitative Aspects of Unit Cells, Points, Lines, and Planes

11.8.1 Unit Cell Parameters and Crystallographic Axes



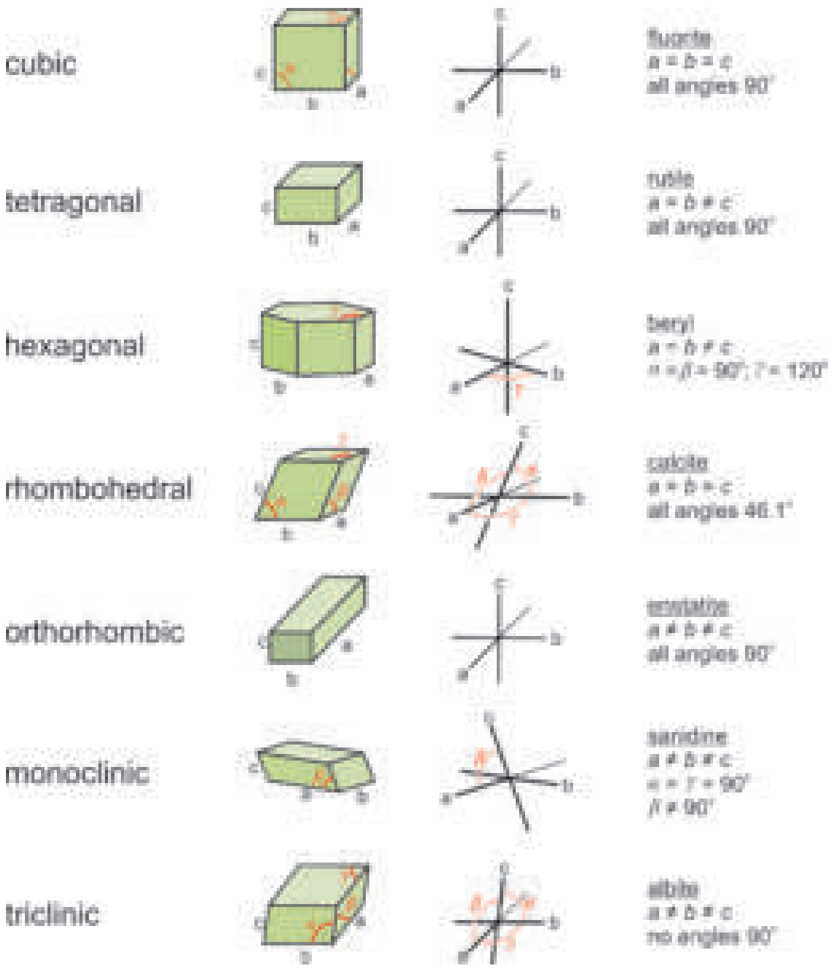
11.54 Coordinate systems from mineral crystals

Earlier in this chapter, we introduced the unit cell parameters *a, b, c, α, β,* and *γ*. *a, b,* and *c* are the lengths of unit cell edges; *α, β*, and *γ* are the angles between the edges. *α* is the angle between *b* and *c, β* is the angle between *a* and *c*, and *γ* the angle between *a* and *b* (Figure 11.54*a*).

Unit cell edges define a coordinate system used by crystallographers when they wish to describe the locations of atoms or other features within a cell. Some crystal systems are orthogonal (cubic, tetragonal, orthorhombic) but others are not. Cubic crystals, and others that belong to an orthogonal system, use a standard Cartesian coordinate system. Figure 11.54*a* shows an example.

Figure 11.54*b* shows axes that are inclined with respect to each other. In this example, they correspond to a triclinic unit cell. *α, β,* and *γ,* the angles between axes, are not equal to 90° and (in contrast with the cube) the edges of the unit cell have different lengths along different axes.

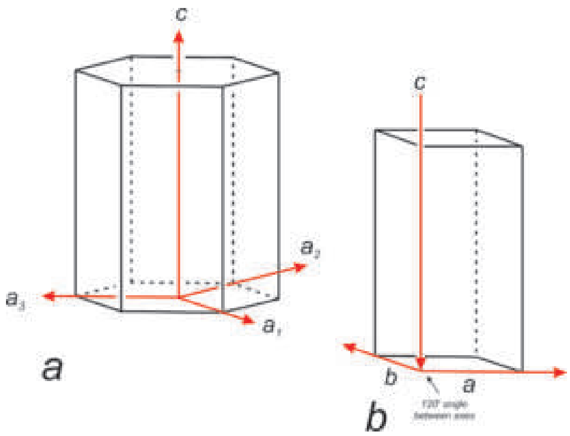
Figure 11.55 shows coordinate axes for each of the crystal systems. We have labeled all angles in the top drawing (a cube); in the other drawings, only the non-90° angles are identified. In the orthogonal systems, *α, β,* and *γ* all equal 90°. In the hexagonal and rhombohedral systems, *β* = 120° and the other angles are 90°. Other constraints are in the right-hand column of this figure. We used calcite as an example of a rhombohedral mineral. In much of the literature, however, calcite’s unit cell is described using a hexagonal prism.



11.55 Coordinate systems for different crystal systems

Although it makes no practical difference which edges of a unit cell we call *a, b,* or *c,* or which angles are *α, β*, and *γ*, mineralogists normally follow certain conventions. In triclinic minerals, none of the angles are special and *a, b,* and *c* are all different lengths. Although the literature contains exceptions, by modern convention edges are chosen so that $c < a < b$. In monoclinic minerals, such as sanidine, only one angle in the unit cell is not 90°. By convention, the non-90° angle is *β*, the angle between *a* and *c*. For historical reasons, this convention is called the *second setting for monoclinic minerals*. In orthorhombic crystals, we choose axes so that $c > a > b$. In tetragonal and hexagonal crystals, the *c*-axis always corresponds to the 4-fold or 6-fold axis.

In this book we use a, b, and c to designate the three crystallographic axes, but crystallographers sometimes use subscripts to indicate axes, and thus cell edges, that must be identical lengths because of symmetry. Instead of a, b, and c, the three axes of cubic minerals might be designated a_1, a_2, and a_3. The axes of tetragonal crystals can be designated a_1, a_2, and c.



11.56 Two choices for axes in hexagonal crystals

For hexagonal crystals, crystallographers have historically used four axes: a_1, a_2, a_3, and c (Figure 11.56*a*). The three a-axes, a_1, a_2, and a_3, are parallel to edges of a nonprimitive hexagonal unit cell. Although the third a-axis is redundant for describing symmetry or points in 3D space, it has been included in the past to emphasize that there are three identical a-axes perpendicular to the c-axis. Because only three axes are used in much of the modern literature (Figure 11.56*b*), we will only briefly mention the fourth axis in the rest of this chapter.

Although mineralogists historically used angstroms (1 Å = 10^{-10} m) to give cell dimensions, much recent literature uses nanometers (1 nm = 10 Å). Typical mineral unit cells have edges of 2 to 20 Å (0.2 to 2 nm). The angles α, β, and γ are normally given as a decimal number of degrees (for example, 94.62°). These angles between edges vary greatly, although unit cells are often chosen so that angles are close to 90°.

Instead of using angstroms (or nanometers) to give distances, we may also use unit cell dimensions as a scale. For example, we might say that a certain plane intersects the axes at distances of 3*a*, 2*b*, and 2*c* from the origin. It is implicit that 3*a* refers to a distance equal to three unit cell edge lengths along the a-axis, 2*b* a distance equal to two unit cell lengths along the b-axis, and 2*c* a distance equal to two unit cell lengths along the c-axis.

The symmetry of a unit cell always affects the relationships between *a, b,* and *c*. So, in the cubic system, $a = b = c$, but in the tetragonal and hexagonal systems $a = b \neq c$. The relationships implied by crystal systems mean that, for systems other than triclinic, we need not give six values to describe unit cell shape. For example, for orthorhombic, hexagonal, tetragonal, and cubic minerals, we do not specify any angles because they are all defined by the crystal system. The table below gives examples of unit cell parameters for minerals from each of the crystal systems; unnecessary information has been omitted. These same example minerals are the ones listed in Figure 11.55.

<table>
<tr><th colspan="7">Unit Cell Parameters (<i>a, b, c, α, β,</i> and <i>γ</i>), <i>Z</i> (number of formulas per unit cell), and <i>V</i> (unit cell volume) for One Mineral from Each of the Crystal Systems*</th></tr>
<tr><th>fluorite
CaF_2</th><th>rutile
TiO_2</th><th>beryl
$Be_3Al_2Si_6O_{18}$</th><th>calcite
$CaCO_3$</th><th>enstatite
$Mg_2Si_2O_6$</th><th>sanidine
$KAlSi_3O_8$</th><th>albite
$NaAlSi_3O_8$</th></tr>
</table>

cubic $Z = 4$ $a = 5.46$ $V = 162.77$	tetragonal $Z = 2$ $a = 4.59$ $c = 2.96$ $V = 62.36$	hexagonal $Z = 2$ $a = 9.23$ $c = 9.19$ $V = 2034.09$	rhombohedral $Z = 2$ $a = 4.98$ $c = 17.06$	orthorhombic $Z = 4$ $a = 18.22$ $b = 8.81$ $c = 5.21$ $V = 836.30$	monoclinic $Z = 4$ $a = 8.56$ $b = 13.03$ $c = 7.17$ $\gamma = 115.98$ $V = 799.72$	triclinic $Z = 4$ $a = 8.14$ $b = 12.8$ $c = 7.16$ $\alpha = 94.33$ $\beta = 116.57$ $\gamma = 87.65$ $V = 746.01$

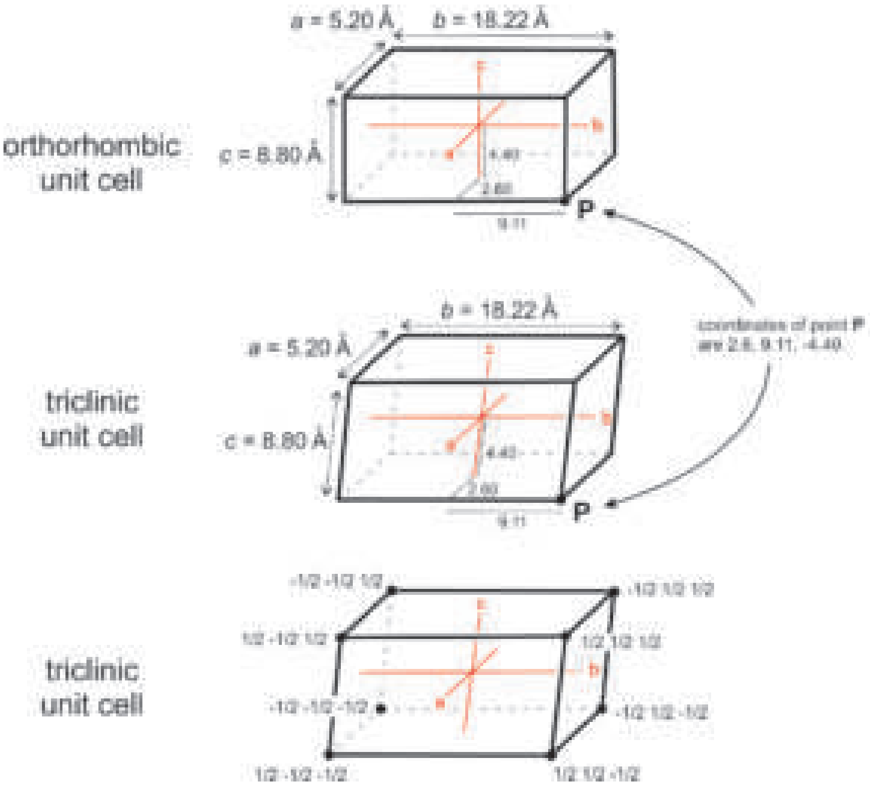
*a, b, and c are in angstroms; α, β, and γ are in degrees; and V is in cubic angstroms.

Consider the triclinic mineral albite, a feldspar with composition $NaAlSi_3O_8$. The last column in the table lists albite’s unit cell parameters. Because none of the angles are special and none of the cell edges are equal, we need six parameters to describe the cell shape. In contrast, fluorite (the first column of the table) has a cubic unit cell, so we need to give only one cell dimension, the length of the cell edge. It is implicit that all angles are 90° and all cell edges are the same length.

Physical dimensions do not completely describe a unit cell. We must also specify the nature and number of atoms within the unit cell. To provide some of this information, the table above lists two other things besides dimensions and angles: mineral formulas and Z, the number of formulas in each unit cell. For example, fluorite has the formula CaF_2 and $Z = 4$.

This means there are 4 CaF_2 molecules (4 Ca and 8 F atoms) in each unit cell. Albite has the formula $NaAlSi_3O_8$ and $Z = 4$. This means that four $NaAlSi_3O_8$ formulas are in each unit cell. In other words, each unit cell contains 4 Na atoms, 4 Al atoms, 12 Si atoms, and 32 O atoms.

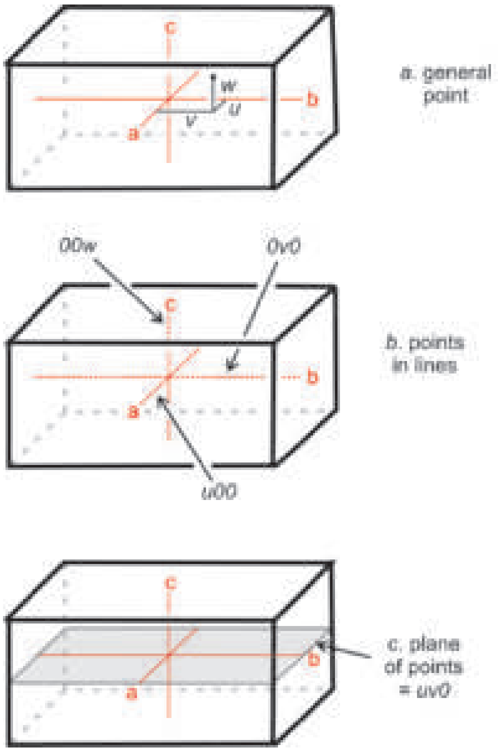
11.8.2 Points in Unit Cells



11.57 Coordinates of points in unit cells

Mineralogists describe the locations of atoms or other points in unit cells by giving their coordinates. As examples, consider the orthorhombic and triclinic crystals shown in Figure 11.57. In the orthorhombic crystal the three axes (shown in red) intersect at 90°, in the triclinic crystal they do not. Assume both crystals have cell dimensions a = 5.20 Å, b = 18.22 Å, and c = 8.80 Å, and the axes’ origins are at the center of the unit cells as shown. The coordinates of point **P**, at the lower right-hand corner in drawings *a* and *b*, are therefore 5.20/2 = 2.60 Å, 18.22/2 = 9.11 Å, and 8.80/2 = -4.40 Å. The negative sign arises because the points are in a negative direction from the origin along the c-axis.

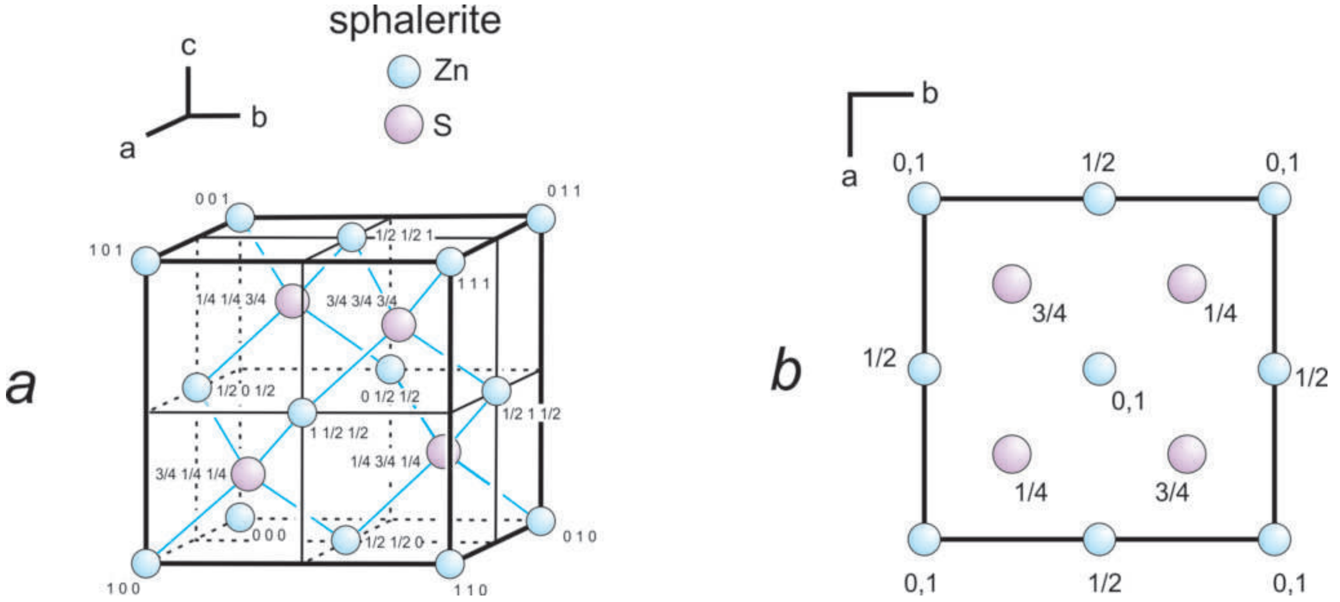
We do not, however, normally report coordinates in angstroms (Å). Instead, we report distances relative to unit cell dimensions. Another way to describe the location of point **P** in Figure 11.57*a* and *b* would be to say it has coordinates 1/2*a*, 1/2*b*, -1/2*c*. Typically, we normalize coordinates to unit cell dimensions by dropping the *a, b,* and *c*. The coordinates then become 1/2 , 1/2 , -1/2. The points at the corners must have coordinates ±1/2, ±1/2, ±1/2, if the origin is at the center of the unit cell (Figure 11.57*c*). Note that the system to which a crystal belongs does not affect coordinate values.



11.58 General points and special points in unit cells

Traditionally, crystallographers have used the variables *u, v,* and *w* to represent the coordinates of a point if the coordinates are rational numbers, and *x, y,* and *z* if irrational. For simplicity, in this text we will use *uvw* in all instances (Figure 11.58*a*). We can say that *uvw* represents a general point anywhere in the cell.

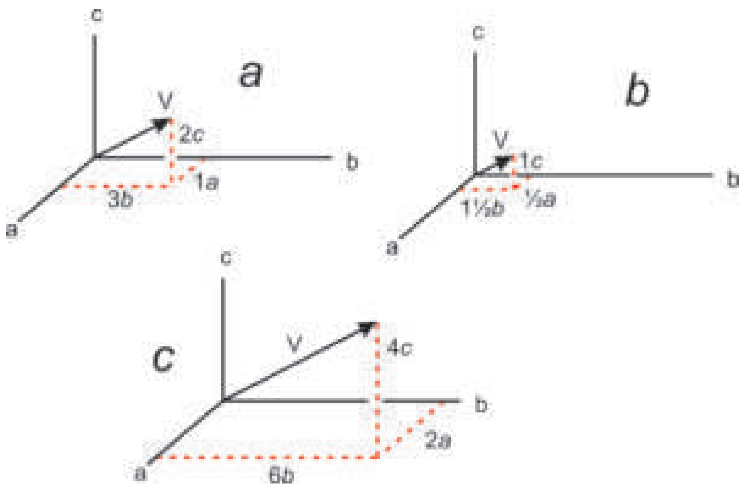
Suppose two coordinates, for example *v* and *w*, are zero. All the points described by the coordinates *u*00 constitute a set of special points, lying along the a-axis (Figure 11.58*b*). Similarly, 0*v*0 and 00*w* refer to sets of special points on the b- and c-axes, respectively. If only one coordinate equals zero, a point lies in a plane including two axes. We might, for example, talk about special points located at *uv*0. These are points on a plane that includes the a- and b-axes, as shown in Figure 11.58*c*. Note that no parentheses or brackets are used when giving coordinates of a point.



11.59 The atoms in a sphalerite unit cell

Figure 11.59*a* shows a unit cell of sphalerite, ZnS, with *uvw* coordinates for each atom. The axes origin is in the bottom back left corner. Because three-dimensional drawings are sometimes difficult to draw and see, crystallographers often use projections, which contain the same information in a less cluttered manner (Figure 11.59*b*). In the projection, which is a view down the c-axis, we need not specify *u* and *v* values because they can be estimated from the location of the atoms in the drawing. The numbers are *w* values. Sometimes we omit *w* values for atoms at unit cell corners; by convention, this means the atoms are found on both the top and bottom of the cell as it appears in projection.

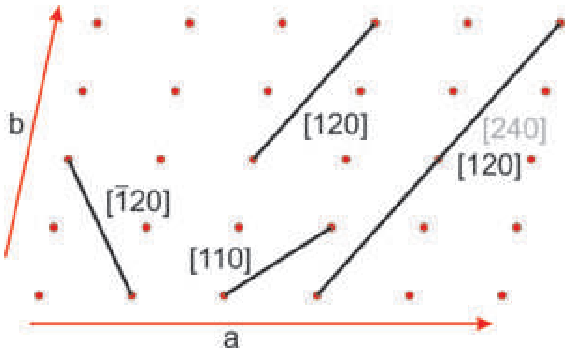
11.8.3 Lines and Directions in Crystals



11.60 Vector directions

The absolute location of a line in a crystal is not often significant, but directions (vectors) have significance because they describe the orientations of symmetry axes, zones, and other linear features. Crystallographers designate directions with three indices in square brackets, [*uvw*]. As with point locations, we give numbers describing directions in terms of unit cell dimensions. In Figure 11.60*a*, direction **V** has indices [132] – it goes from the origin to a point at 1*a*, 3*b*, 2*c*.

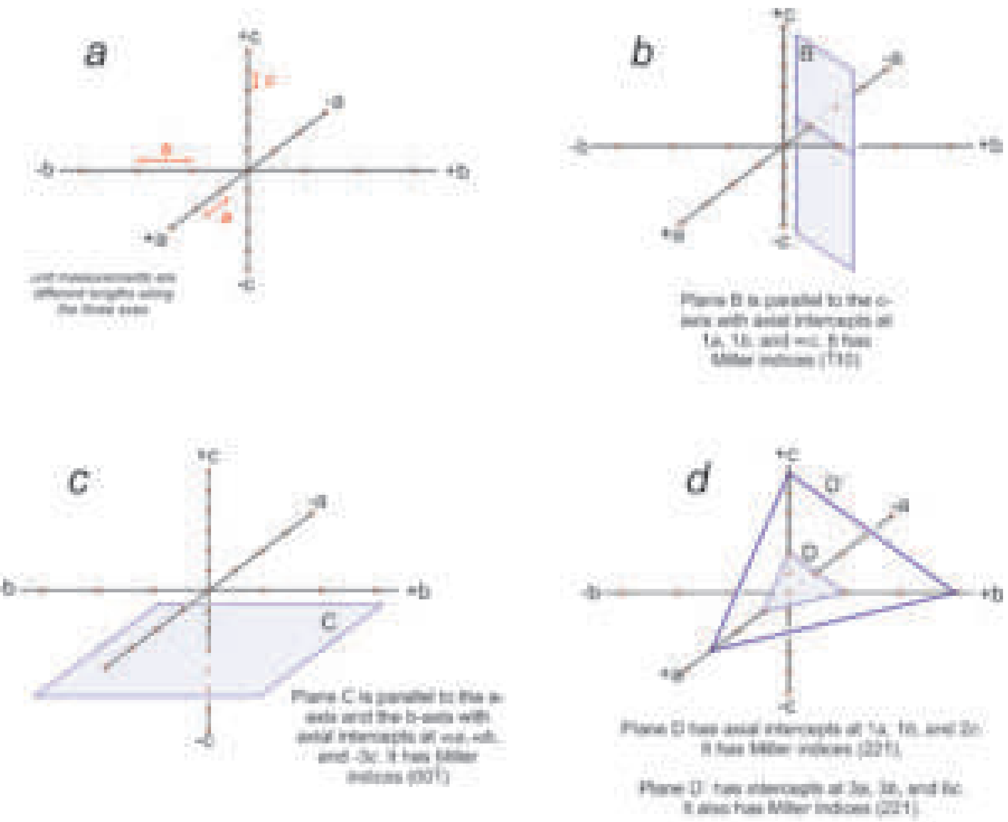
The drawings in 11.60*b* and 11.60*c* show other vectors pointing the same direction as [132]. We clear fractions and divide by common denominators when giving the indices of a direction. So directions [½ 1½ 1] and [264] would be simplified and described as [132]. Although no commas are included in [132], reading sequentially, as we do for point locations, we articulate it “one-three-two.” By convention, commas separate indices only if they have more than one digit.



11.61 Examples of line indices

Figure 11.61 shows several lines on a two-a dimensional lattice. Parallel lines have identical indices, and choosing an origin is unimportant. The direction [240] is the same as [120], and when we clear the common denominator [240] becomes [120]. For line [$\bar{1}$20], the bar over the 1 is equivalent to a negative sign, indicating that the line goes in the negative a-direction. We articulate the indices as “bar-one-two-zero.” Because all directions in Figure 11.61 lie in the a-b plane, they have indices [*uv*0]. This notation indicates that the first two indices may vary, but the third is 0.

11.8.4 Planes in Crystals



11.62 Axial intercepts and Miller indices

While crystals and crystal faces vary in size and shape, Steno’s law tells us that angles between faces are characteristic for a given mineral. The absolute location and size of the faces are rarely of significance to crystallographers, while the relative orientations of faces are of fundamental importance. We can use face orientations to determine crystal systems and point groups, so having a simple method to describe the orientation of crystal faces is useful.

Figure 11.62*a* shows three axes with different unit cell lengths; small red dots show unit increments along the axes. The axes are orthogonal, so this arrangement corresponds to the orthorhombic system. Consider a plane parallel to a crystal face. Such a plane may be parallel to one axis (Figure 11.62*b*), parallel to two axes (Figure 11.62*c*) or it may intersect all three axes (Figure 11.62*d*).

We can describe the orientation of a plane by listing its intercepts with the axes. For a face running parallel to an axis, the intercept is at ∞ (because the face never intersects the axis). In Figure 11.62*b*, the plane is parallel to the c-axis but intersects the a-axis and b-axis one unit from the origin. So, it has axial intercepts 1*a*, 1*b*, and ∞*c*, which we shorten to 1, 1, ∞. In Figure 11.62*c*, the plane is parallel to two axes and has axial intercepts ∞*a*, ∞*b*, 3*c*, or simply ∞, ∞, 3.

Crystal faces are commonly parallel to axes, but the use of ∞ to describe their orientations can be confusing and awkward. A second problem with using intercepts to describe face orientation is that parallel planes, such as plane D and plane D´ Figure 11.10*d*, have different intercepts. Crystallographers find this inconvenient because crystals may be large or small, but face orientation, not size, is generally the feature of greatest significance. To avoid these and other problems, crystallographers do not report axial intercepts. They use *Miller indices* instead.

11.9 Miller Indices

Miller indices were first developed in 1825 by W. Whewell, a professor of mineralogy at Cambridge University. We use them to describe the orientation of crystal faces, and also the orientations of cleavages and other planar properties. They are named after W. H. Miller, a student of Whewell's, who promoted and popularized their use in 1839. The general symbol for a Miller index is (*hkl*), in which the letters *h, k,* and *l* each stand for an integer. Parentheses enclose the resulting Miller index. As with directions, bars above numbers show negative values and we do not include commas unless numbers have more than one digit.

We calculate Miller indices for a plane from its axial intercepts (Figure 11.62). The procedure is as follows:

- First, we invert axial intercept values. (∞ becomes zero after inversion.)
- Then we clear all fraction by multiplying by a constant.

·And we divide by a constant to eliminate common denominators.

Consider the plane in Figure 11.62*b*. It has intercepts 1, 1, ∞. Inverting these values gives us (110), the Miller index of the plane. And the plane in Figure 11.62*c* has axial intercepts ∞, ∞, 3. Inverting these values gives us 0, 0, $^1/_3$. Clearing the fraction gives us (001), the Miller index. We articulate it as “oh-oh-one.”

Figure 11.62*d* contains two planes. One has intercepts 1, 1, 2. The other has intercepts 3, 3, 6. Inverting intercepts for the first plane gives us 1, 1, $^1/_2$. Clearing fractions yields the Miller index (221). Inverting intercepts for the second plane gives $^1/_3$, $^1/_3$, $^1/_6$. Clearing fractions yields (221). So we see that parallel planes have the same Miller index. If the planes shown in this figure were crystal faces, we would call them the “two two one face” no matter their size or shape. Thus the Miller index describes the orientation of a crystal face with respect to crystallographic axes, but not the absolute size or location of the face. The relationship between planes and directions in a crystal depends on the crystal system. Except in the cubic system, the direction [*uvw*] is neither perpendicular nor parallel to planes with the Miller index (*uvw*).

Because crystal faces are parallel to rows of lattice points, they are parallel to planes that intercept crystal axes at an integral number of unit cells from the origin. Consequently, inversion of intercepts and clearing fractions always yields integers. This observation is known as the *Law of Rational Indices*. Another observational law, called *Haüy’s Law:*

- Miller indices of faces generally contain low numbers.

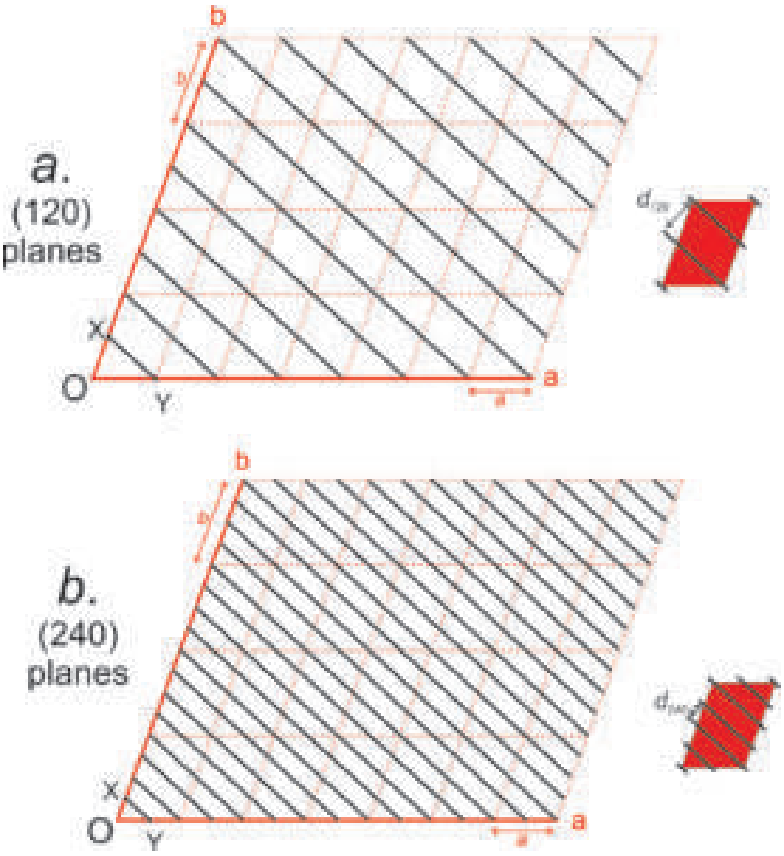
For example, (111) is a common face in crystals, while (972) is not. Haüy’s law is really a corollary to the *Law of Bravais,* already discussed, which states that faces form parallel to planes of high lattice point density; planes with low values in their Miller index have the greatest lattice point density.

As mentioned previously, crystallographers have in the past used four axes for crystals in the hexagonal system. This yields a Miller index with four numbers (*hkil*). One of the first three values *h, k,* or *i* is redundant because we can always describe the location of a plane in three-dimensional space with three variables. In all cases: $h + k + i = 0$. Because of the redundancy, and to be consistent with other crystal systems, many crystallographers today use only three indices for hexagonal minerals.

11.10 The Miller Indices of Planes within a Crystal Structure

We use Miller indices to describe the orientation of crystal faces, but we also use them to describe planes within a crystal structure. For example, we may be interested in knowing which planes in a unit cell contain the most atoms. For planes within a cell, we calculate Miller indices as we do for crystal faces, except that we do not clear common denominators after inversion of axial intercepts.

For example, if we calculate an index of (633) for a set of planes, we do not divide by 3 to give (211), as we do when calculating a Miller index for a crystal face. We do not do this because, besides orientation, the spacing and location of planes are important when we are talking about atomic arrangements and other aspects of crystal structures, and not talking about crystal faces.



11.63 Planes in unit cells

Figure 11.63*a* shows some two-dimensional unit cells cut perpendicular to the c-axis. The plane passing through points X and Y (and perpendicular to the page) has axial intercepts 1, $^1/_2$, ∞, so its Miller index is (120). Because all unit cells are equivalent, we know identical (120) planes exist in all the unit cells.

Drawing *a* shows all equivalent (120) planes; when we discuss (120) planes within a crystal, we refer to this entire family, not just to one plane. As shown in the red inset drawing, four (120) planes intersect each unit cell. Two pass through the inside of the cell, and two through corners. Note that the axial intercepts of the (120) plane closest to the origin (O) are 1, $^1/_2$, ∞, equivalent to $^1/_h$, $^1/_k$, $^1/_l$ for the entire family of planes. This relationship holds true for any family of (*hkl*) planes.

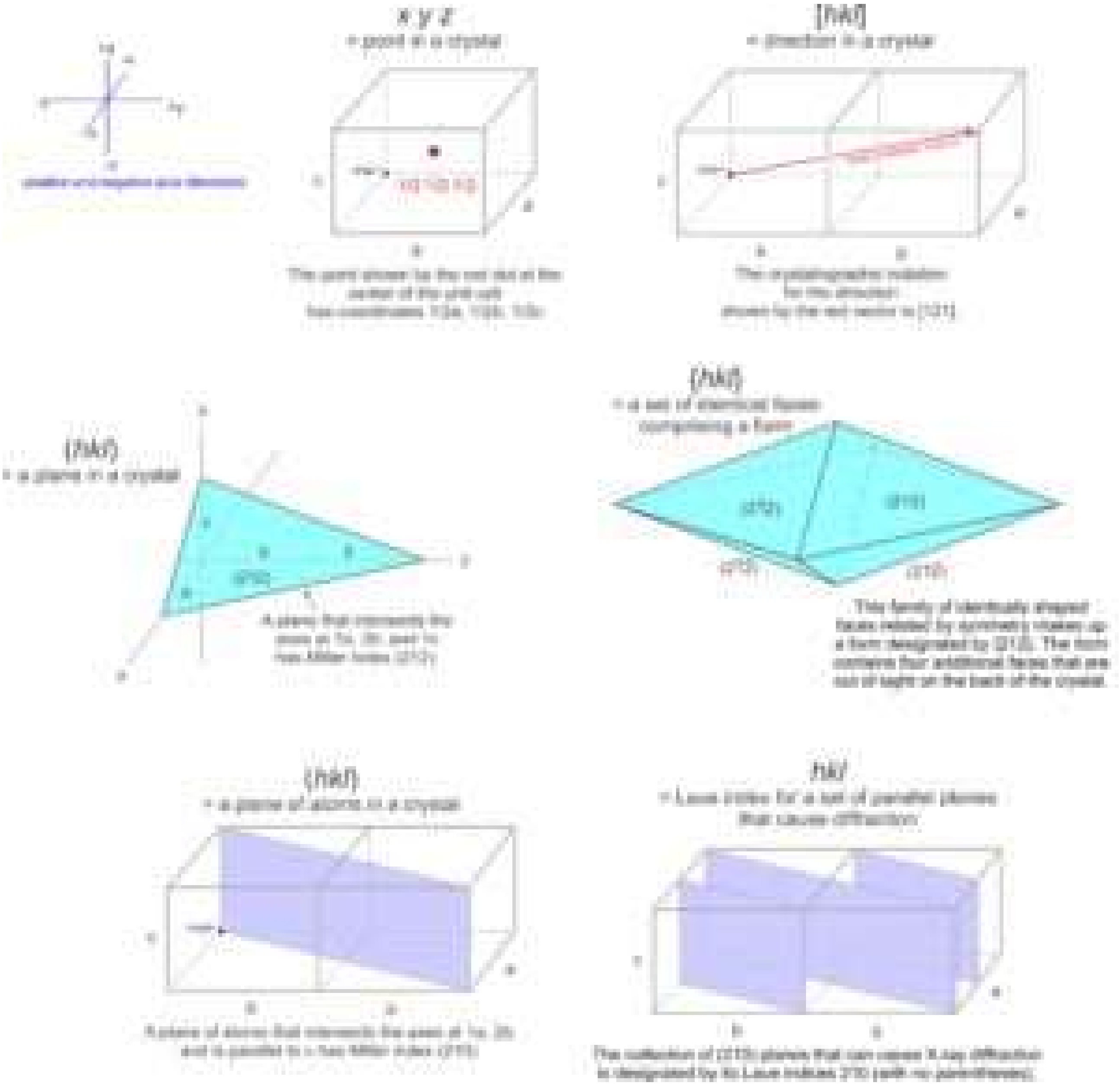
Different families of planes, with the same orientation but different spacings, have different indices. The drawings in Figure 11.63*b* show planes spaced half as far apart as the (120) planes; $d_{240} = {}^1/_2\, d_{120}$. The plane closest to the origin has intercepts ${}^1/_2$, ${}^1/_4$, ∞. Inversion gives the Miller index (240). We do not clear the common denominator (divide by 2) because the families of (240) and (120) planes, although parallel, are not identical. There are twice as many (240) planes. The red inset drawing shows that seven planes intersect each unit cell – two at opposite corners; the rest pass through the cell interior.

Because the Miller indices (120) and (240) are proportional, the two families of planes are parallel but the (240) planes are spaced apart half as much as the (120) planes. This is always the case – proportional indices mean planes are parallel and larger indices mean planes are closer together. If we are considering a set of planes that cause X-ray diffraction (discussed in detail in the next chapter), we describe them with *Laue indices*. These indices are the same as Miller indices, but we omit the parentheses. Thus we can have 120 or 240 diffraction, and the angle of diffraction is different because the two families of planes have different spacings.

11.11 Confusing Notations

As just discussed, crystallographers designate points, lines, and planes using different kinds of notations. The different notations, however, are somewhat similar, and this can be confusing. So, Box 11-2 summarizes the standard notations used, and gives examples.

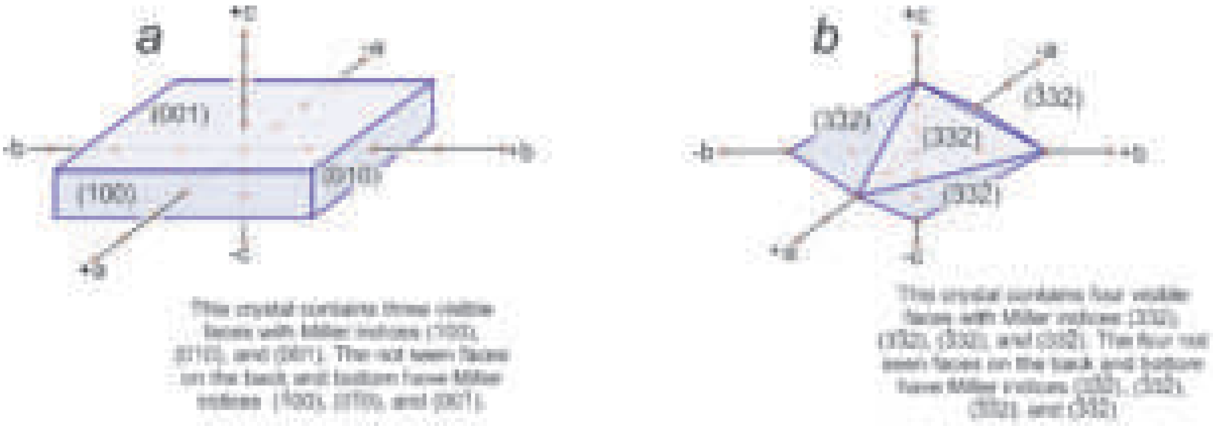
- **Box 11-2 Summary: Different Kinds of Crystallographic Notations**



11.10 Crystal Forms and the Miller Index

The replacement of unknown or variable numbers in a Miller index with *h*, *k*, or *l* allows us to make generalizations. The index (*hk*0) describes the family of faces with their third index equal to zero. A Miller index including a zero describes a face is parallel to one or more axes (Figure 11.64). The family of faces described by (*hk*0) is parallel to the c-axis

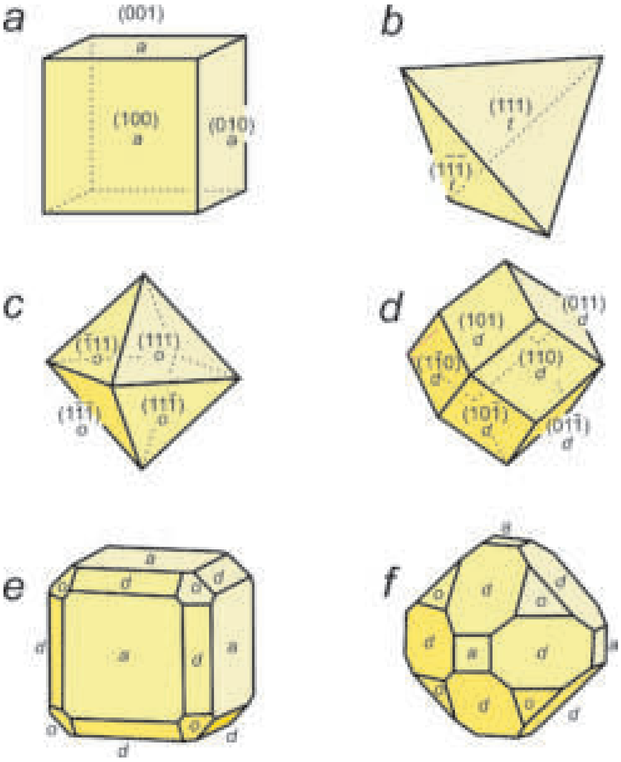
(Figure 11.63); faces with the Miller index (00*l*) are parallel to both the a-axis and the b-axis (Figure 11.62*c*).



11.64 Forms and Miller indices

Figure 11.64*a* shows an orthorhombic prism with six faces. Some faces cannot be seen, but the Miller indices of all six are (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0), and (00$\bar{1}$). Although this crystal contains three forms, indices for all faces contain the same numbers (two zeros and a one) but the order of numbers and the + or – sign changes.

Figure 11.64*b* shows an orthorhombic dipyramid. It contains only one form, and all the faces have the same numbers in their Miller index (332). This is always true for faces that belong to the same form; they always have similar Miller indices. This relationship is especially clear for crystals in the cubic system because high symmetry means that many forms may contain many identical faces.



11.65 Some forms in the cubic system

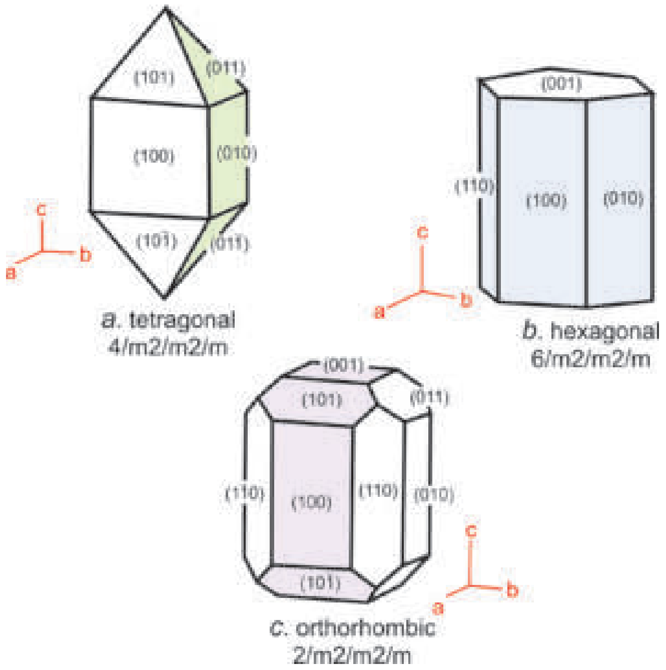
The six identical faces on the cube in Figure 11.65*a* have indices (001), (010), (100), (00$\bar{1}$), (0$\bar{1}$0), and ($\bar{1}$00). We symbolize the entire form {100}, and the { } braces indicate the form contains all faces with the numerals 1, 0, and 0 in their Miller index, no matter the order.

The four faces on the tetrahedron in Figure 11.65*b*, and the eight faces on the octahedron in Figure 11.65*c* are all equilateral triangles. For both, the form is {111}. As Figure 11.65*b* and *c* demonstrate, two crystals of different shapes can have the same form if they belong to different point groups. The tetrahedron in Figure 11.65*b* belongs to point group $\bar{4}3m$; the octahedron in Figure 11.65*c* belongs to point group $^4/_m\bar{3}^2/_m$. If we know the point group and the form, we can calculate the orientation of faces. If a crystal contains only one form, we then know the shape of the crystal. Note that the cube, octahedron, and dodecahedron all belong to point group $^4/_m\bar{3}^2/_m$. The cubic form is {100}, the octahedral form is {111}, and the dodecahedral form in Figure 11.65*d* is {110}.

Figure 11.65*e* shows a crystal containing three forms: cube {100}, octahedron {111}, and dodecahedron {110}. Because they all belong to point group $^4/_m\bar{3}^2/_m$, we know the faces are oriented as shown. However, the crystal in Figure 11.64*f* belongs to the same point group and contains the same forms, but the size and shape of corresponding faces are different. We do not know the crystal shape if more than one form is present, unless we know some extra information.

Crystallographers sometimes label faces of the same form with the same letter as we have done in Figure 11.65. For some forms, the letter is just the first letter of the form name. For example, *o* indicates the octahedral form and *d* the dodecahedral form in the cubic system. Usually, however, the symbols are less obvious (we normally designate cube faces, for example, by the letter *a*); labels also vary from one crystal system to another.

11.10.1 Zones and Zone Axes



a. tetragonal 4/m2/m2/m

b. hexagonal 6/m2/m2/m

c. orthorhombic 2/m2/m2/m

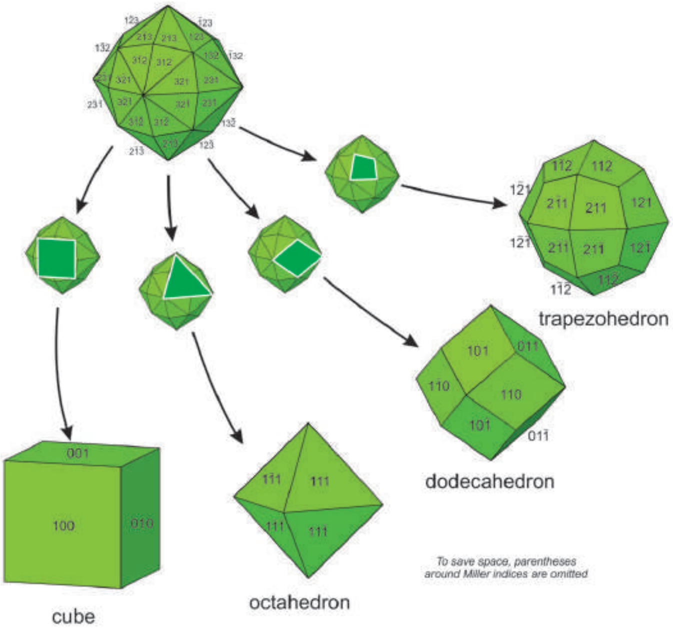
11.66 Zones and zone axes

As discussed in Chapter 9, a set of faces parallel to a common direction defines a *zone*. We designate zones by the common direction, which we call the *zone axis*. Figure 11.66 shows examples of tetragonal, hexagonal, and orthorhombic crystals. The green faces in the tetragonal crystal (Figure 11.66*a*) form a zone. The faces are parallel to the a-axis. Three other faces, not visible are also part of the zone. The zone axis is [100], parallel to a. Zones may contain faces from more than one form, as in this example.

Figure 11.66*b* shows a common zone in hexagonal minerals: 6 (blue) faces (three not seen) are parallel to the c-axis. The zone axis is [001]. And in Figure 11.66*c*, the zone (purple faces) comprises three forms and the zone axis is [010]. In all three drawings, additional zones are present besides those just mentioned. In these three examples, the zones axes have simple indices because they are parallel to crystal axes. Zones need not be parallel to axes, and consequently the indices may contain values other than 0 and 1.

● Box 11-3 General Forms, Special Forms, and Miller Indices

The relationship between special forms and general forms is the same as the one between special points and general points discussed in the previous chapter. Faces of a general form are neither parallel nor perpendicular to any symmetry element, while faces of special forms are. Thus, in special forms, symmetry relates fewer equivalent faces.



11.67 Hexoctahedron and related special forms

The *hexoctahedron* (Figure 11.67) is the general form in the $^4/_m\bar{3}^2/_m$ point group; its Miller index contains three different values. The simplest index is {123}, indicating that $h \neq k \neq l$ and that none of the indices are zero. The hexoctahedron contains 48 triangular faces. We can think of this form as octahedron with each of its eight faces replaced by six smaller triangular faces; hence, its name.

All other forms with the same symmetry are special forms in the hexoctahedral class. Crystals in this class may contain any of 15 forms singly or in combinations. Figure 11.67 shows four examples. See Box 10-3 and the table in Chapter 10 for other examples.

Special forms have two or more identical indices in their Miller index, or have an index with value zero; Figure 11.67 contains examples. For example cube faces belong to the {*h*00} form; octahedron faces belong to the {*hhh*} form. The dodecahedron faces belong to the {*hh*0} form. Another related form, the trapezohedron, has Miller index {*hkk*}, signifying that two of its indices have the same value and that none are zero. *h*, *k*, and *l* can have any integer values and these relationships will hold.

As shown in Figure 11.67, if we combine groups of faces on a hexoctahedron and replace them with a single face, we get a cube, octahedron, dodecahedron, or trapezohedron with no change in symmetry.

Faces of the special forms all coincide with symmetry elements – that is what makes them special. Cube faces are perpendicular to 4-fold rotation axes, octahedron faces are perpendicular to 3-fold rotoinversion axes, dodecahedron faces are perpendicular to 2-fold axes, and trapezohedron faces are perpendicular to mirror planes.

The examples seen in Figure 11.67 are all from a single point group, $^4/_m\bar{3}^2/_m$. But the principles discussed apply to all 32 point groups. However, symmetry relationships and the nature of special forms are more difficult to see for some point groups, especially those with little symmetry.

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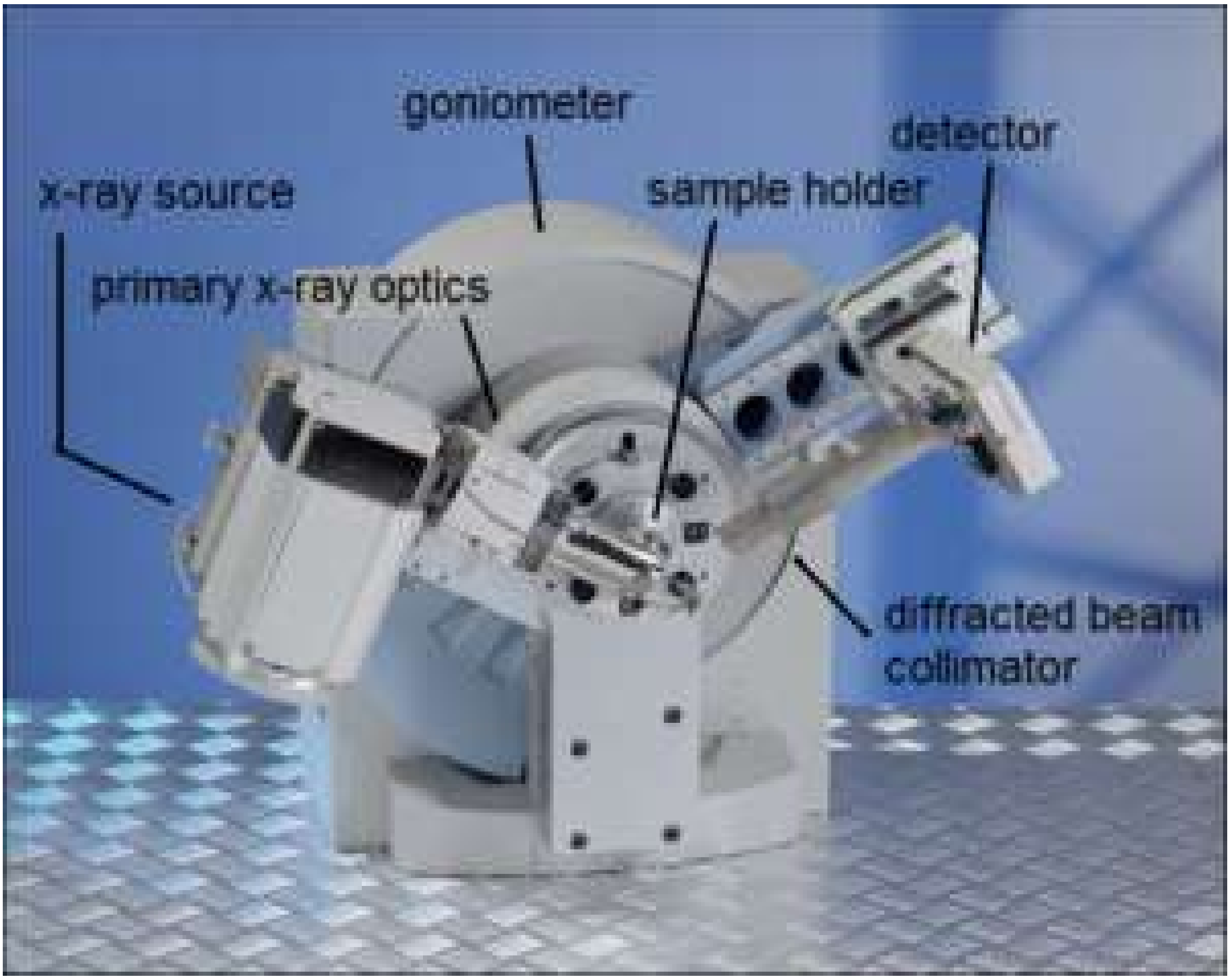
11.38 Spinel in marble, anonymous, Wikimedia Commons
11.39 Garnet in schist, Robert M. Lavinsky, Wikimedia Commons
11.40 Tetrahedrite with malachite and azurite, erocks.com
11.47 Calcite scalenohedra, Robert M. Lavinsky, Wikimedia Commons
11.48 Calcite rhombohedron, Géry Parent, Wikimedia Commons
11.49 Calcite on fluorite, Géry Parent, Wikimedia Commons
11.50 Calcite on galena, Géry Parent, Wikimedia Commons
11.51 Calcite with orpiment, Marie-Lan Taÿ Pamart, WikimediaCommons
11.52 Calcite with siderite, Didier Descouens, Wikimedia Commons
Video 11-1: Bravais lattices, Keith Putirka, YouTube
Video 11-2: Space groups, Keith Putirka, YouTube

12 X-ray Diffraction and Mineral Analysis



12.1 A powder X-ray diffractometer

12 X-ray Diffraction and Mineral Analysis

KEY CONCEPTS

- X-radiation, discovered in 1895 was the key to understanding atomic arrangements in crystals.
- X-rays may have many different wavelengths but for diffraction studies we isolate one.

- When X-rays interact with atoms, the rays are scattered in all directions; coherent scattering by multiple atoms produces X-ray diffraction.
- Directions of diffraction tell us the spacings between planes of atoms in a crystal; intensities of diffraction tell us the number of atoms on those planes.
- We use a powdered sample for routine mineral identification.
- Compositional variations cause slight variations in X-ray patterns.
- Single crystal diffraction data allow crystallographers to figure out where atoms are in a unit cell.
- Scanning electron microscopes allow high-magnification imaging of mineral crystals and of thin sections.
- Electron microprobe data yield mineral compositions based on X-ray intensities.
- Other important analytical techniques include X-ray fluorescence, atomic absorption, inductively coupled plasma mass spectrometry, ion microprobe, Mössbauer spectroscopy, visible and infrared spectroscopy, and Raman spectroscopy.

12.1 X-ray Diffraction

12.1.1 The Discovery of X-rays and Diffraction

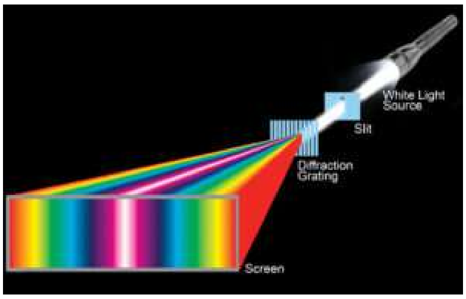
Scientists studied minerals for hundreds of years before the discovery of X-rays. By the late nineteenth century, mineralogists knew that crystals had ordered and repetitive crystal structures. They hypothesized about atomic arrangements and the nature of crystal structures, but they lacked direct evidence. Some ideas about crystal structure were generally accepted, while others were poorly understood and hotly debated. Without a way to test hypotheses, development of an understanding of atomic arrangement and of bonding in crystals was stalled.

12.2 Röntgen at work in
1896

Wilhelm Conrad Röntgen’s discovery of X-rays in 1895 allowed mineralogists to proceed with their studies and eventually led to a greater understanding of crystal structures. Mineralogists quickly discarded many hypotheses disproved by X-ray studies; just as quickly, they developed and tested new ones. In less than two decades, scientists developed a firm theoretical basis for understanding how atoms are arranged in minerals.

Today we accept without question the idea that atoms bond together in regular arrangements to make crystals. We draw pictures, make enlarged models, and study the details of crystal structures of thousands of minerals. All this knowledge would have been unobtainable if Röntgen and his coworkers had not recognized the importance of some curious phenomena they observed while studying cathode ray tubes (early versions of television tubes) in 1895.

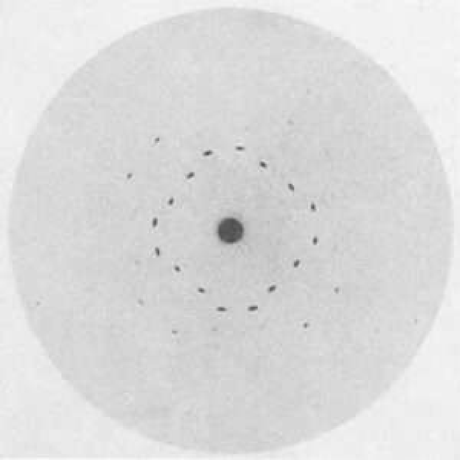
Röntgen taught and studied physics at the University of Würzburg in Germany. He was studying the relationship between matter and force as charged particles flowed from a heated filament in an evacuated glass tube. By chance, he observed that a nearby piece of barium platinocyanide fluoresced when he turned on the tube. Röntgen deduced that electrons interacting with the walls of the tube produced a high-energy form of radiation, and he showed that the radiation could penetrate paper and even thin metals. Because the radiation seemed to behave differently from light, he thought it a completely different phenomenon, calling it *X-radiation*. Various physicists searched for an understanding of the nature of X-radiation. X-rays became inextricably involved with mineralogy when Max von Laue successfully used crystals as a tool in this search.



12.3 Diffraction gratings containing fine slits disperse light into different colors

The diffraction of light was well understood at the time. Physicists routinely measured the wavelengths of colored light using finely spaced *diffraction gratings*. The gratings consist of many parallel slits (or sometimes grooves), typically spaced between 0.0002 and 0.03 mm apart. Light passing through the grating is *dispersed* – which means it is separated into different colors that go in different directions (Figure 12.3).

In 1911, von Laue, a physics professor in Münich, determined that lines in diffraction gratings were not spaced closely enough to diffract X-rays. This partly explained Röntgen's confusion about the relationship between light and X-rays. Von Laue hypothesized that the distance between atoms in crystals, being much less than the distance between lines in diffraction gratings, could lead to X-ray diffraction. And so he ushered in the field of X-ray crystallography.



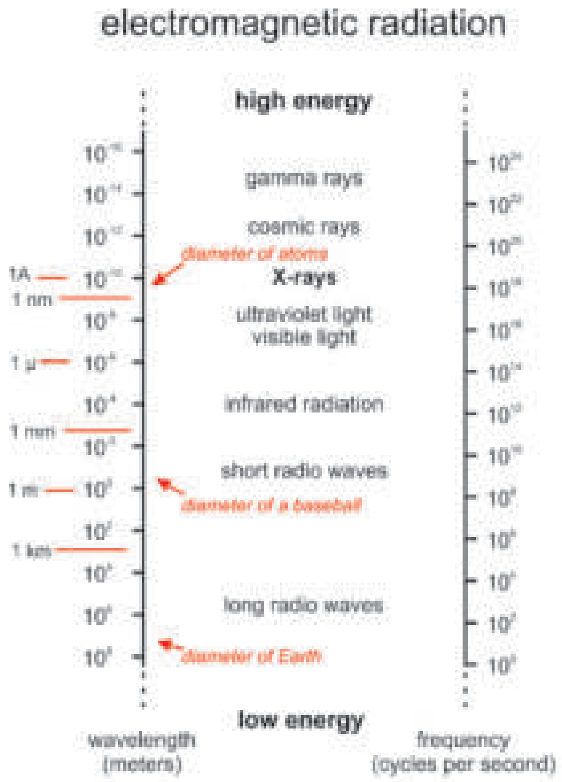
12.4 Diffraction pattern of sphalerite recorded by Friedrich and Knipping

In 1912, Walter Friedrich and Paul Knipping confirmed von Laue’s ideas when they caused X-rays to pass through crystals of copper sulfate ($CuSO_4$) and sphalerite (ZnS) and recorded diffraction patterns on film (Figure 12.4). Their studies showed that X-rays are electromagnetic waves similar to light, but with much shorter wavelengths. They also confirmed that crystals must have a regular crystal structure.

The impact of the work by von Laue and his students was immense. Paul Debye and Paul Scherrer soon improved X-ray techniques. They showed that all crystals have a lattice and that lattices vary in their symmetry. In 1913 William H. Bragg and his son William L. Bragg determined the arrangement of atoms in sphalerite, ZnS, using data obtained with X-ray studies. For the first time, mineralogists knew the actual locations of atoms within a crystal. Similar studies on other crystalline compounds soon followed as Linus Pauling and other scientists realized the power of X-ray diffraction.

Early X-ray studies were tedious. Scientists could spend an entire career determining the atomic arrangement in only a few minerals. Today, with sophisticated equipment and high-speed computers, crystal structure analyses are often routine and can be completed in less than a day. It is important to remember, however, that without the pioneering work of Röntgen, von Laue, the Braggs, Pauling, and others, we would have no detailed knowledge of how atoms are arranged in minerals. In 1901 Röntgen received the first Nobel Prize for Physics; von Laue received the same prize in 1914, and both Braggs were the recipients in 1915.

12.1.2 What are X-rays?



12.5 Electromagnetic radiation

X-rays are a form of electromagnetic radiation (Figure 12.5). Whereas the wavelengths of visible light are 10^{-7} to 10^{-6}

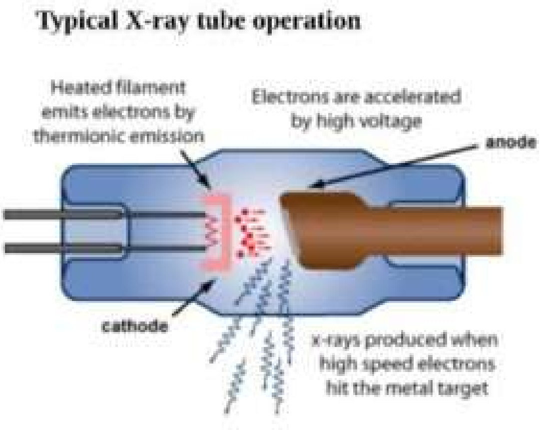
meters, X-ray wavelengths are only 10^{-11} to 10^{-8} meters. Long-wavelength X-rays grade into ultraviolet light; shorter wavelengths grade into cosmic and gamma rays. Mineralogists usually give X-ray wavelengths in angstroms (1Å equals 10^{-10} meters). The copper radiation commonly used in X-ray studies has λ = 1.5418Å.

The frequency (v) and wavelength (λ) of electromagnetic radiation are inversely related. *Planck's law* relates them to energy:

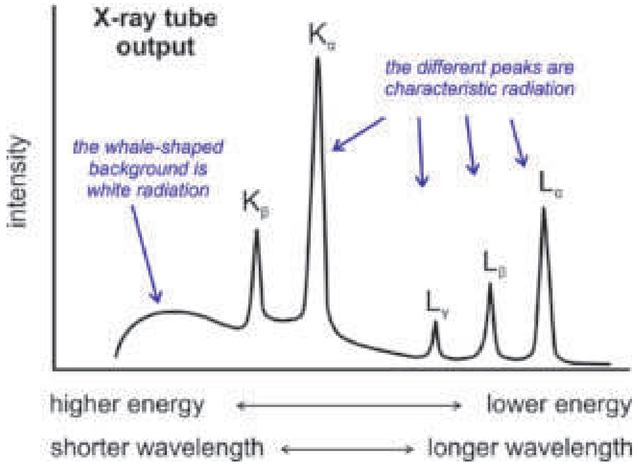
$$E = h\upsilon = hc/\lambda$$

In this equation h is Planck's constant and c is the speed of light in a vacuum. Because of their short wavelengths and high frequencies, X-rays have high energy compared with visible light and most other forms of electromagnetic radiation. High energy allows X-rays to penetrate many natural materials, as observed by Röntgen in 1895.

X-rays of highest energy, called *hard radiation*, are used in many manufacturing and industrial applications, such as checking steel for flaws. X-rays of relatively low energy, called *soft radiation*, are used by mineralogists and for medical diagnoses. Soft radiation is the most dangerous to people because rather than passing through tissue like many hard X-rays and gamma rays, soft X-rays interact with atoms in cells and tissues, causing damage. Because of the potential health hazards, crystallographers take special care to avoid exposure to the X-rays in their experiments.



12.6 An X-ray tube



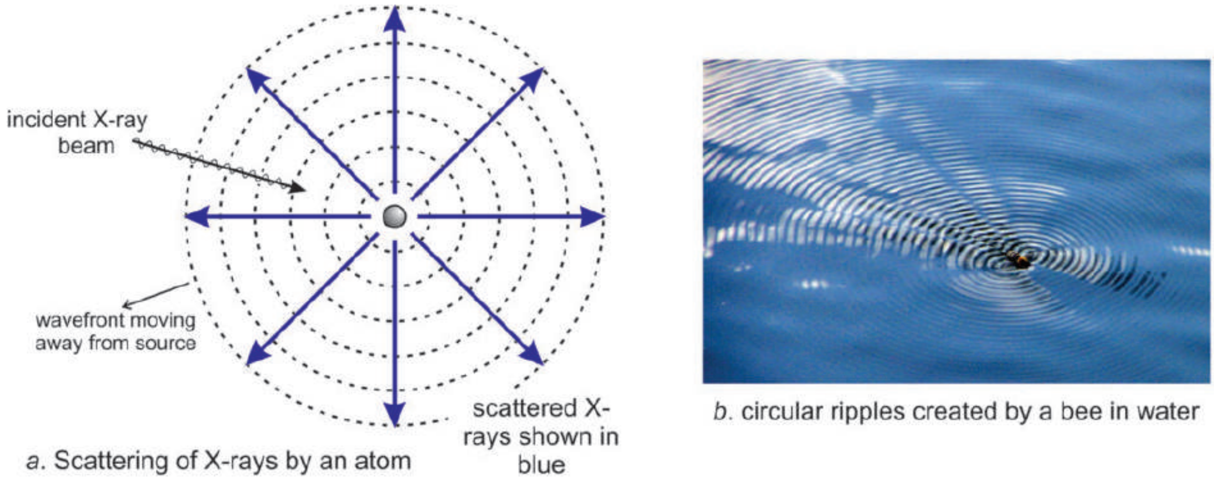
12.7 Typical X-ray emissions from an X-ray tube

Mineralogists use X-ray tubes (Figure 12.6) to generate X-rays for diffraction studies. In the tubes, a heated filament releases a beam of high-velocity electrons that strike a metal target. Some of the high-velocity electrons that hit the target cause emission of a continuous spectrum of X-rays called *continuous radiation* or *white radiation* (the “whale-shaped” hump in Figure 12.7).

Other electrons collide with electrons orbiting atomic nuclei in the target material and bump the electrons temporarily into a high energy level. As the target electrons return to lower energy levels, they emit energy as X-rays. The energy difference between the two levels is proportional to the energy and frequency, and inversely proportional to the wavelength, of X-rays emitted. Because some electrons are elevated to higher levels than others, and because they do not all return to the same levels, typical X-ray tubes emit *characteristic radiation* (the peaks in Figure 12.7) having several different wavelengths. The wavelengths of the characteristic radiation depend on the metal in the target of the X-ray tube. So, X-ray tubes emit *polychromatic* radiation, radiation having a range of wavelengths, but most of the energy is channeled at specific wavelengths. We designate the different characteristic X-ray wavelengths using combinations of English (*K*, *L*, *M*) and Greek (*a*, *β*, *γ*) letters. The most intense peak is designated *Kα* (Figure 12.7).

The most common X-ray tubes have a copper target. Copper has more than one characteristic X-ray wavelength, but interpretation of diffraction results is easiest if we use one (*monochromatic radiation*). So we use copper's most intense radiation, $K\alpha$, for most routine X-ray studies. To isolate $K\alpha$ radiation from the other wavelengths, X-ray machines have filters, monochromators, or solid-state monochromatic detectors. X-ray tubes emit two nearly equal wavelengths of Cu $K\alpha$ radiation: the wavelength of $K\alpha_1$ is 1.5401Å and the wavelength of $K\alpha_2$ is 1.5443Å. They are so similar that, although two wavelengths are present, for most applications the radiation is effectively monochromatic, and we take a weighted average of $K\alpha_1$ and $K\alpha_2$. We assume a λ value of 1.5418Å.

12.1.3 Interactions of X-Rays and Atoms



a. Scattering of X-rays by an atom

b. circular ripples created by a bee in water

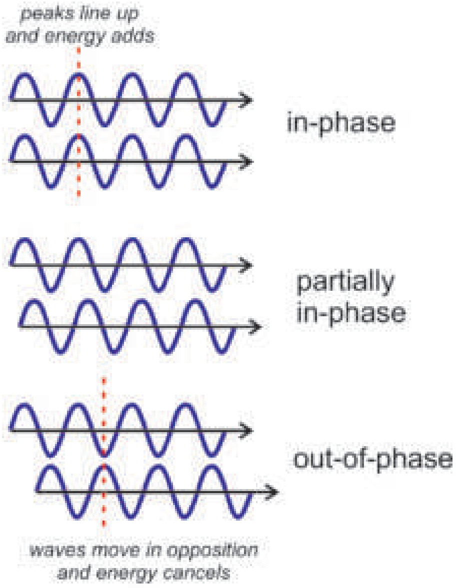
12.8 X-ray scattering

When an X-ray strikes an atom, the wavelike character of the X-ray causes electrons, protons, and neutrons to vibrate. Heavy protons and neutrons vibrate less than much lighter electrons. The oscillating electrons reemit radiation, called *secondary radiation*, at almost the same frequencies and wavelengths as the incoming beam. This creates X-ray *wavefronts* (dashed lines in Figure 12.8) that travel in all directions from the atom, much the same way that circular ripples disperse in water (Figure 12.8*b*). The difference in radius of adjacent wavefronts is the wavelength, λ. This process, called *scattering*, is not the same for all elements, nor is it the same in all directions.

Because heavy elements have atoms with more electrons, they scatter more efficiently than light elements, and scattering by heavy elements can completely mask scattering by light ones. As a result, X-ray crystallographers often have trouble measuring the effects of light atoms, such as hydrogen, when X-rays interact with crystal structures. As X-rays scatter in different directions, they interact with electron clouds in various ways. Overall, those scattered at high angles to the incident beam are less intense than those scattered at low angles.

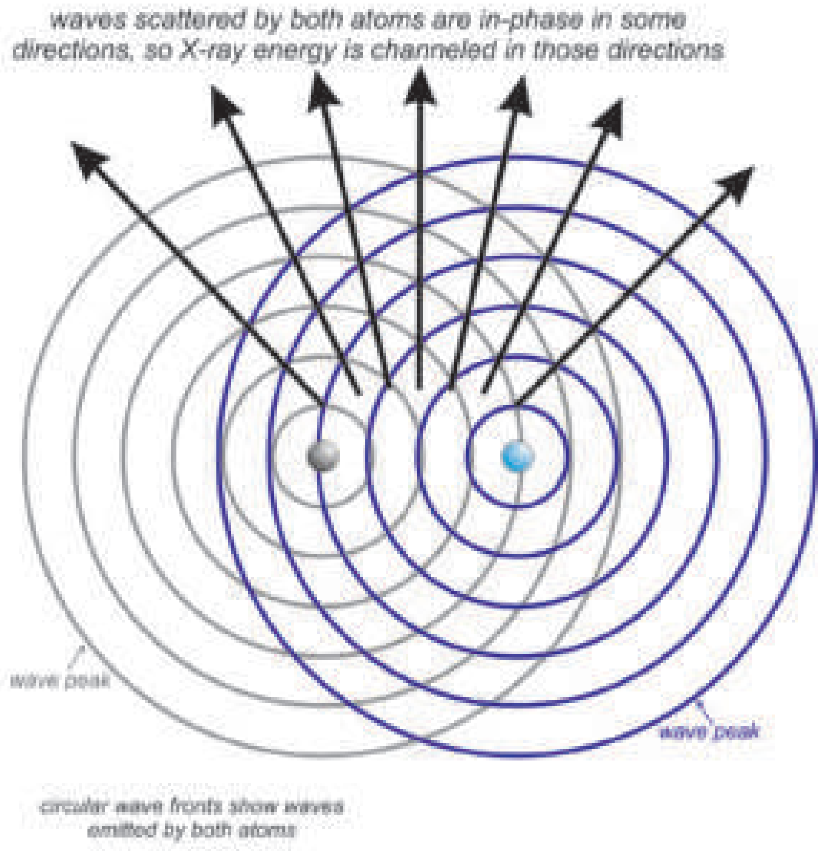
Besides being scattered, when X-rays interact with atoms in a crystal, some electrons temporarily bump up to higher energy states. As the electrons return to their normal state, a release of radiation characteristic of the element comprising the target atom (in the crystal) occurs. This process, called *X-ray fluorescence* (*XRF*), is similar to the interaction of electrons and atoms in the target metal of an X-ray tube, but results from interaction of X-rays and atoms in the crystal. X-ray fluorescence, while not widely used by mineralogists, is the basis for a common analytical method used by petrologists and geochemists.

12.1.4 Interference of X-Ray Waves



12.9 Wave interference

Just like visible light, X-rays propagate in all directions and may interact, or *interfere*, with each other (Figure 12.9). Two parallel X-rays of the same wavelength can exhibit *constructive interference or destructive interference*. If constructive, it means that the waves are in phase – that their wave peaks coincide. In such a case, wave energies add, increasing X-ray amplitude. Destructive interference occurs when waves are *out of phase* – one is moving up while the other is moving down. When destructive interference occurs, waves can cancel. Often, waves are partially in phase and partially out of phase.



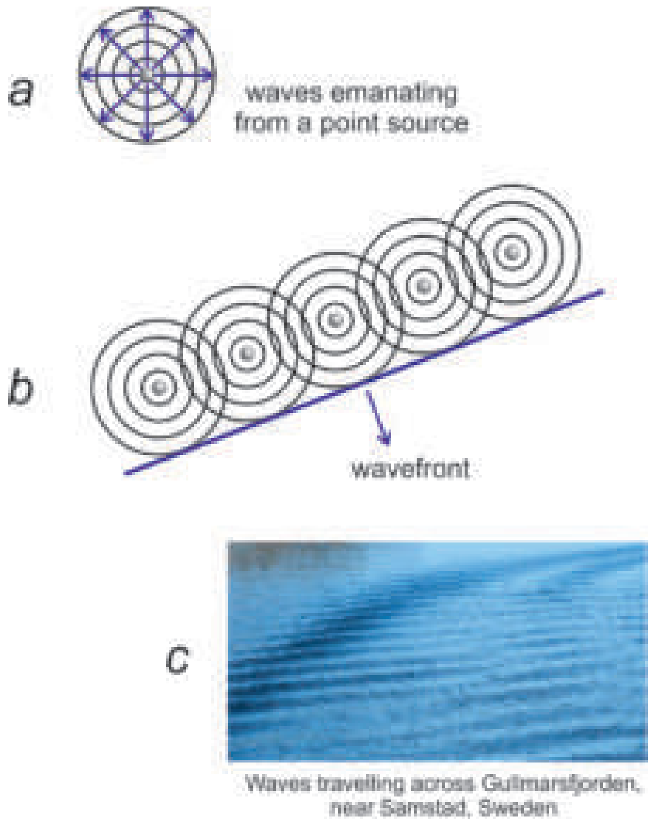
12.10 Interference of waves from two atoms

Figure 12.10 shows two atoms emitting monochromatic X-radiation. The solid lines show wavefronts moving away from each atom. If we could move an X-ray detector around the atoms, we would find that energy is intense in some directions (where wave peaks coincide and waves interact constructively). In other directions, the detector would register no X-rays due to destructive interference. This channeling of energy in specific directions is *diffraction*. The directions of diffraction depend on X-ray wavelength and distance between the two X-ray sources.

A narrow slit, a series of parallel grooves in a diffraction grating, regularly spaced atoms in a crystal, and many other things can cause diffraction. The main requirement is that two or more sources emit, or scatter, monochromatic waves.

In principle, all electromagnetic radiation can be diffracted, but unless the spacing of atoms, slits, or gratings is similar to the wavelength of the radiation, diffraction will not occur. Fortunately for mineralogists, atoms have radii on the order of angstroms. Because atoms pack closely together in crystals, space between atoms is of the same magnitude. So, atomic radii and spacing are about the same dimension as the wavelength of X-rays. Consequently, X-rays interacting with atoms in crystals can lead to intense X-ray diffraction. This is the understanding that led von Laue and his coworkers to their successful experiments.

12.1.5 Diffraction by a Row of Atoms



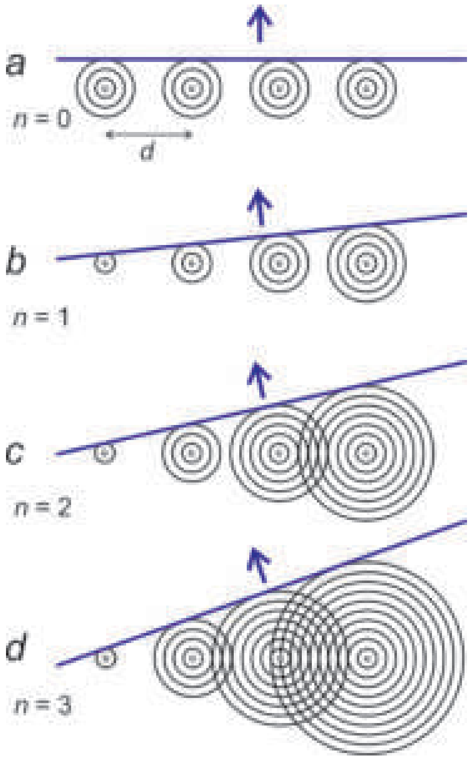
12.11 Diffraction by a row of atoms

To discuss diffraction by a row of atoms, we can use the analogy of a group of campers standing on a lake dock. One camper throws a rock in the water, producing wave fronts that spread out in concentric circles before eventually dying out (Figure 12.11*a*).

Next, five campers on the dock all drop rocks into the water at different times, making many circular wavefronts. The wavefronts work with each other constructively in some directions and destructively in others. Most are out-of-phase and the waves disappear quickly.

But then they try an experiment. Five campers stand on the dock and all drop a rock into the water simultaneously. Each rock produces a circular wavefront. The five different wavefronts are in phase and together create a straight wavefront that moves across the lake before eventually losing energy (Figure 12.11*b*). The rocks produce waves similar to a parallel set of wind-driven waves that might move across the ocean or across a lake (Figure 12.11*c*). If you are in a boat and see the waves coming toward you, you cannot tell that they were created by multiple in-phase point sources.

When a row of atoms scatters an X-ray beam, the atoms can produce a coherent wavefront similar to the one produced when rocks hit water simultaneously. Figure 12.11*b* could be showing a row of atoms each emitting X-ray waves with identical wavelengths. If all the atoms emit a wave simultaneously, the waves will create a straight wavefront moving away from the row. This is what happens when an incident X-ray beam strikes a row of atoms. The atoms scatter X-rays and create coherent wave fronts even if the incident wave hits the row of atoms at an angle. So, constructive interference produces a wavefront moving perpendicularly away from the row of atoms. And, as we will see shortly, wavefronts also travel in other directions.

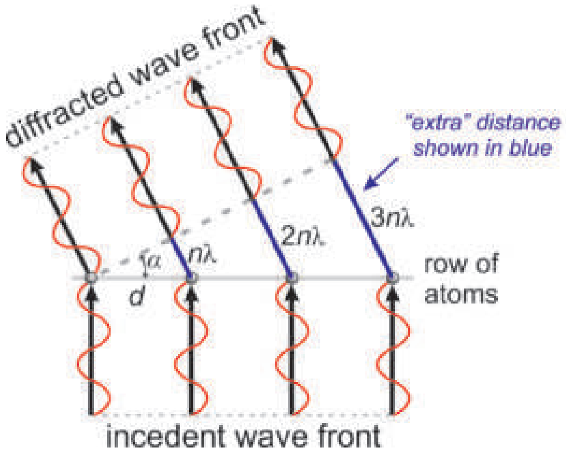


12.12 Higher order diffraction

Figure 12.12*a* shows circular wavefronts emitted by atoms in a row. The difference in radius of adjacent wavefronts is the wavelength, λ. As described above, the waves, which have all traveled the same distance, combine to form straight wavefronts moving perpendicular to the row.

But because one cycle of a wave is the same as any other, it does not matter if waves have traveled different distances. If their peaks correspond, they are in phase. So, Figures 12.12 *b, c*, and *d* show that coherent wavefronts also move in other directions. In Figure 12.12*b*, waves emitted by adjacent atoms differ in travel distances by 1λ; in Figure 12.12*c* by 2λ; and in Figure 12.12*d* by 3λ.

Thus, we see that diffraction by a row of atoms in 2D produces wave fronts traveling in many directions. This is the same when 3D crystals diffract X-rays – diffracted rays go in many directions in 3D space.

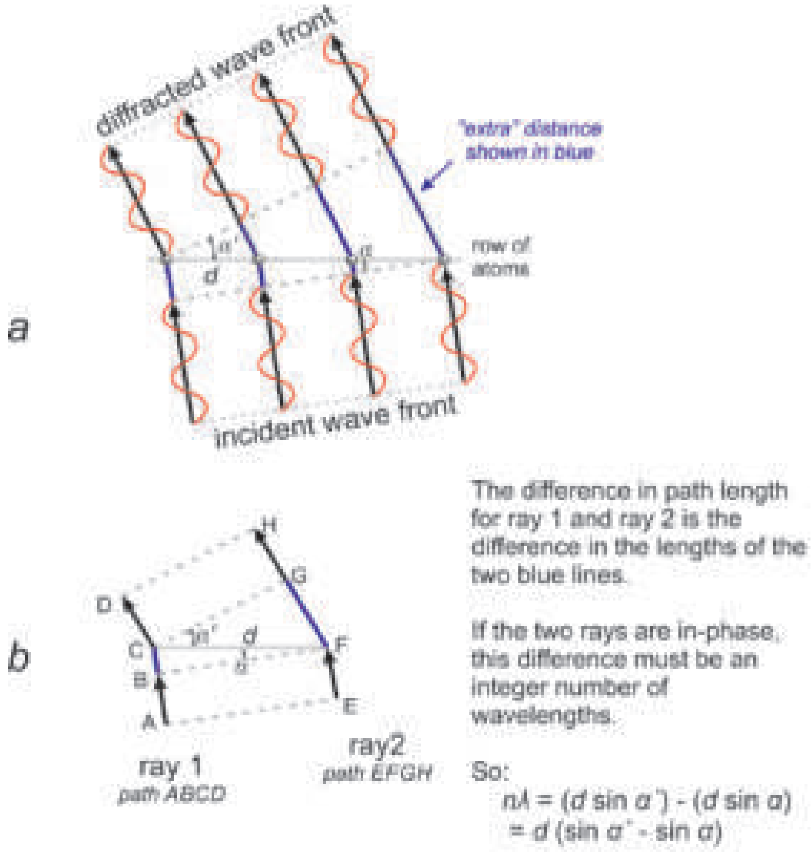


12.13 Incedent and diffracted wave fronts

The geometry in Figure 12.12 yields a simple relationship between wavelength (λ), atomic spacing (d), and the angle of diffraction (α). In Figure 12.13, n is the number of wavelengths that each wave is behind (or ahead of) the one next to it. Application of trigonometry gives:

$$n\lambda = d \sin \alpha$$

n is called the *order of diffraction*. When $n = 0$, 0th order diffraction occurs and α must be 0. When $n = 1$, 1st-order diffraction occurs; when $n = 2$, 2nd-order diffraction occurs, and so on. As n increases, the angle between the diffracted wavefront and the row of atoms increases. The maximum value of $n\lambda$ corresponds to $\sin \alpha = 1$ (when $\alpha = 90°$), so $n\lambda$ must always be less than d. Because $n \geq 1$, λ must be less than or equal to d for diffraction to occur. These limits explain why atoms in crystals do not diffract visible light: the wavelengths of light are too long compared with the atomic spacings.



The difference in path length for ray 1 and ray 2 is the difference in the lengths of the two blue lines.

If the two rays are in-phase, this difference must be an integer number of wavelengths.

So:
$n\lambda = (d \sin \alpha') - (d \sin \alpha)$
$= d (\sin \alpha' - \sin \alpha)$

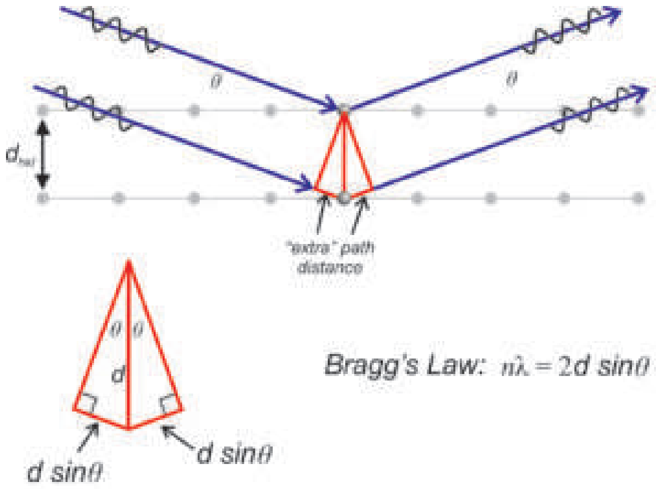
12.14 Deriving the Laue Equation

The preceding discussion assumed that an incident X-ray beam struck a row of atoms at 90°, but this is rarely the case. When the incident radiation strikes a row of atoms at another angle, coherent diffraction will still occur in any direction where X-rays are in phase (Figure 12.14*a*). To analyze this situation, we need only consider two rays (Figure 12.14*b*). They will be in phase if the difference in their path lengths, the difference between paths ABCD and EFGH, is an integral number of wavelengths ($n\lambda$). For the geometry shown in Figure 12.14*b*, we can easily verify that the rays will be in phase when:

$$d\ (\sin \alpha' - \sin \alpha) = n\lambda$$

where d is the atomic spacing, α' and α are the angles of the diffracted and incident wave with the row of atoms, n is the order of diffraction, and λ is the wavelength. This is the general equation for diffraction by a row of atoms in 2D space. Von Laue was the first to derive this equation, and he derived similar equations for diffraction by three-dimensional structures. We call these the *Laue equations*.

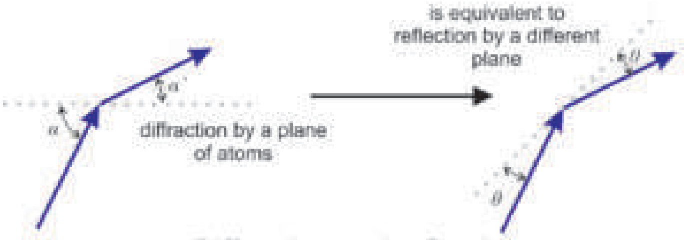
W. L. Bragg developed a simpler mathematical treatment describing diffraction. His final equations are just as valid as von Laue’s, but the derivations avoided some unnecessary complexities. Although diffraction and reflection are two different processes, Bragg noted that diffracted X-rays behave as if they were reflected from planes within a crystal. To model this “reflection,” Bragg considered two parallel planes of atoms separated by distance d_{hkl} (Figure 12.15).



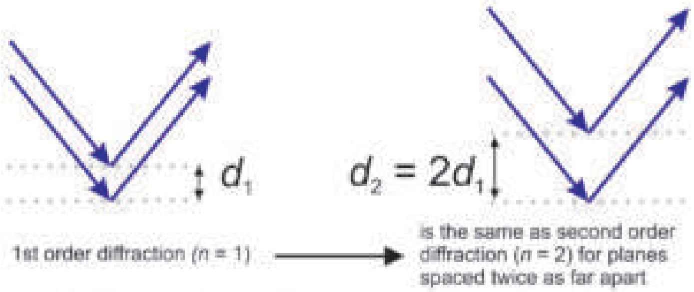
12.15 Bragg’s Law

The blue lines in Figure 12.15 represent parallel monochromatic X-ray beams striking and reflecting from two (hkl) planes of atoms planes. The angle of incidence and the angle of reflection are both θ. The geometry in the inset photo shows how we can calculate the extra distance followed by the bottom ray. The path lengths of the two beams must vary by an integral number of wavelengths if diffraction is to occur. So, the extra path distance followed by the bottom ray must equal $n\lambda$, and:

$$n\lambda = 2d_{hkl} \sin\theta$$



a. Diffraction and reflection



b. First-order and second-order diffraction

12.16 Assumptions and Bragg’s Law

We call the equation above *Bragg’s Law*. Bragg demonstrated that we need not consider situations in which incident and diffraction angles are different (Figure 12.16*a*). Because we can always describe diffraction using reflection geometry, although diffraction and reflection are different phenomena. The angle of “reflection” θ is related to the incident angle (α) and the diffraction angle (α') by

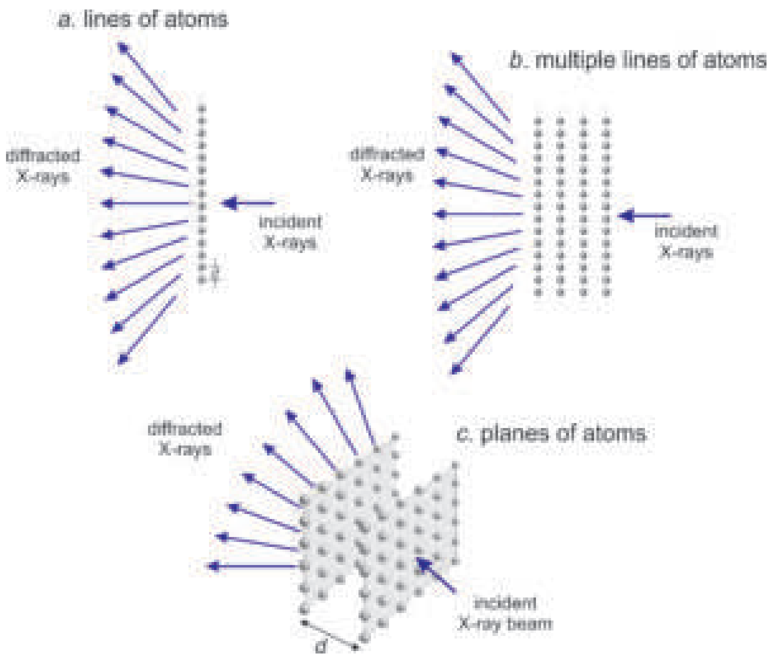
$$\theta = (\alpha - \alpha')/2$$

Examination of Bragg’s Law reveals that if we double the value of n (the order of diffraction) and we double the value of d_{hkl}, θ will not change (diffraction will occur at the same angle.) So, 1st-order diffraction by planes with spacing d_{hkl} occurs at the same angle as 2nd-order diffraction by a set of planes spaced twice as far apart. Figure 12.16*b* shows this relationship. Because we have no way to know diffraction order (n) when conducting routine X-ray studies, assuming 1st-order is simplest. In other applications of Bragg’s Law, the order of diffraction is important.

For a video that further explores Laue patterns, Bragg’s Law and diffraction, check out the video linked below:

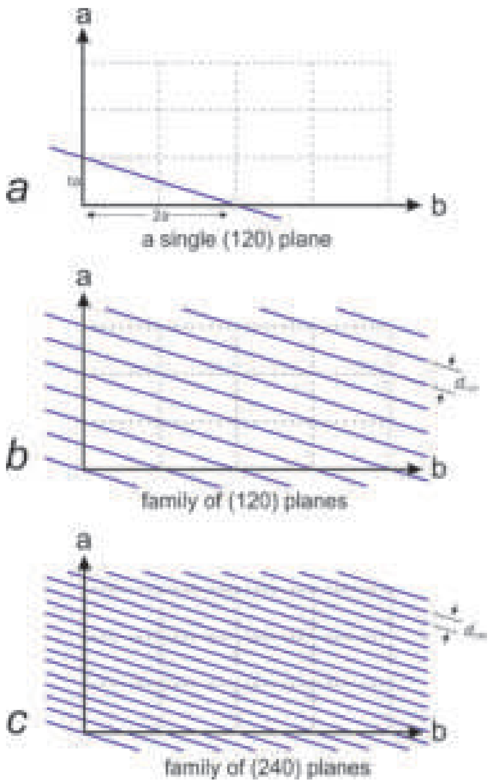
▶️ Video 12-1: Laue Patterns and Bragg’s Law (10 minutes)

12.1.6 Diffraction by Planes of Atoms



12.17 Diffraction from 2D (rows of atoms) to 3D (planes of atoms)

A regularly spaced line of atoms provides a simple model for describing diffraction (Figure 12.17*a*). However, in two dimensions crystals contain multiple identical unit cells. So, crystals have many identical lines of atoms, all causing diffraction at the same angles (Figure 12.17*b*). In three dimensions, a crystal contains many identical 3D unit cells, all containing planes of atoms that cause diffraction at the same angles (Figure 12.17*c*). A distance d_{hkl} separates the planes of atoms, and they diffract at angles we can calculate with Bragg’s Law. Although not clearly shown in Figure 12.17*c*, diffracted X-rays are not constrained to a plane but may go in any direction in 3D space.



12.18 Miller indices and the distance between planes

As discussed in Chapter 11, crystallographers use Miller indices (*hkl*) to describe planes of atoms in crystals. d_{hkl} is the perpendicular distance between (*hkl*) planes. Let’s consider planes perpendicular to this page.

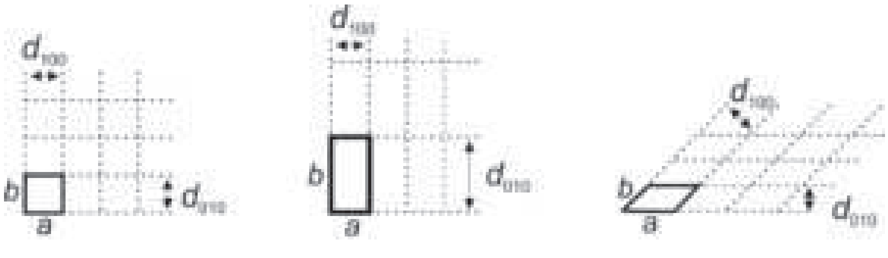
Figure 12.18*a* shows a single (120) plane. Every unit cell is identical, so Figure 12.18*b* shows an entire family of (120) planes separated by the perpendicular distance d_{120}. Different families of planes, with the same orientation but different indices, have different *d*-values. Figure 12.18*c* shows the family of (240) planes; they parallel (120) but are half as far apart. For all crystal systems, d_{120} is twice d_{240}. Planes with higher numbers in their Miller indices are closer together than planes with lower numbers, and in general:

$$d_{hkl} = n\ d_{h'k'l'}$$

where $h' = nh$, $k' = n$k, and $l' = nl$.

The relationship between Miller indices, unit cell lengths (*a, b, c*), and *d*-values depends on the crystal system. Box 12.1 gives equations relating unit cell parameters to *d*-values. Derivation of equations for orthogonal systems (cubic, tetragonal, and orthorhombic) is simple compared with derivations for the other systems. For orthogonal systems:

$d_{100} = a$
$d_{010} = b$
$d_{001} = c$

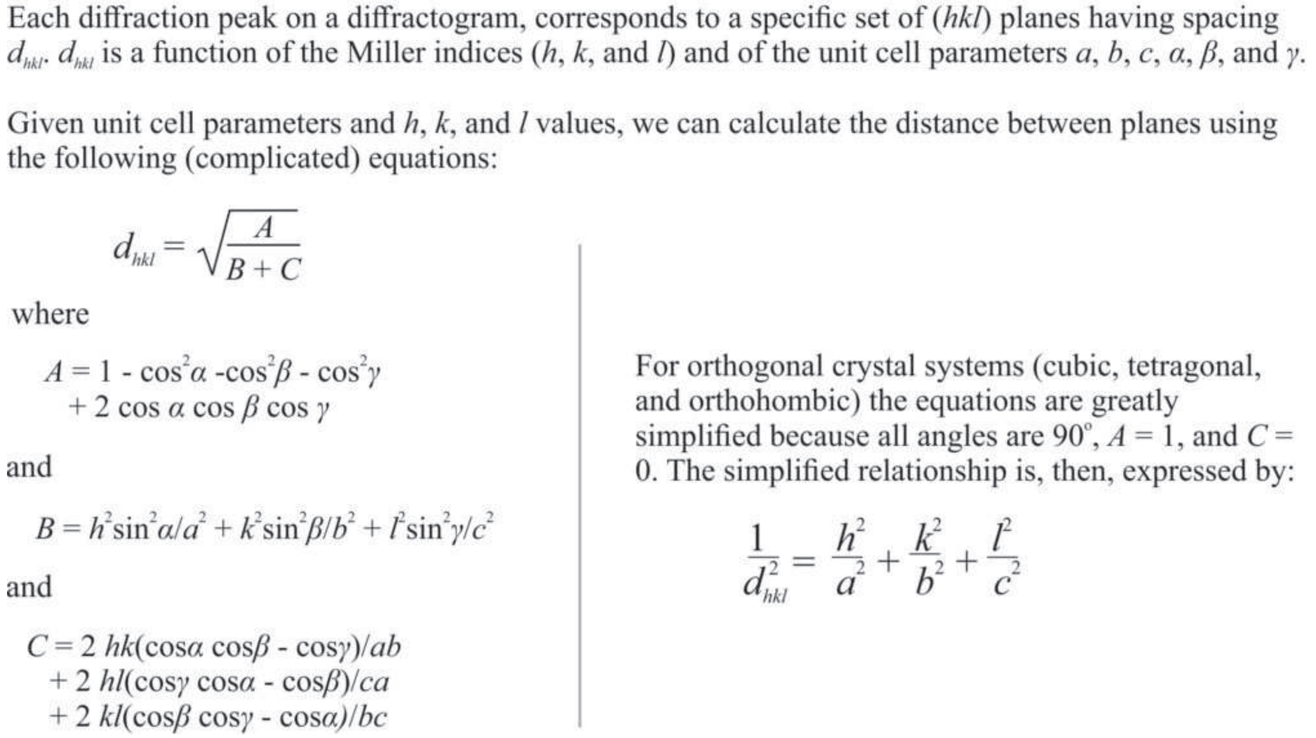


a. square cell b. rectangular cell c. monoclinic cell

12.19 d-values and unit cell parameters

For the other systems, we must also consider the angles *α, β,* and *γ*. Figure 12.19 shows this by comparing *d*-values with unit cell lengths for square, rectangular, and monoclinic cells. For the orthogonal cells, $d_{100} = a$, but for the monoclinic cell it does not.

● Box 12-1 Calculating *d*-Values from Cell Parameters and Miller Indices



Each diffraction peak on a diffractogram, corresponds to a specific set of (*hkl*) planes having spacing d_{hkl}. d_{hkl} is a function of the Miller indices (*h*, *k*, and *l*) and of the unit cell parameters *a*, *b*, *c*, *α*, *β*, and *γ*.

Given unit cell parameters and *h*, *k*, and *l* values, we can calculate the distance between planes using the following (complicated) equations:

$$d_{hkl} = \sqrt{\frac{A}{B + C}}$$

where

$$A = 1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma$$

and

$$B = h^2\sin^2\alpha/a^2 + k^2\sin^2\beta/b^2 + l^2\sin^2\gamma/c^2$$

and

$$C = 2\,hk(\cos\alpha\cos\beta - \cos\gamma)/ab + 2\,hl(\cos\gamma\cos\alpha - \cos\beta)/ca + 2\,kl(\cos\beta\cos\gamma - \cos\alpha)/bc$$

For orthogonal crystal systems (cubic, tetragonal, and orthohombic) the equations are greatly simplified because all angles are 90°, $A = 1$, and $C = 0$. The simplified relationship is, then, expressed by:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

12.1.7 Routine X-Ray Analysis: Powder Diffraction

12.20 A powder diffractometer

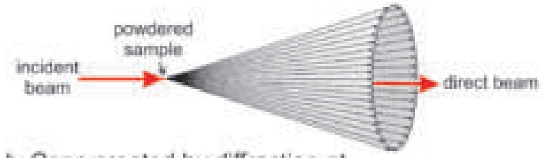
There are two fundamental X-ray diffraction techniques: *powder diffraction* and *single-crystal diffraction*. Powder diffraction is much more common; we use it for routine mineral identification and for determining unit cell dimensions. We can also sometimes use this technique to learn the proportions of different minerals in a rock or other mineral mixture. Single crystal diffraction provides information necessary for determining a crystal’s space group and the arrangement of atoms in a crystal’s unit cell. We do not normally use powder diffraction to figure out atomic arrangements in crystals because powder diffraction data are more ambiguous for this purpose than single crystal data. Different X-ray peaks correspond to different crystals in the powdered sample, and the data do not reveal the orientations of crystals or planes causing diffraction. The *Rietveld method*, an extension of normal powder diffraction analysis, sometimes overcomes these complications.

For now, we will focus our discussion on powder diffraction and return to single-crystal techniques later. Figure 12.20 shows a typical powder diffractometer. The cabinet is about 2 meters tall.

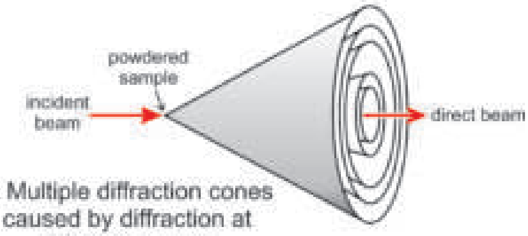
12.21 A sample holder being loaded with a powdered sample

To prepare a sample for powder diffraction, we grind it to a fine powder. The goal is to have a near-infinite number of fine crystallites in random orientations. We load the powder into holders, such as the one in Figure 12.21 or put it on a glass slide. When lots of crystals in different orientations are X-rayed, many crystals will satisfy Bragg’s law for every set of (*hkl*) planes. Thus, when an X-ray beam hits the sample, hundreds or thousands of diffracted beams will go in different directions. Some diffracted beams will have high intensity and others will have medium or low intensity.

a. Diffraction at an angle of 17.74° to the direct beam in 2D



b. Cone created by diffraction at 17.74° to the direct beam in 3D

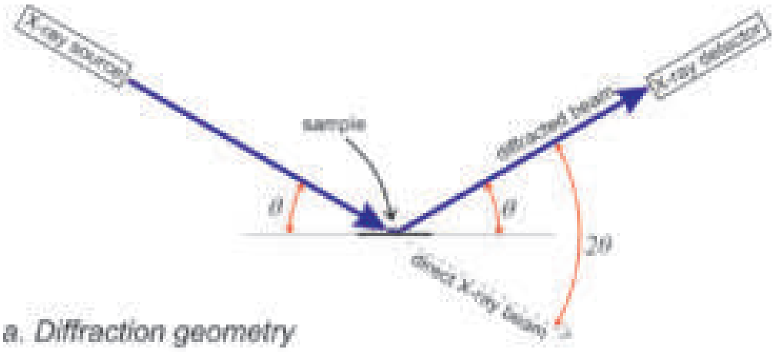


c. Multiple diffraction cones caused by diffraction at different angles

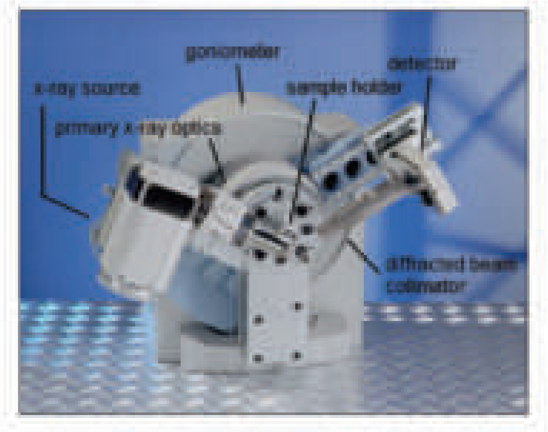
12.22 Diffraction cones

Consider a powdered sample of some mineral with (111) planes having a *d*-value of 5.0 Å. For Cu *Kα*, then, Bragg's Law tells us this will cause diffraction at a 2θ angle of 17.74°. When we X-ray the sample, many crystals will be oriented to cause diffraction at 17.74° to the incident X-ray beam. Figure 12.22*a* shows this in two dimensions. But, diffraction can go in any direction at 17.74° to the beam and, consequently, diffracted beams create a diffraction cone in three dimensions (Figure 12.22*b*)

In most crystals, a large number of *d*-values cause measurable diffraction. Each produces a cone at a different 2θ angle to the X-ray beam. Figure 12.22*c* shows a small number of cones corresponding to different *d*-values – minerals typically produce many more than shown here. The cones are all concentric with the direct X-ray beam.



a. Diffraction geometry



b. An X-ray diffractometer

12.23 X-ray diffraction geometry and a modern diffractometer

Because we powdered the sample and get diffraction cones instead of separate rays going in discreet directions, we do not have to measure angles and intensities in 3D space. Some diffractometers are slightly different, but Figure 12.23*a* shows the basic geometry of diffraction. The photo in Figure 12.23*b* shows a modern diffractometer with this geometry. Besides an X-ray source (tube) and a detector (which measures the intensity of diffracted X-ray beams), the device includes several collimators and filters that enhance analysis.

In most diffractometers, the sample is at a fixed location (although it may be rotated by a device called a *goniometer*). The tube and detector, move in a circular arc, usually vertically, to measure diffraction intensities for 2*θ* values from very low angles to some high value. In practice, most diffractometers cannot measure peaks at angles below 1 or 2° *2θ* because the direct X-ray beam bombards the detector. The upper 2*θ* limit of measurement usually depends on the need of the mineralogist, but for most purposes we do not need data above 60° to 70° 2θ.

During analysis, the incident X-ray beam strikes the sample at many different θ angles while the detector moves to maintain Bragg Law (reflection) geometry. The angle of incidence and the angle of reflection are the same, so after being diffracted an X-ray beam travels at an angle of 2θ from the incident beam. Because a crystal contains many differently spaced atoms, diffraction occurs at many 2θ angles.

If a diffracted beam is to hit the detector, two requirements must be met:

- A family of planes with d_{hkl} must be oriented at an angle (θ) to the incident beam that satisfies Bragg's Law.
- The detector must be at the correct angle (2θ) from the incident beam to intercept the diffracted X-rays.

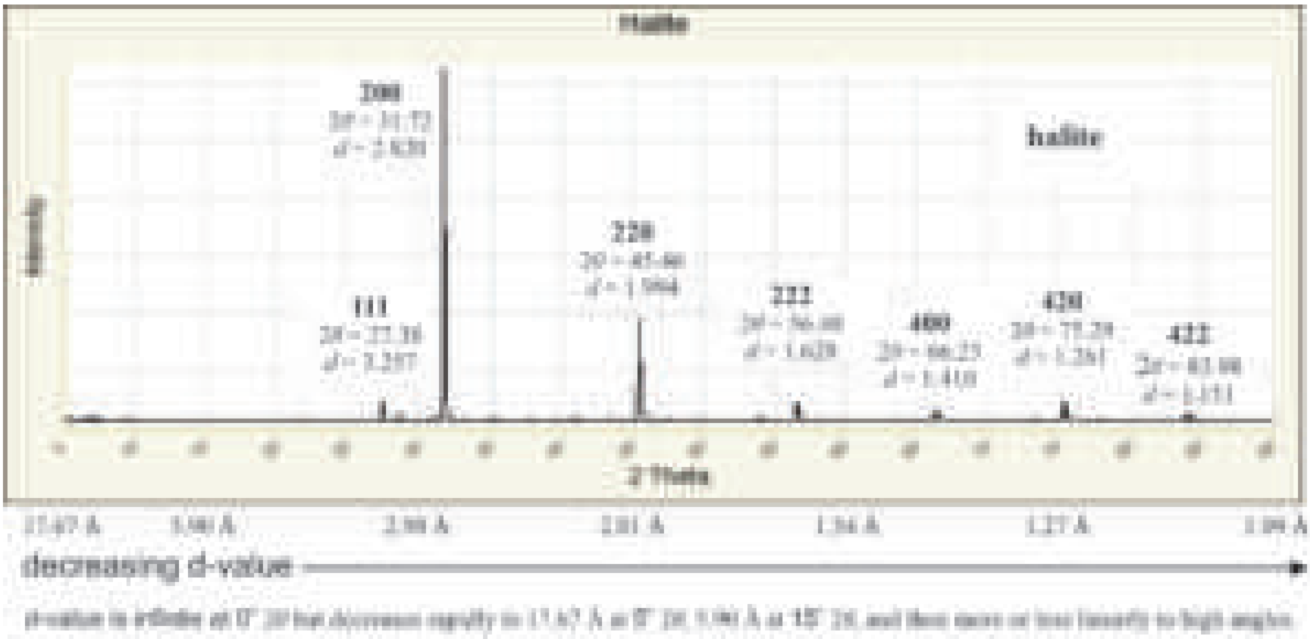
Because the angle between the detector and the X-ray beam is 2θ, mineralogists usually report X-ray results as peak intensities for different 2θ values. For example, reference books list the two most intense diffraction peaks of fluorite (using Cu $K\alpha$ radiation) as 28.3° and 47.4° 2θ. We must remember to divide 2θ values by 2 before we use them with Bragg's Law to calculate *d*-values.

12.1.8 Data and Processing

When we X-ray a powdered sample, we obtain a *powder diffraction pattern*. The key information from the pattern is a list of *d*-values with diffraction intensities. Each *d*-value corresponds to sets of planes, and the intensity is a measure of how many atoms are on those planes. Because different minerals have different atomic arrangements, they yield different patterns.

Computers controlling powder diffractometers collect and process data automatically. They compare diffraction results with data bases to identify the mineral or minerals present. The most comprehensive reference, the *X-ray Powder Diffraction File* (*PDF*) compiled by the International Centre for Diffraction Data, is available in computerized databases and contains information on almost 6,000 minerals and tens of thousands of other inorganic and organic crystalline compounds. Simple mineral identification may require only a few to 10s of minutes. For extremely precise results, however, data collection may take hours or longer. However, a shortcoming of computer interpretations is that they are “black box” procedures; they do not improve our knowledge or understanding of powder diffractometry and may occasionally produce misidentifications. And, for mixes of more than one mineral, computer programs always give an analysis but it is sometime difficult to evaluate the accuracy of the results.

To visualize diffraction measurements, we typically look at a *diffraction pattern* like the one below in Figure 12.24. It shows a diffraction pattern, also called a *powder pattern*, or a *diffractogram*, for halite. In standard diffraction patterns like this one, the X-axis is 2θ in degrees and the Y-axis is the intensity of diffraction. Following Bragg’s Law, d-value is infinite at 0° 2θ but decreases quickly with increasing angle. It is less than 20 Å at 5° 2θ, and then falls slowly to about 1 Å at 90° 2θ.



12.24 Diffractogram for halite

The peaks in Figure 12.24, also called *reflections*, are labeled with the *2θ* angles at which diffraction occurs. They are also labeled with associated *hkl* indices, called *Laue indices,* and *d*-values. By convention, when talking about diffraction directions, we use Laue indices with no parentheses (because we are labeling a reflection and not a family of planes) as is done in this figure. Note that, according to Bragg's Law, the peak labeled 222 (at 56.48°) in Figure 12.24 may be due to 1st-order diffraction by (222) planes (that have a spacing of 1.628 Å). However, 2nd-order diffraction by (111) planes (that have a spacing of 3.257 Å) also occurs at the same angle (discussed at the end of section 12.1.5, above). Higher-order diffraction from other families of planes, too, can cause diffraction at 56.48°. Because we have no way to distinguish 1st-order from higher-order diffraction, we label the peak 222, assuming 1st-order. So, Laue indices are not the same as Miller indices, but are close.

We always assign the strongest peak an intensity of 100% and calculate other intensities compared with that peak. In this pattern, halite's 200 peak at 31.7° is most intense (100%). The

220 peak (45.5°) is about 35% as intense, and other peaks are all small. Minerals with high symmetry, such as halite (which is cubic), generally have fewer than 30 measurable reflections in their powder patterns. Minerals of low symmetry have more.

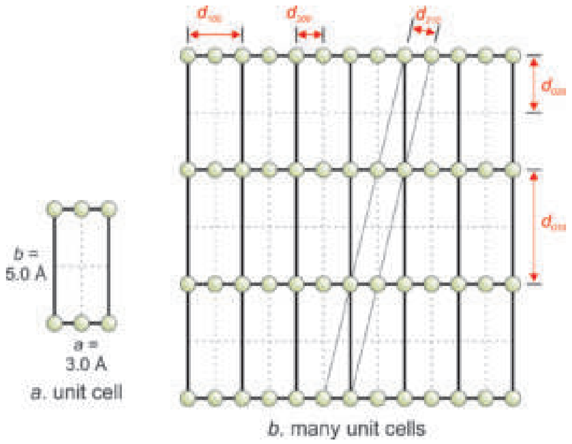
12.1.9 Effects of Different X-ray Wavelengths

All X-ray patterns seen in this chapter were obtained using a copper X-ray tube that produced Cu $K\alpha$ radiation with wavelength 1.5418Å. Sometimes mineralogists use other kinds of tubes that produce a different X-ray wavelength. If so, the angles of diffraction will be different. The diffraction pattern will look the same but will be systematically shifted to higher or lower 2θ values. Nevertheless, when we calculate d-values using Bragg's Law, the values come out the same no matter the X-ray tube and radiation used.

12.1.10 Intensity of Diffraction

When discussing planes in unit cells, h, k, and l may have any integer values, which implies the possibility of an infinite number of d_{hkl} values that could satisfy Bragg's Law. However, intense diffraction will only occur if many atoms occupy the (hkl) planes; without atoms no electrons are present to scatter X-rays. So, while Bragg's Law tells us the angle at which diffraction could occur for any particular d_{hkl} value, it does not tell us anything about diffraction intensity.

Mineral unit cells contain a finite number of atoms, which restricts the number of d-values corresponding to planes of high atomic density. Therefore, the number of angles at which intense diffraction occurs is limited. An example in two dimensions will make this point.



12.25 Hypothetical arrangement of atoms in a 2D crystal

Consider the hypothetical unit cell shown in Figure 12.25*a*. All atoms are on top and bottom edges. The unit cell has dimensions of a = 3.0Å and b = 5.0Å. Ignoring the third dimension (or assuming that all planes are perpendicular to the page), we can say that d_{100} = 3.0Å and d_{010} = 5.0Å.

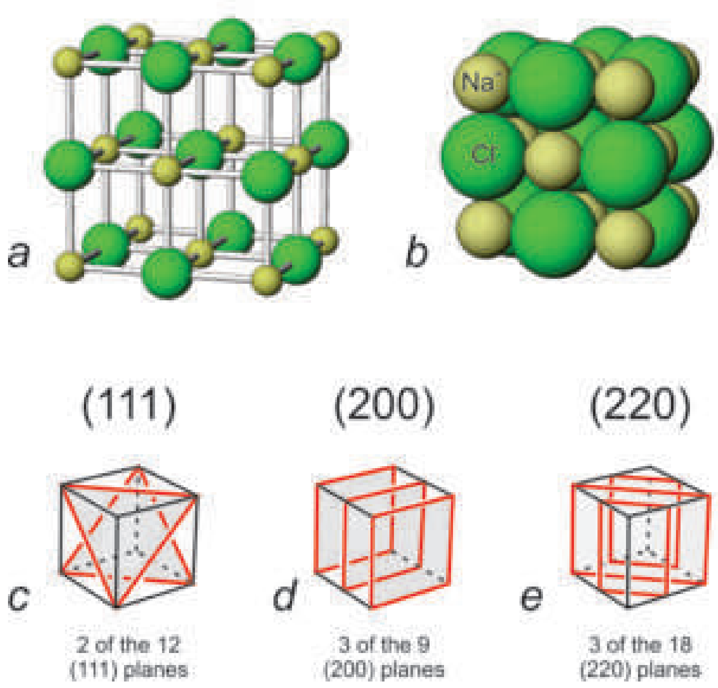
If we imagine a structure made of many of these unit cells (Figure 12.25*b*), we see that many atoms are in rows 5.0Å apart, and diffraction corresponding to d_{010} (5.0Å) should be quite intense. We can also expect apparent diffraction by the (020) planes (d = 2.5Å) to be intense, although no atoms occupy every other (020) plane. This is because we have no way of knowing diffraction order, and 2nd-order (n = 2) diffraction by (010) planes occurs at the same angle as 1st-order diffraction by (020) planes. So we will identify 2nd order (010) diffraction as (020).

Besides 010 and 020, 200 diffraction (d_{200} = 1.5Å) will be quite intense because many atoms occupy the (200) planes. Note also that the (210) plains (diagonal in the figure) contain many atoms and should diffract almost as much as the (200) planes. Applying the equation in Box 12-1 above, we find that d_{210} = 1.43Å, just about the same as d_{200}.

(*hkl*)	***d***	***2θ***
(210)	1.43	65.2°
(200)	1.50	61.9°
(020)	2.50	35.9°
(100)	3.00	29.8°

For our hypothetical crystal, (010) planes will cause very strong diffraction. (210), (200), and (020) planes will also cause significant diffraction. Applying Bragg’s Law to these *d*-values (see the table) tells us that the strongest diffraction will occur for a *2θ* value of 29.8°. Strong diffraction will occur for *2θ* = 65.2°, 61.9°, and 35.9°. But many other planes in this crystal will produce moderate or weak diffraction too.

12.1.11 Intensity of Diffraction: Halite



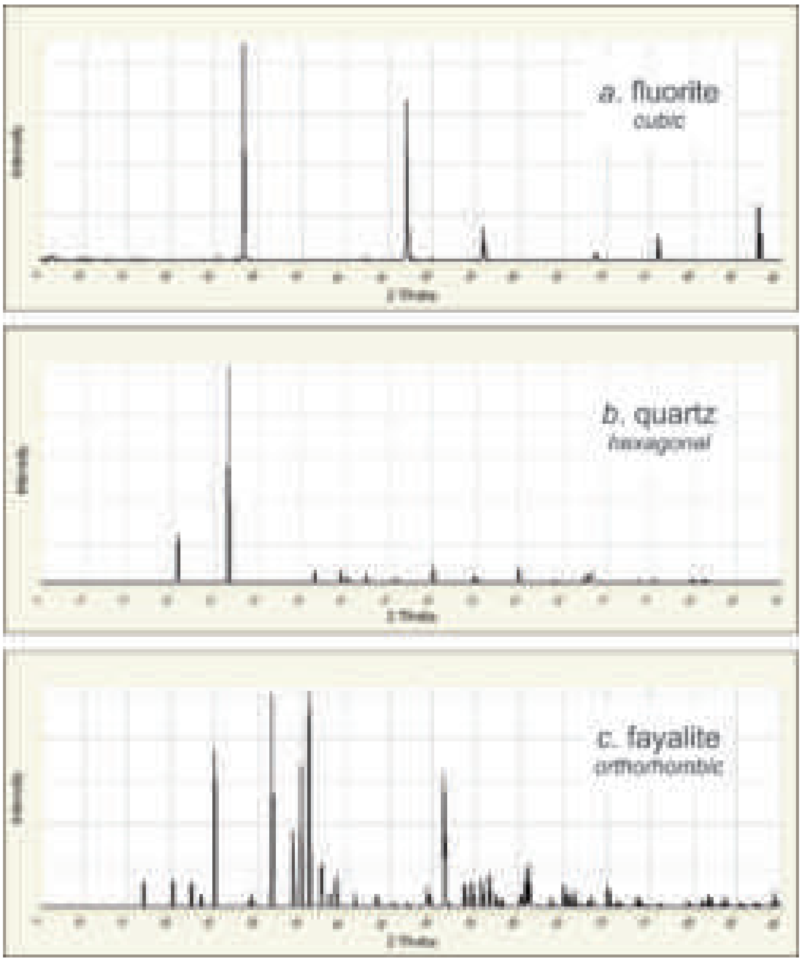
12.26 Atomic arrangement in halite and some planes in a unit cell

The preceding discussion was about a hypothetical 2D mineral. For a 3D example, let’s reconsider halite. Drawings *a* and *b* in

Figure 12.26 show two different depictions of the atomic arrangement in halite. The diagrams in the bottom of the figure highlight (in red) some of the (111), (200), and (220) planes.

Halite is cubic and has lots of symmetry. Consider the (200) planes shown in drawing 12.26*d*. Equivalent planes with equal spacing (not shown) can be parallel to the top and bottom faces, or parallel to the front and back faces. We omitted them for clarity. So, these drawings only show a few of many equivalent planes with equal *d*-values. In total, a cubic crystal like halite contains 12 different orientations for planes equivalent to (111), 9 different orientations for planes equivalent to (200), and 18 different orientations for planes equivalent to (220). If we X-ray halite, diffraction by (111) planes is relatively weak. The (200) and (220) planes produce the most intense reflections because there are many of those planes and they contain many atoms (as seen in the atomic drawings in this figure). You can verify this by looking at the diffraction pattern for halite in Figure 12.24.

12.1.12 X-ray Patterns, Symmetry and Mineral Identification

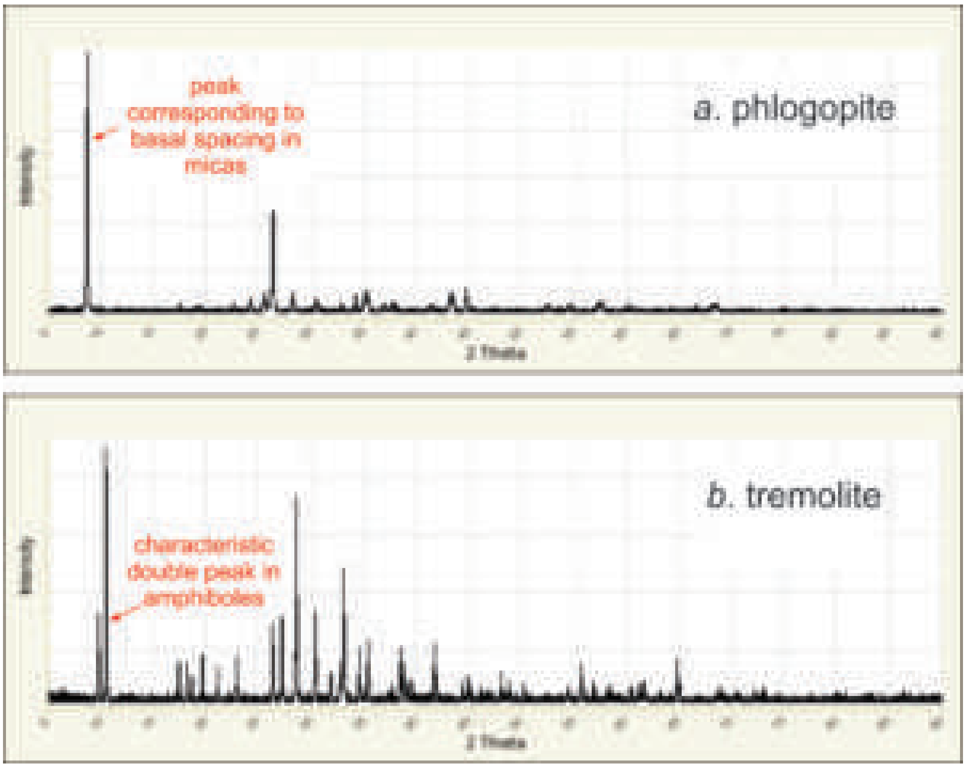


12.27 Diffraction patterns and symmetry

Different minerals produce different diffraction patterns because patterns depend on mineral composition and on the locations of atoms in unit cells. So, space symmetry, which relates to atom location, has great influence on diffraction patterns. Crystals with high symmetry contain identical planes of atoms in multiple directions. Consequently, fewer *d*-values cause diffraction – there are fewer diffraction peaks – than for crystals with low symmetry. And for crystals with high symmetry, X-ray peaks may seem somewhat regularly spaced on diffractograms. In contrast, low crystal symmetry means diffraction occurs in many more directions and diffraction patterns are irregular.

Figure 12.27 shows diffraction patterns for fluorite, quartz, and fayalite. Fluorite is cubic, quartz is hexagonal, and fayalite is orthorhombic. So, crystal symmetry increases downward in the figure. The number of reflections increases from fluorite to quartz to fayalite, and the patterns for fluorite and quartz appear to have a more even spacing of peaks.

An experienced crystallographer can often tell the crystal system with one look at a diffraction pattern, even if they do not know what the mineral is. This is most easily done for high-symmetry systems (such as cubic, hexagonal, or orthorhombic) and may be impossible for monoclinic or triclinic patterns. Experienced crystallographers also learn to identify common minerals quickly. Quartz, for example, has a strong peak at 20.8° 2θ, a stronger peak at 26.6°, and no other significant reflections (Figure 12.27*b*). That is enough to identify it. Graphite also has few peaks with its strongest at about 26.7°, but it lacks a peak near 20.8°. Calcite has a very strong peak just below 30°. And many other minerals have specific peaks that crystallographers quickly spot.



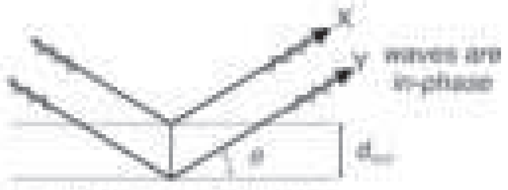
12.28 Diffraction pattern for phlogopite

Even if we cannot identify a mineral with a quick look, we can sometimes figure out the general kind of mineral that was X-rayed. For example, many minerals have no X-ray peaks below 20° *2θ*, and most minerals have no peaks below 10°. But clay minerals have broad peaks in the 5° to 7° range, and phlogopite and other micas have very large peaks at around 9° *2θ*. Figure 12.28 shows an example pattern for phlogopite, a mica; the strongest peak is at 8.7°. Diffraction patterns for amphiboles, too, have a distinguishing characteristic – a double peak at 10-11° *2θ* characterizes tremolite and most other amphiboles. Figure 12.28*b* shows a typical diffraction pattern for an amphibole.

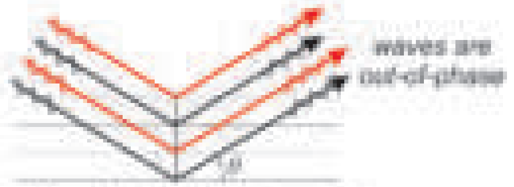
The low-angle reflections produced by clays and micas correspond to large *d*-values. The large values are due to the layered atomic arrangements in these mineral groups. The repeat distance between layers, called the *basal spacing*, is around 10 Å in most micas and repeat distance can be significantly greater in clays. The unit cells for most other kinds of minerals are too small to permit such large repeat distances and large *d*-values. So, if crystallographers see peaks at or below 10°, they often know what general kind of mineral they have.

12.1.13 Extinctions

a. cubic unit cells with atoms at corners and centers



b. diffraction by (010) planes



c. diffraction by (010) planes and planes of atoms between them

d. diffraction by (020) planes

12.29 Destructive interference and extinction

Sometimes, due to destructive interference, planes containing many atoms do not produce diffraction. We term this phenomenon a *systematic absence*, or an *extinction*. Figure 12.29*a* shows a two-dimensional drawing of a structure in which atoms occupy the corners (grey atoms) and the center (red atoms) of each unit cell. As shown in Figure *b*, when 010 diffraction occurs at angle θ, beam X and Y are completely in phase. If the diffraction is 1st order, beam Y travels exactly 1λ farther than beam X.

However, the constructive interference cannot prevail when we account for the (red) atoms between the (010) planes. X-rays scattered by these atoms travel $^1/_2\,\lambda$ more or less than those scattered by the adjacent (010) planes. This produces waves that are out-of-phase and we get perfect destructive interference, shown in Figure *c*. No X-rays will be found at the angle θ although it satisfies Bragg’s Law for d_{010}. This effect is *extinction*, and we would say the 010 diffraction peak is extinct.

Although (010) planes do not diffract, (020) planes do. But the smaller d_{020} compared with d_{010} results in the larger diffraction angle shown in Figure *d*. The atomic arrangement we saw earlier in this chapter in Figure 12.25 also produces extinctions. 100 diffraction is absent because additional atoms occur halfway between the (100) planes.

Figures 12.25 and 12.29 show two-dimensional examples of structures that result in extinctions due to end-centered and body-centered unit cells. In three dimensions, end-centered, body-centered, and face-centered arrangements also produce extinctions. We often describe extinctions using arithmetical rules. For body centering, the rule is that an *hkl* peak will only be present if $h + k + l$ is an even number.

Besides centering, screw axes and glide planes also cause extinction because they, like centering, result in planes of atoms between other planes. The systematic extinction of certain X-ray peaks, then, is one way we figure out space group symmetry. Box 12-2 gives more examples of extinction rules.

● Box 12-2 Extinction Rules

Lattice centering can cause X-ray extinctions. Screw axes and glide planes do too. Arithmetical rules involving h, k, and l describe which peaks can be present. (Although called *extinction rules*, the rules usually describe which peaks are present, not which peaks are extinct.)

The table below lists the affected peaks and gives rules for their presence. This table includes only some of the many possible screw axes. Rules for other screw axes can be inferred by analogy with the ones listed here.

For lattice centering, extinction rules affect all hkl reflections. But screw axes and glide planes only affect some. For example, as listed in the table below, a 2_1 screw axis parallel to the a-axis causes extinction of $h00$ peaks if h is an odd number. If h is an even number, the peak will be present, and other (not $h00$) peaks are not affected at all.

Symmetry Element	Affected Reflection	Condition for Reflection to Be Present
Lattice Centering		
primitive lattice (P)	hkl	always present
body-centered lattice (I)	hkl	$h + k + l$ = even
end-centered lattice (A)	hkl	$k + l$ = even
end-centered lattice (B)	hkl	$h + l$ = even
end-centered lattice (C)	hkl	$h + k$ = even
face-centered lattice (F)	hkl	h, k, l all odd or all even
Screw Axes		
2-fold screw, 2_1 parallel to a	$h00$	h = even
4-fold screw, 4_2 along parallel to a	$h00$	h = even
6-fold screw, 6_3 parallel to c	$00l$	l divisible by 3
3-fold screw, 3_1 or 3_2 parallel to c	$00l$	l divisible by 3
6-fold screw, 6_2 or 6_4 parallel to a	$h00$	h divisible by 4
4-fold screw, 4_1 or 4_3 parallel to a	$h00$	h divisible by 4
6-fold screw, 6_1 or 6_5 parallel to c	$00l$	l divisible by 6
Glide Plane Perpendicular to the B-axis		
a glide	$h0l$	h = even
c glide	$h0l$	l = even
n glide	$h0l$	$h + l$ = even
d glide	$h0l$	$h + l$ divisible by 4

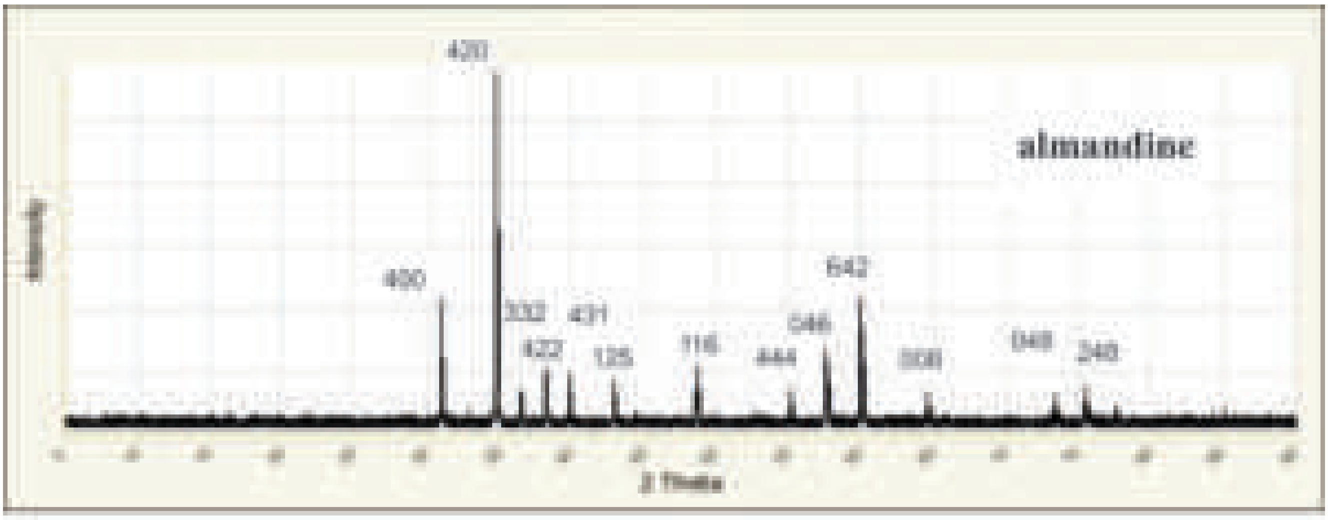
To see the importance of extinctions, consider almandine, a garnet. Almandine is cubic and its crystals have symmetry $^4/_m\bar{3}\,^2/_m$. But the atomic arrangement has a body centered unit cell, a screw axis (4_1), and two glide planes (*a* and *d*); it belongs to space group = I $4_1/a\ \bar{3}\ ^2/_d$.

For cubic minerals we can calculate *d*-values from the relationships in Box 12-1:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

So, we can calculate *d*-values for all combinations of *h*, *k*, and *l*. If we only consider combinations that could give X-ray peaks for $2\theta < 90^\circ$, we get 726 possibilities. That is a lot. However, when we apply the extinction rules for body centering, the screw axis, and the two glide planes, most reflections go away. We are left with only 51 possibilities! And some of these correspond to planes that contain no, or few, atoms – so they produce no reflections.

The diagram below (Figure 12.30) shows a standard reference pattern for almandine. It contains fewer than 15 visible peaks. Some appear spaced regularly, but gaps (missing peaks) correspond to extinctions.



12.30 Diffraction pattern for almandine

12.1.14 Indexing Patterns and Determining Cell Parameters

We have labeled the peaks on the X-ray pattern in Figure 12.30 with *hkl* indices corresponding to the planes causing diffraction. For identifying unknown minerals, we do not need to know which *hkl* indices correspond to which *d*-values, but for other purposes, such as determining unit cell dimensions, we must.

The process of matching *d*-values to *hkl* indices is called *indexing*. The easiest way to index a pattern – unless a computer does it – is to compare it with one for a similar mineral already indexed. For instance, if we measure a pattern of an unknown garnet, it will have the same general appearance as the one in the figure above, so we can easily assign *hkl* indices to the peaks. This is quick and simple. Without a pattern to compare, the process becomes more complex and, except perhaps for cubic minerals, computer programs are desirable or necessary. In the past it was different, but today analyzing a diffraction pattern is automated. With *d*-values for many peaks (the more the better), computer programs use the equations in Box 12.1 and a least-squares approach to derive the six cell parameters (*a, b, c, α, β, γ*). The programs then assign *hkl* indices to each peak.

12.1.15 Uncertainties

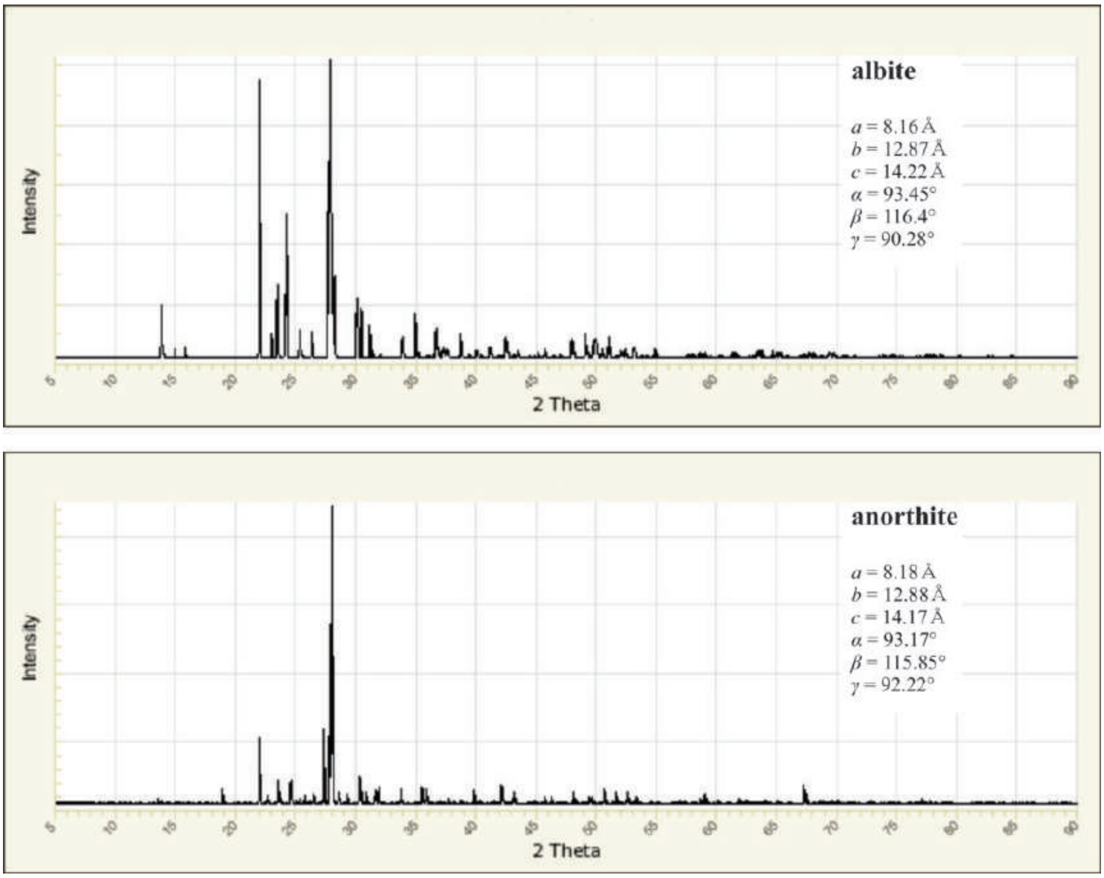
Powder diffraction is not always an exact process, and several things may cause X-ray patterns to deviate from those in reference files. Proper sample preparation is crucial to obtaining accurate patterns. Complications arise when we do not grind a sample properly, or when powdered crystals are not in truly random orientations. For example, because micas are hard to grind and their tiny flakes may align parallel to each other, obtaining random orientation and a good X-ray pattern is difficult for micas. A second problem is that compositional variations can affect X-ray patterns (see Box 12-3 below). Despite these complications, the PDF data contains adequate reference patterns for most mineralogical uses.

● Box 12-3 Compositional Control on Diffraction Patterns

Powder patterns for quartz, fluorite, and other minerals with fixed compositions vary little from those in reference data bases. This is not the case for minerals that form solid solutions.

For example, consider plagioclase. Figure 12.31 in this box shows X-ray patterns for albite and anorthite, the two main plagioclase end members. Unit cell parameters for each are also given. These two minerals have almost, but not quite, the same unit cell size and shape. They also have atoms in the same places within their unit cells. So the two patterns have peaks at about the same angles. (You may have to look closely to see this because albite and anorthite are triclinic which means the patterns are a bit chaotic.)

Peak intensity, however, is significantly different for the two feldspars. This difference is because the minerals have different compositions. The same (*hkl*) planes cause diffraction, but because atoms on those planes are different elements, diffraction intensity by the planes is different. Plagioclase feldspars can have any composition between albite and anorthite and consequently may produce many different looking diffractograms.



12.31 Comparing diffraction patterns for albite and anorthite

12.1.16 Single Crystal Diffraction

12.32 A single crystal diffractometer

For powder diffraction, we grind a sample so we have many crystallites contributing to the diffraction pattern. *Single-crystal diffraction* instead, as the name implies, uses only a single crystal. The technique involves measuring directions and intensities of diffraction when a collimated X-ray beam strikes a carefully oriented small crystal. Crystals are typically 50 to 250 microns (0.05 to 0.25 mm) in longest dimensions. The diffractometer rotates the crystal and moves the detector to measure intensities of all diffraction peaks in 3D space. Typically, a detector moving in a sphere or hemisphere around the crystal measures diffraction intensity. Figure 12.32 shows an example of such a diffractometer. Data collecting can be time-consuming, but modern single crystal diffractometers are computer controlled and can collect diffraction intensities for thousands of directions – sometimes as many as 20,000 – in a few hours. Computers store the data and process it automatically.

We use the data obtained from single-crystal diffraction studies to determine crystal structures. If we know the composition of a mineral, we know how many atoms of which elements are present in a unit cell. Computer programs figure out where atoms are relative to each other, based on the diffraction data. We call this process a *crystal structure* *determination* or *crystal structure refinement*. Crystal structure determination involves many complexities, but automation and high-speed computers have simplified the process considerably since the Braggs determined the first crystal structure in 1913.

12.2 Obtaining a Mineral Analysis

X-ray diffraction has historically been, and still is, a very important technology used by mineralogists. It also has important applications in solid-state physics, biophysics, medical physics, chemistry, and biochemistry. It allowed Watson and Crick to discover the structure of DNA in 1953. Yet, diffraction rarely tells us what elements a mineral contains, instead telling us how atoms are arranged. So, petrologists and mineralogists use other approaches to obtain chemical analyses.

Until about 1960, geologists obtained mineral and rock analyses primarily using an approach called “wet chemistry.” To obtain a wet chemical analysis, we can dissolve samples in acid and then analyze them by reactions involving precipitation, titration, or colorimetry. *Gravimetric analysis* involves reacting the acid solution with reagents to produce a precipitate. We then weigh the precipitate, and the weight tells how much of an element of interest was present in the original sample. *Volumetric analysis* involves titrating the sample until a specific reaction occurs. The volume of reagent necessary to make the reaction occur is proportional to the amount of the element of interest that is present. *Colorimetric analysis* involves reaction with a reagent that changes the color of the solution. The color intensity is proportional to the amount of the element of interest present, which we quantify by comparison to standards. The advantage of wet chemical analysis is that we can analyze just about any element. However, different elements require different approaches, the technique requires large samples that are destroyed during analysis, and analyses are difficult and time-consuming to do with accuracy. For these reasons and because other, simpler techniques are now available for most purposes, wet chemical analysis is rarely done today.

In the 1960s, researchers developed several new kinds of instruments that made mineral and rock characterization and analysis easier, while also providing new and different kinds of information. Today, we use many different kinds of analytical techniques and devices; for a good summary, go to https://serc.carleton.edu/research_education/geochemsheets/browse.html. The development of *electron microscopes* and *electron microprobes* was of particular importance – we discuss these instruments below.

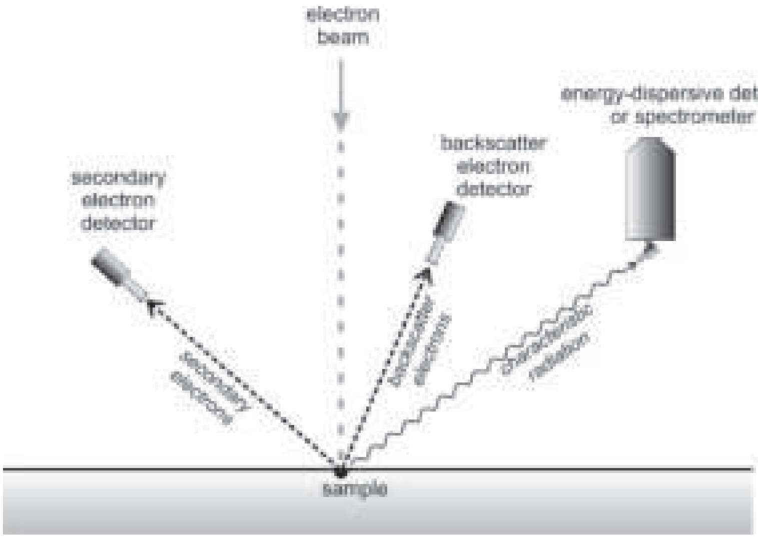
12.2.1 Electron Microscopes

12.33 An electron microscope

Conventional microscopes use visible light to examine a small specimen, or sometimes a thin section. An *electron microscope* uses a beam of electrons instead of light. Electron microscopes can magnify samples thousands of times more than conventional light microscopes, allowing us to see very fine mineral grains and details. The greater magnification and resolution are possible because the effective wavelength of an electron is much smaller than the wavelength of light. Consequently, electron optics can focus on much smaller areas than light optics.

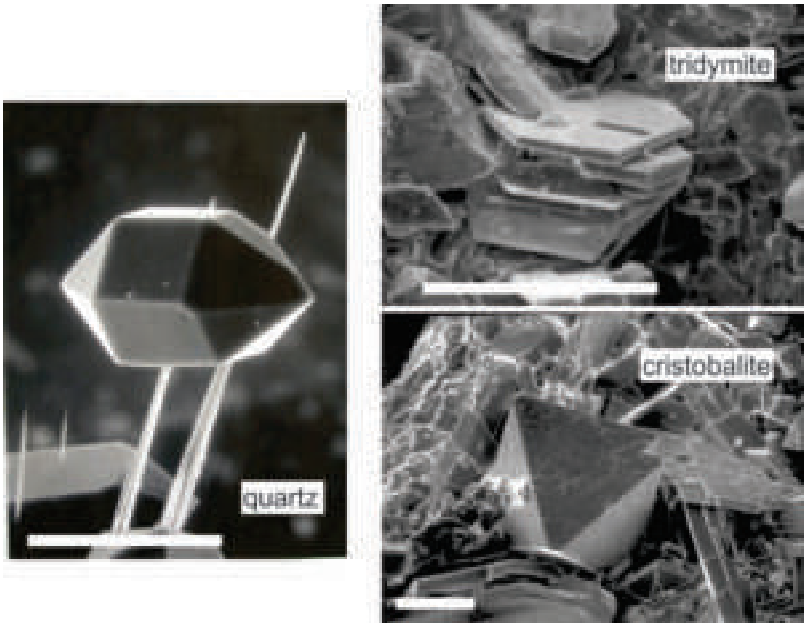
There are several different kinds of electron microscopes; *scanning electron microscopes* (*SEMs*) are by far the most common. In a scanning electron microscope, such as the one shown in Figure 12.33, high energy (typically 15–20 keV) electrons are generated at the top of the column on the left. The electrons are focused into a narrow beam that scans back and forth (*rasters*) across a sample at the bottom of the column to produce an image. SEMs can scan very small areas, operating over a wide range of magnifications, up to 250,000x when properly optimized. They can resolve topographical or compositional features just a few nanometers in size. Several different kinds of images can be displayed on a monitor screen depending on the user’s needs.

12.2.1.1 SEM Images



12.34 Inside a scanning electron microscope

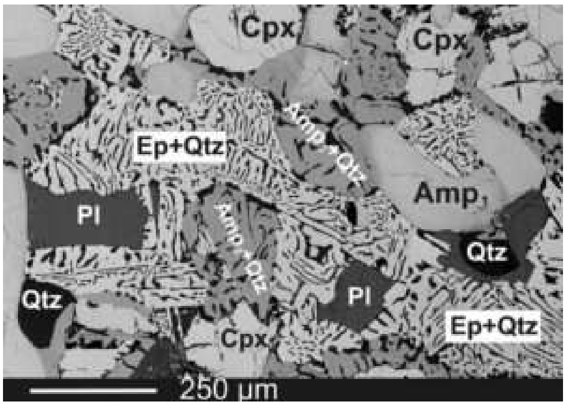
Several important things occur as the electron beam interacts with a sample (Figure 12.34). Some electrons will reflect from the sample surface with no loss of energy. We call these electrons *backscatter electrons*. Additionally, ionization produces lower-energy *secondary electrons* when the original high energy electrons interact with valence electrons in the sample. To obtain standard SEM images, a detector measures the intensity of secondary electrons (SE) emitted by the sample as the beam rasters across it. This allows creation of an image with brightness proportional to the number of electrons reaching the detector.



12.35 Secondary electron images of three SiO_2 polymorphs. The white bars are 0.01 mm long.

Most SEMs also have a separate detector for creating backscatter electron (BSE) images. For both SE and BSE images, the number of electrons emitted, and thus the brightness or darkness of an image, depends on sample topography and on the composition of the sample. The emission of secondary electrons is particularly sensitive to topography, and only slightly affected by composition. In contrast, the emission of backscatter electrons depends significantly on the composition of the sample. Heavier elements backscatter electrons more efficiently than light elements. So, BSE images show compositional variations within a sample as well as surficial features.

Figure 12.35 shows secondary electron images of very small quartz, tridymite, and cristobalite crystals. These SiO_2 polymorphs all belong to different crystal systems and the mineral habits reflect the differences. SE and BSE images, like the images in this figure, sometimes look like conventional photographs but are not the same thing because they do not involve light reflection.



12.36 BSE image of a thin section

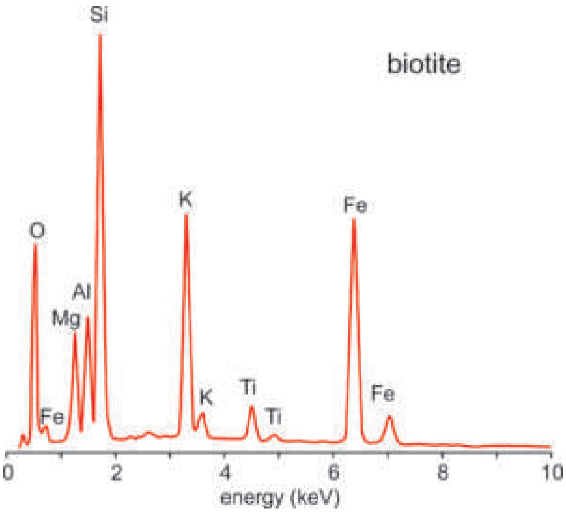
Mineralogists and petrologists sometimes use SEM images to look at rock thin sections. Figure 12.36 shows an example. This is a BSE image of an amphibolite that experienced complex metamorphic reactions. The reactions produced intergrowths of epidote and quartz called *symplectites*. The very small grains and textures would be hard to see in thin section (the bar scale is 0.25 mm long).

In this image, distinct contrast between white and shades of grey reflect mineral compositions. Dark colored minerals (quartz and plagioclase) are those that contain mostly elements with low atomic numbers. The light colored clinopyroxene and epidote contain significant amounts of heavier elements, in particular iron. The amphibole has an intermediate composition.

12.2.1.2 Secondary X-rays and Characteristic Radiation

An additional important phenomenon occurs when beam electrons hit atoms in a sample. The electrons cause the atoms to emit characteristic secondary X-rays with energy that depends on the element. This process is much the same as the way that the target in an X-ray tube emits X-rays. If the sample contains several different elements, it may emit X-rays at multiple wavelengths corresponding to different energies. Because different elements give off characteristic X-rays with different energies, the emission spectrum displays the chemical composition of the specimen. Most SEMs are equipped with energy-dispersive X-ray detectors for measuring X-ray energies and, thus, for identifying elements in a sample. This analytical method is called *energy-dispersive spectroscopy* (*EDS*).

Iron, for example, emits its strongest characteristic radiation (called *Kα radiation*) at 6.4 keV. So, the spectrum for a sample that contains iron emits energy at 6.4 keV, and the intensity of the emission is proportional to the amount of iron in the specimen. Iron also emits characteristic X-rays of other energies, but the intensities are much less than *Kα* radiation and rarely used for analysis.



12.37 EDS spectrum for biotite

Energy dispersive detectors measure X-ray energy and intensity over a wide range of energies simultaneously. Spectra can be collected quickly, perhaps counting X-rays for just a few seconds, to get an idea of the composition of a sample. For more accurate results, counting times must be longer. Figure 12.37 shows a spectrum for biotite. Some elements produced more than one peak but the strongest peak for any element is always *Kα*. This is a typical spectrum for biotite, but biotite varies in composition so the relative heights of the peaks are not the same for all specimens.

A computer takes a spectrum such as the one in Figure 12.37 and quickly analyzes the intensities of all X-ray peaks to produce an EDS chemical analysis for the sample. EDS analyses are generally semiquantitative at best, but often that is all that we need.

12.2.2 Electron Microprobes

For the most accurate chemical analyses, we use *wavelength dispersive X-ray spectroscopy* (*WDS*) instead of EDS. Special detectors called *spectrometers* measure the intensity of X-rays having specific wavelengths, characteristic of specific elements. Because most scanning electron microscopes do not have spectrometers, they cannot produce WDS analyses.

12.38 An electron microprobe

Electron microprobes, more properly called *electron probe micro analyzers* (*EPMAs*), are instruments similar to SEMs but specifically designed for obtaining WDS analyses (Figure 12.38). Microprobes have a more intense electron beam than SEMs, and may have four or more spectrometers besides imaging and EDS analytical capabilities. However, we cannot obtain WDS analyses as quickly as EDS analyses because a spectrometer only measures one element at a time. For the most accurate results, we analyze standards to compare with unknowns, adding additional time to the procedure. The WDS approach is much more accurate than EDS and can detect elements present in smaller amounts, with precision about 1 to 2% of the amount present (for major elements). The analytical accuracy depends primarily on how well we have standardized the microprobe. Today’s microprobes can do all the same imaging that an SEM can do. The four monitors in Figure 12.38 allow viewing of different kinds of images and analytical data simultaneously.

Scanning electron microscopy and electron microprobe analysis have several major advantages over most other analytical techniques and are therefore widely used. First, they allow us to examine rocks, mineral grains, or thin sections with little sample preparation. Second, microprobe analysis is a nondestructive analytical technique. So, we analyze samples without destroying them. Perhaps most important, microprobe analyses focus on very small spots. We can analyze single mineral grains, or many spots in the same grain, to look at very small-scale changes in chemistry. No matter the exact technique used, because the electron beam typically excites a sample volume of only 30 cubic microns, it can resolve very fine compositional features. Additionally, individual X-ray peaks may be isolated to construct elemental maps, showing the distribution of different elements in different parts of the sample.

One shortcoming of both EDS and WDS analysis is that elements with low atomic number are difficult to analyze. This problem arises because low-numbered elements emit X-rays of low energy. For several reasons, such X-rays may not make it to the detector or spectrometer, or may not be measurable once they get there. Technology varies, but even the best EDS detectors cannot analyze elements lighter than boron. WDS analysis can, in principle, analyze elements from Be to U but technical complications occur at both extremes.

An additional complication arises because most geological materials do not conduct electricity. Unless we coat them with a conducting material, static charge builds up, distorting images and analyses. So, we vaporize gold, carbon, or other conducting material in a vacuum and let it precipitate on our specimen. Gold coatings work very well for some applications, producing excellent images. However, we cannot easily remove the gold, and it interferes with analyses. So mineralogists and petrologists generally use carbon coating instead. Unlike gold, we can remove the carbon coating from a thin section by light polishing. Instead of coating samples, we can reduce or eliminate charging problems by using an *environmental scanning electron microscope* (*ESEM*) instead of a standard SEM. ESEM is a technology that, unlike a conventional SEM, does not require that the sample be under a high vacuum. A small amount of gas (up to 20 torr/2.7 kPa) provides a medium to conduct electrons away from the sample. ESEMs require no sample coating and many permit examination of large samples, larger than conventional SEMs. The quality of images and analyses, however, is reduced compared with conventional SEMs.

12.2.3 Other Analytical Techniques

Mineralogists and petrologists use many other analytical techniques besides those described above. All are destructive techniques, and most are more useful for analyzing rocks than individual minerals because they require large samples. A farily comprehensive list of analytical techniques can be found at https://serc.carleton.edu/research_education/geochemsheets/browse.html. Some of the most important are:

> *X-ray fluorescence (XRF)* is a technique used mainly for analyzing rocks. It requires relatively large samples melted with a flux to make a glass disk. The disc is placed in the machine, where a high-energy X-ray beam hits it. Atoms in the sample fluoresce, producing characteristic X-rays that are analyzed using EDS or WDS detectors. We compare unknowns with well-characterized standards to obtain quantitative results.
>
> *Atomic absorption spectroscopy (AAS)* is based on the absorption of light by an atomized sample. We dissolve samples in an acid solution or flux that we then introduce to a hot (2,000 °C/3,600 °F) flame or graphite furnace. The flame atomizes the liquid, converting it to a gas phase. We use special light sources to pass light of different wavelengths, characteristic of different elements, through the gas. We compare light absorption of unknown samples and standards to determine the concentration of the element of interest. We can use AAS to analyze most metals but not nonmetals.
>
> *Inductively coupled plasma (ICP)* is used mostly to analyze rocks, not individual minerals. After we dissolve it in acid, or in a flux, we heat the sample in a plasma (6,000 °C/11,000 °F), ionizing its atoms. At 6,000 °C, the atoms emit light at wavelengths that depend on the elements present. We measure the intensity of light emission at different wavelengths to calculate the concentrations of each element present. ICP analysis is very sensitive and can measure elements present at the parts-per-billion level.
>
> *Inductively coupled plasma mass spectrometry (ICP-MS)* is a variant of ICP analysis. Instead of analyzing the emitted light, displaced ions are analyzed using a mass

spectrometer to measure concentrations of individual isotopes. ICP-MS can be used with a laser that ionizes small spots on individual mineral grains. ICP-MS is very sensitive and can analyze many elements at concentrations as low as 1 part per trillion.

Ion microprobes, also called secondary ion mass spectrometers (SIMS), analyze small spots (on the order of a few microns) on a sample. A focused beam of ions bombards the sample, burning a pit as it creates a plasma and releases ions. The ions then travel to a mass spectrometer for analysis. Ion microprobes are much more sensitive than electron microprobes and we use them to measure the concentrations of very light elements that we cannot analyze with a microprobe. However, standardization is problematic and limits accuracy.

Mössbauer spectroscopy is a limited but very valuable analytical technique. We use it to determine the oxidation state and coordination of Fe in minerals. A sample is exposed to gamma radiation emitted by an ^{57}Fe source, and a detector measures how much of the radiation is absorbed by Fe as it passes through the sample. The gamma-ray source is accelerating back and forth, changing the energy slightly due to the Doppler effect. The absorption at different velocities (energies) reflects Fe valence and coordination number in the specimen. We could use Mössbauer spectroscopy to analyze a few other elements besides Fe, but none are generally of geological interest.

Visible and infrared spectroscopy is an analytical technique based on the absorption of visible light or infrared radiation (IR) by a sample. Samples are prepared in one of several ways to make them thin enough for light/ radiation to pass through. We shine a beam of light through the sample and measure the absorption of different wavelengths. Absorption of visible light can tell us the oxidation state and coordination number of important transition metals. Absorption of IR radiation helps identify minerals, and reveals the relative amounts of H_2O and OH^-, or of CO_2 and $CO_3{}^{2-}$, in a specimen.

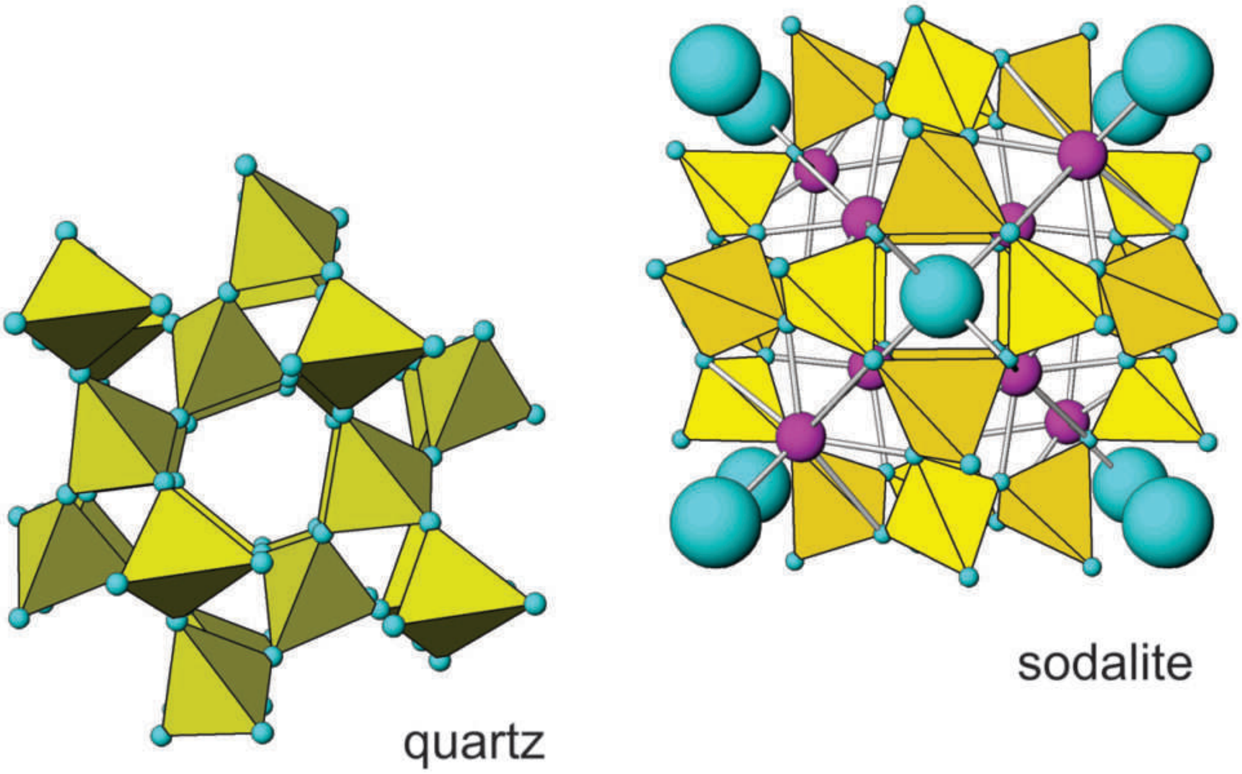
Raman spectroscopy is based on inelastic (Raman) scattering of light from a sample. A monochromatic laser beam is focused on a small spot on the sample, and most light photons bounce off with the same wavelength as the original light (elastic scattering). The few that do not will have slightly increased or decreased wavelengths and energies. The difference in energy, called the *Raman shift*, reflects the presence of specific ions and atoms in the sample. It also tells us the coordination numbers of some elements, helps distinguish polymorphs from each other, and provides a measure of the crystallinity of a specimen.

●Figure Credits

Uncredited graphics/photos came from the authors and other primary contributors to this book.

12.1 An X-ray diffractometer, xrpd.eu
12.2 Röntgen at work in 1896, crtsite.com
12.3 Diffraction gratings, educatingphysics.com
12.4 Diffraction pattern of sphalerite, www.nature.com
12.6 X-ray tube, designworldonline-dot-com
12.8b Bee making ripples Bogdan Giuşcă, Wikimedia Commons
12.11c Ripples on lake, W.carter, Wikimedia Commons
12.20 A powder diffractometer, serc.carleton.edu
12.21 Powder diffraction sample holder, USGS
12.23b X-ray diffractometer, xrpd.eu
12.24 to 12.30 Diffraction patterns from rruff.info
12.32 Single crystal diffractometer, geo.arizona.edu
12.33 Electron microscope, jeolusa.com
12.35 SEM images, George Rossman
12.36 BSE image. Belyanin et al. (2014)
12.38 An electron microprobe, cameca.com
Vide0 12-1: Laue patterns and Bragg’s Law, Keith Purtirka, YouTube

13 Crystal Structures



13.1 The atomic arrangements in quartz and sodalite

13 Atomic Structures

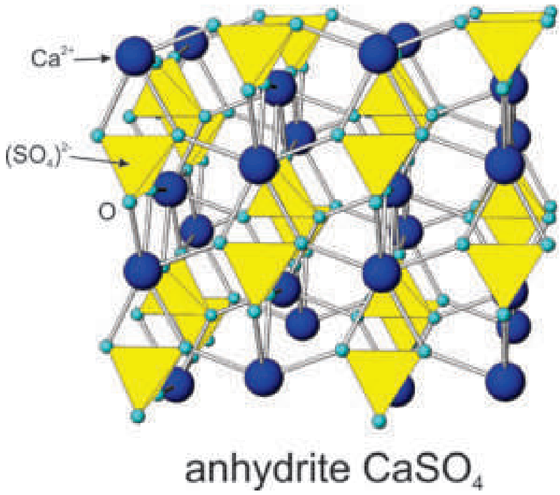
KEY CONCEPTS

- The development of X-ray diffraction techniques allowed mineralogists and chemists to directly investigate the nature of crystal structures.
- Minerals have highly ordered and repetitive atomic arrangements.
- We can model many crystal structures as being spherical atoms held together by ionic bonds.
- Ionic crystals contain anions packed around cations and vice versa.
- The key controls on ionic bonds are ionic size and charge.
- An atom’s coordination number is the number of other

atoms that it bonds to.

- Most common cations bond to 3, 4, 6, or 8 anions; alkalis and other large ions bond to more.
- The strength of an ionic bond is an ion's charge divided by its coordination number.
- Atoms pack tightly together in some minerals; in others, atoms are in networks with geometric shapes.
- Compositional variations in silicate minerals are directly related to the nature of the crystallographic sites in their structures.

13.1 The Impact of X-ray Crystallography



13.2 The atomic arrangement in anhydrite

We cannot overstate the importance of the discover of X-rays and the subsequent studies by Röntgen, von Laue, and the Braggs. Before their pioneering work, scientists could not test competing hypotheses for the nature of crystal structures. Within a few decades after the discovery and development of X-ray diffraction techniques, most of the basic principles of crystal structures were well known. Figure 13.2 shows the arrangement of atoms in anhydrite ($CaSO_4$). This arrangement was first described by J.A. Wasastjerna in 1925 based on X-ray studies. Blue spheres are Ca^{+2} ions and yellow tetrahedra are sulfate (SO_4) groups. This model has passed the test of time and is accepted as the atomic arrangement in anhydrite today.

While crystallographers were working on crystals, chemists were developing atomic theory. The Bohr model of the atom, the Schrödinger wave equation, and theories of ionic and covalent bonding were firmly established by the 1920s. And things came together. Crystallographers used the new knowledge of bonding to analyze minerals. At the same time, Linus Pauling (see Box 13-1) and other chemists realized the importance of X-ray techniques and conducted X-ray studies in efforts to further understand crystal structure and bonding. In 1939, Pauling published *The Nature of the Chemical Bond*; he subsequently won the Nobel Prize in Chemistry in 1954.

● Box 13-1 Who Was Linus Pauling?

13.3 Linus Pauling with a friend

Linus Carl Pauling was a prolific American chemist and, in his later years, a peace and health activist. His success as a scientist stemmed from his ability to cross traditional discipline boundaries, an uncanny ability to identify key questions, and courage to put forth new, although sometimes incorrect, ideas.

Born in Portland, Oregon, on February 28, 1901, Pauling received a B.S. in chemical engineering from Oregon State University in 1922 and a Ph.D. from California Institute of Technology (Cal Tech) in 1925. For several years he was a postdoctoral fellow in Europe, where he worked with such renowned scientists as Niels Bohr, Erwin Schrödinger, and Sir William Henry Bragg. He returned to the United States and began his career as a professor of chemistry at Cal Tech in 1927.

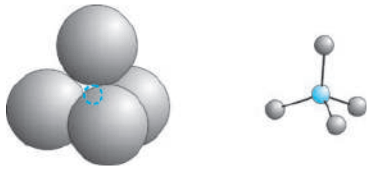
In 1963 he left Cal Tech to join the Center for the Study of Democratic Institutions Santa Barbara, California, where he spent his time working for world peace. In the late 1960s he worked for a brief time at the University of California – Santa Barbara before moving to Stanford University. He died in Big Sur, California, on August 29, 1994, at the age of 93.

Pauling’s chemical studies covered many fields, including both organic and inorganic chemistry. One of the first to interpret crystal structures using quantum mechanics, he was also a pioneer of X-ray diffraction. His studies of chemical bonding resulted in the publication of his book *The Nature of the Chemical Bond* in 1939.

In the 1930s and 1940s, Pauling turned his attention to molecular chemistry, producing significant papers concerning blood, proteins, and sickle cell anemia. In 1954 he received the Nobel Prize in Chemistry “for research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.” During his later years, Pauling received acclaim for his investigations of vitamin C. His vitamin C studies resulted in many publications including the books *Cancer and Vitamin C* and *Vitamin C and the Common Cold,* published in the 1970s.

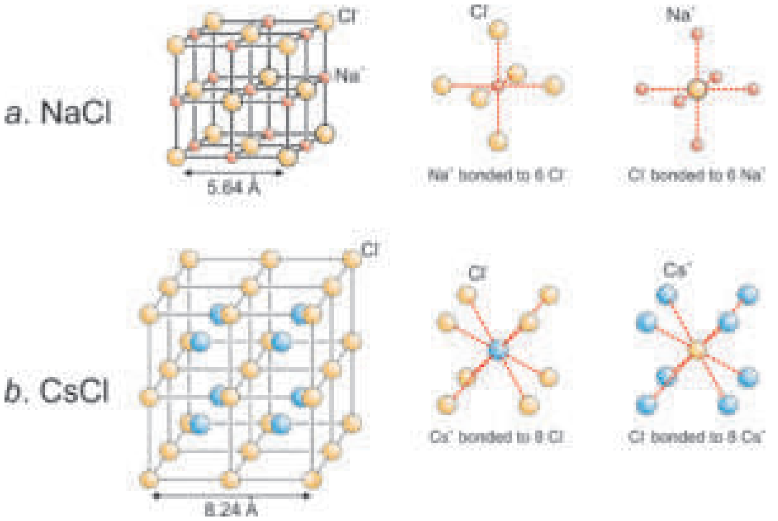
With the development of nuclear weapons, Pauling became concerned about potential world destruction. In 1958 he published *No More War!*, and during the same year he delivered a petition urging the end of nuclear testing signed by more than 11,000 scientists to the United Nations. In 1962 he received the Nobel Peace Prize, making him one of only a few individuals ever to win two Nobel prizes. During his long career he received many other honors, including the Mineralogical Society of America’s Roebling Medal in 1967.

13.2 Ionic Crystals



13.4 A cation bonded to four anions

Ionic crystals are those composed of cations and anions held together primarily by ionic bonds. They have overall electrical neutrality, or else electrical current would flow until they obtained charge balance; so the total number of electrons in the structure is equal to the total number of protons. Anions repel anions, cations repel cations, so ions of similar charge stay as far apart from each other as possible. Consequently, an organized and repetitive atomic arrangement, with cations packed around anions and anions packed around cations, typifies ionic crystals. Figure 13.4, for example, shows two views of a cation (blue) surrounded by four anions. The drawing on the left does a better job of showing the relative sizes of the cation and anions but the one on the right is more clear about bond angles and distances.



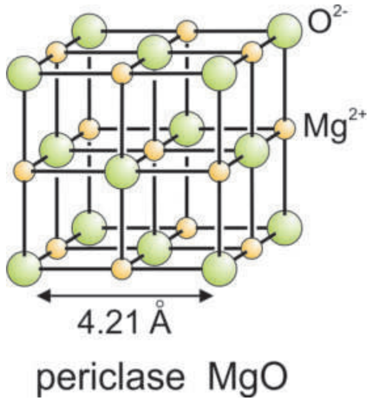
13.5 The atomic arrangements in NaCl

and CsCl

Consider the mineral halite, NaCl, which contains an equal number of Na and Cl atoms (Figure 13.5*a*). Mineralogists have determined its atomic arrangement through X-ray studies, finding that Na^+ and Cl^- ions pack around each other in an alternating three-dimensional structure. As shown in the enlarged views, each Na^+ bonds to six Cl^- and vice versa. Bonds around one ion are all equal length and at 90° to each other. Unit cells are therefore cubic, containing four Na^+ and four Cl^- ions in a face-centered arrangement. Halite salt crystals, including the ones that come out of your salt shaker, are often perfect cubes.

Besides halite (NaCl), other alkalis combine with chlorine to produce alkali chlorides. Figure 13.5*b,* for example, shows the atomic arrangement in CsCl. The arrangement, like halite’s, is cubic. But in contrast with the halite structure, eight anions surround the alkali cation (Cs^+). The difference is because Cs^+ is larger than Na^+. It requires more room in the crystal structure. Because there are equal numbers of Cs^+ and Cl^- in CsCl, if eight anions surround every Cs^+, eight cations must surround every Cl^-, as shown in the enlarged views.

The ionic bonds between alkalis and Cl^- are not terribly strong. They break easily when salts dissolve in water, releasing free alkalis and Cl^- ions. High solubility in water is characteristic of highly ionic crystals, especially those in which the ions only have charges of ±1. If concentrations of dissolved Na^+ and Cl^- reach high enough levels, perhaps due to evaporation, halite may precipitate from solution.

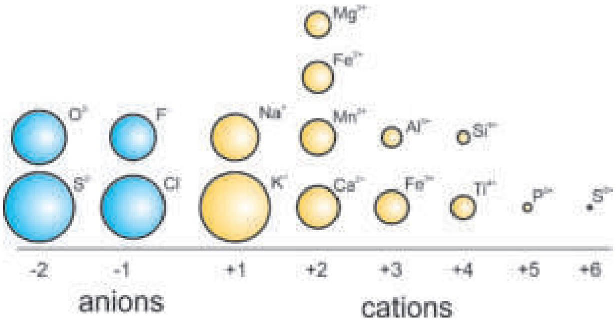


13.6 The atomic arrangement in periclase

Other minerals have different atoms but have atomic structures and bonding similar to halite’s; sylvite (KCl) and periclase (MgO) are both examples. In periclase (shown in Figure 13.6), however, the ions are divalent, having a charge of ±2 (in contrast with the ions in halite and sylvite which are monovalent), and the bonds are 25% covalent. The stronger, more covalent bonds mean that periclase is harder and has lower solubility than sylvite and halite.

In some minerals, tightly bonded molecular ions, for example carbonate $(CO_3)^{2-}$, sulfate $(SO_4)^{2-}$, or phosphate $(PO_4)^{3-}$ are present instead of simple anions. These molecules alternate with cations just as O^{2-} and Mg^{2+} alternate in periclase. The molecular ions may not dissociate, even if a mineral dissolves in water, because covalent bonds hold them together. Calcite, $CaCO_3$, is a good example. In the calcite structure, carbonate groups and Ca^{2+} ions alternate in three dimensions. However, the carbonate units are triangular, so the overall symmetry is not cubic like halite’s. When calcite dissolves, the ionic bonds between calcium and carbonate break easily, but the carbonate group itself does not dissociate into C and O. Consequently, dissolved species are Ca^{2+} and $(CO_3)^{2-}$, and sometimes $(HCO_3)^{-}$.

13.2.1 Ionic Radii



13.7 Comparing the sizes of common cations and anions

Ions consist of nuclei with electron clouds around them. The electrons are constantly moving; sometimes they are farther from the nucleus than at other times, so we can never know the exact size of the electron cloud. However, ions often behave as if they have fixed radii, and we can understand many crystal properties by thinking of crystals as collections of spherical ions packed together. The spacing between them, and the way they pack together, are functions of their size. Knowing their *effective ionic radius* is therefore useful. Figure 13.7 shows average effective ionic radii for common anions and cations.

How can we determine ionic radii if ions really do not have a fixed radius? We estimate size by studying bond lengths in crystals. Consider the mineral periclase (MgO) shown in Figure 13.6. Through X-ray diffraction studies we have learned that the distance between the centers of the Mg^{2+} and O^{2-} ions is about 2.11 Å, so the sum of the effective ionic radii of Mg^{2+} and O^{2-} is 2.11 Å. A standard value for the radius of O^{2-} is 1.32 Å, so this yields a radius of 0.79 Å for Mg^{2+} in periclase. Crystallographers have also measured the radius of an Mg atom by using X-ray to learn the distance between neighboring Mg atoms in Mg metal. Mg metal is not, however, ionically bonded, and the results do not tell us the radius of

Mg^{2+}, although they do tell us that metallic Mg has a radius of about 1.60 Å.

If we study many compounds, it becomes possible to learn the effective ionic radii of all individual elements in their most common ionic forms. Consider the alkali oxides. They have the general formula R_2O, and R can be any alkali element. Oxygen bonds to each alkali ion, and chemists and mineralogists have determined the bond lengths through X-ray studies. Since the radius of O^{2-} is common to all alkali oxides, variations in bond length must be due to variations in the radii of the alkalis. If we assume O^{2-} has a constant radius of 1.32 Å, we get the cation radii in the table below. The alkalis are in column 1 (Group 1) of the Periodic Table. It should be no surprise that alkali radius increases as we move down the column because we know elements with higher atomic numbers have more protons and electrons, and so are larger atoms.

Radii of Alkali Cations in Alkali Oxides

cation	**Li^+**	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
at. no.	3	11	19	37	55
radius Å	0.82	1.40	1.68	1.81	1.96

The table above shows radii of alkali cations increasing with atomic number (down a row in the Periodic Table). Radii also vary systematically across a row of the Periodic Table (see the table below). Cation radii are always smaller than uncharged atoms of the same species. As we move from the left margin of the Periodic Table toward the center, cation charge increases and cations get smaller because more charge means attraction between electrons and protons increases.

Radii of Common Ions in the Third Period (Row) of the Periodic Table

cation	**Na^+**	**Mg^{2+}**	**Al^{3+}**	**Si^{4+}**	**P^{5+}**	**S^{6+}**	**S^{2-}**	**Cl^-**	**Ar^0**
at. no.	11	12	13	14	15	16	16	17	18
radius Å	1.18	0.79	0.55	0.41	0.25	0.20	1.72	1.70	—

The table above also includes two anions (S^{2-} and Cl^-) from the right-hand side of the Periodic Table; they are larger than the cations because they contain extra electrons in outer orbitals. Anion radii are always larger than uncharged atoms of the same species. Note that we cannot list an ionic radius for argon because it is a noble gas and does not ionize to enter ionic structures.

We can best see the relationship between cation radius and charge by looking at elements that exist in more than one valence state. For example, the tables below give ionic radii for manganese and vanadium cations. As expected, the radii decrease with charge, reflecting the greater pull nucleus protons have on outer electrons with increasing charge.

Radii of Manganese Atoms and Cations

cation	**Mn^0**	**Mn^{2+}**	**Mn^{3+}**	**Mn^{4+}**	**Mn^{6+}**	**Mn^{7+}**
radius Å	1.12	0.97	0.70	0.62	0.35	0.34

Radii of Vanadium Atoms and Cations

cation	**Va^0**	**Va^{2+}**	**Va^{3+}**	**Va^{4+}**	**Va^{5+}**
radius Å	1.31	0.87	0.72	0.67	0.53

Box 13-2 contains a table with effective ionic radii for the most common ions. The table includes more than one value for most ions because radius varies depending on how an ion is bonded. For example, the radius of Na^+ is listed as 1.07, 1.08, and 1.40 Å; these difference reflect different numbers of bonds going to the cation. And the radii of Na^+ given in some tables above are inconsistent because one table refers to alkali oxides, and the other contains average values for many different types of crystals. These differences remind us that the notion of ionic radius is an approximation because the effective radius of an ion depends on several things:

- Most significantly, radii are only constant if bond types are constant. For example, the average ionic radius of Mg^{2+} is 0.88 Å, while its covalent radius is 1.36 Å and its metallic radius is 1.60 Å.
- Additionally, ionic size varies depending on the number of bonds (called the *coordination number*, discussed below) that connect to an ion.
- Another complication may arise because in some structures ions become *polarized* (elongated) in one direction and no longer act as spheres.
- A final ambiguity arises because we assume a value for the radius of O^{2-} to calculate radii for cations bonded to oxygen. Depending on the kind of bonding and several other things, O^{2-} may have an effective radius between 1.27 Å and 1.34 Å, but the values in this book’s tables are based on an assumed radius of 1.32 Å.

● Box 13-2 Coordination Numbers and Effective Ionic Radii

13.8 Effective ionic radii for ions in different coordinations

The chart seen here (*click to enlarge*) gives effective ionic radii for the most common ions. These data are slightly modified from values in Zoltai and Stout (1984) *Mineralogy: Concepts and Principles*. The literature contains many different tables with values that do not match those given here because radii are approximations and may be determined in different ways. For consistency, values from different sources should not be combined.

The first number in every entry below is the coordination number. The second number (for cations) is the effective ionic radius in coordination with O^{2-} having a radius of 1.32 Å. Values for elements in parentheses were not determined.

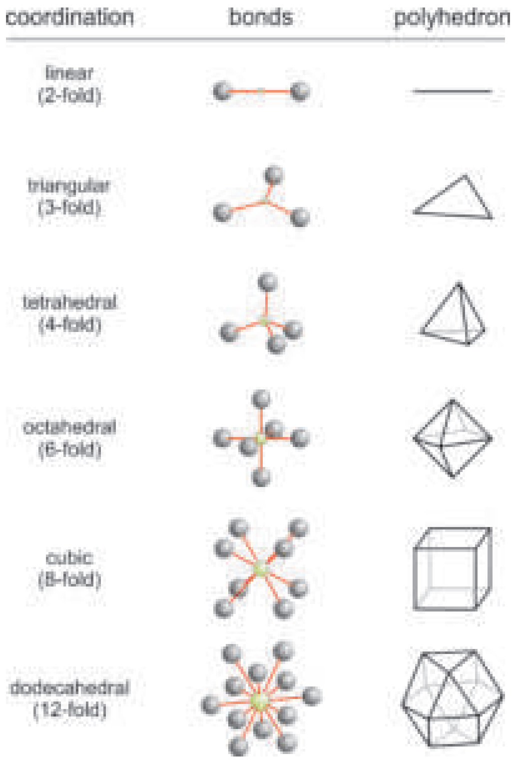
▶ Video 13-1: Further discussion about why ionic radii can vary, even for the same element

13.2.2 Coordination Number

Most minerals, except native elements such as gold or copper, contain anions or anionic molecules. O^{2-}, S^{2-}, $(OH)^{-}$, and $(CO_3)^{2-}$ are especially common. The large size of oxygen and other anions (and molecules) compared with most common cations (Figure 13.7) means that we can often think of crystal structures as large anions with small cations in *interstices* (spaces) between them. Anions are packed in a repetitive structure, with the cations at regular intervals throughout.

The number of anions to which some particular cation bonds is the cation’s *coordination number* (C.N.). Si^{4+}, for example, nearly always bonds to four O^{2-} anions in minerals, and therefore has a C.N. of 4. So we say it is “in 4-fold coordination.”

The size of interstices between anions depends on how the anions are packed. In two dimensions, anions can fit together in symmetrical patterns to form hexagonal or square patterns. In three dimensions, other possibilities, including tetrahedral and cubic arrangements, exist.



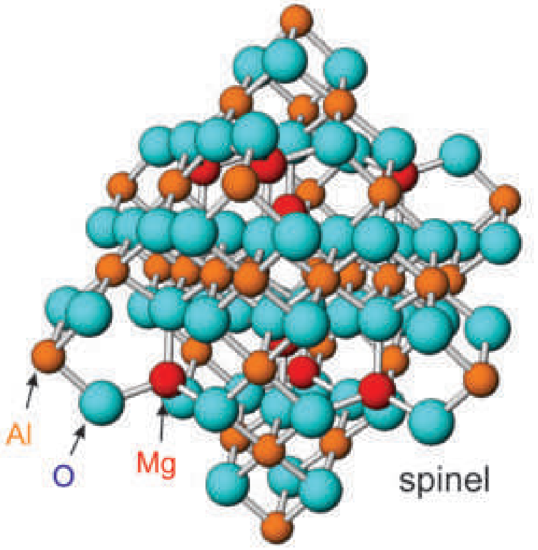
13.9 Different kinds of coordination

Figure 13.4 showed one way a group of identical anions may pack around a single cation. The cation was in 4-fold coordination, but there are other possibilities, shown here in Figure 13.9. Since only one cation and one kind of anion are involved, all bond distances (in red) are the same. We give coordination arrangements geometrical names depending on the shape of the polyhedron created by connecting the centers of the anions.

We call 2-fold coordination *linear* because the ions form a line. We call 3-fold coordination *triangular* because the anions form a triangle. We call 4-fold coordination *tetrahedral* because the four anions form a tetrahedron. We call the 6-fold coordination *octahedral* because the anions outline an octahedron (an eight-sided geometric shape). We call the 8-fold coordination *cubic* because connecting the centers of the anions produces a cube. (Fortunately, we never call cubic coordination *hexahedral* although a cube has six faces.) We call the 12-fold coordination, shown in Figure 13.9, *dodecahedral* because the coordinating polyhedron has twelve vertices.

As coordination number increases, the space inside a polyhedron increases to accommodate larger cations. So, large cations have greater C.N.s than small cations. The coordination polyhedra shown in Figure 13.9 are all regular, meaning the cation-to-anion distance is the same for all anions. Cations also sometimes occupy distorted sites or sites with irregular or unusual coordinations not represented by the drawings in Figure 13.9. Most of the time, regular geometry is present.

Common elements have different coordinations in different minerals. Most atoms in minerals are in 3-, 4-, 6-, or 8-fold coordination, but 5-fold, 7-fold, 9-fold, and 10-fold coordinations are possible. 2-fold coordination is rare or nonexistent. The atoms in some native metals are in 12-fold coordination.



13.10 The atomic arrangement in spinel

Figure 13.10 shows a typical ball-and-stick model for spinel, $MgAl_2O_4$. This model is convenient and easy to examine, and we can count the number of bonds to each atom. But the depiction is incorrect in detail because balls of nearly the same size, separated by large distances, represent all atoms, anions, or cations, and there is lots of unoccupied space. More accurate models of crystal structures could better reflect variations in ionic radii, bond length, and the way that ions fit together. In principle we could construct very exact models, using spheres of correctly proportioned sizes. In practice it is not often done because regular ball-and-stick models are easier to make and examine, and because we know that the notion of ions as spheres is only an approximation.

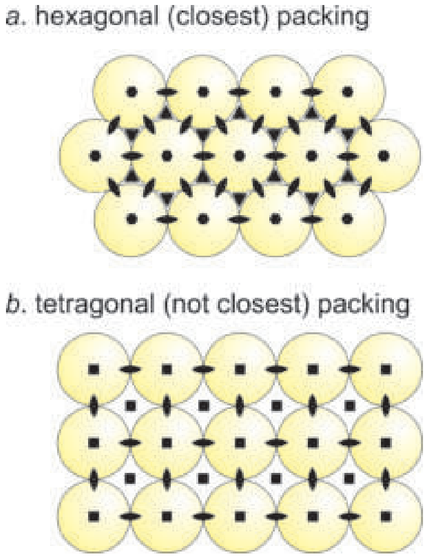
13.2.3 Different Kinds of Bonding

So far, we have focused on ions and ionic bonding. Yet, minerals often contain other kinds of bonds. For example, fluorite has mostly ionic bonds. Bonds in other halides may only be 70% ionic. In contrast, the bonds between metals and oxygen in many minerals are up to 50% covalent. Overall, atoms in covalent bonds are significantly larger than their cations in ionic bonds. These difference can occasionally affect coordination number. Sulfides and native metals have bonds that range from nearly 100% covalent to 100% metallic, but covalent and metallic radii are nearly the same, and the variations in radii may not be significant. Combinations of ionic and metallic bonds are rare and usually minor.

Although bonds in minerals crystals, such as quartz crystals, may be up to 50% covalent, for most purposes consideration of ions and ionic bonding explains mineral properties. An ionic model, although incorrect in detail, works for many sulfides too, even though bonding in them has little ionic character. No matter the kind of bonding, (wholly or partially) positively charged ions alternate with (wholly or partially) negatively charged ions. Because ionic bonds are easier to analyze, and because they explain most mineral properties, we will stick with them for the rest of this chapter.

13.3 Closest Packing

13.3.1 Closest Packing in Two Dimensions



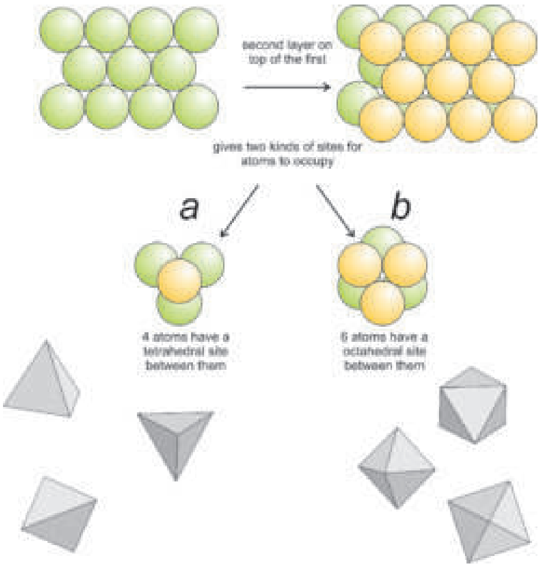
13.11 Packing of ions in 2D

In many crystals, anions pack together in highly regular repetitive patterns. As an analogy, consider a collection of equal-sized marbles. We may arrange the marbles so rows line up and repeat at regular spacing characterized by translational symmetry. Figure 13.11 shows two alternative ways that marbles (shown as circles) can pack together in two dimensions. In Figure 13.11*a* groups of three marbles are arranged so that connecting their centers yields an equilateral triangle. On a slightly larger scale, each marble is surrounded by six others, and connecting their centers makes a hexagon. The total pattern has 2-fold, 3-fold, and 6-fold rotational symmetry (shown by symmetry symbols in the drawing), and also translational symmetry and mirror planes. Figure 13.11*b* shows an alternative arrangement of marbles in two dimensions. This arrangement has 2-fold and 4-fold axes of symmetry (shown by lens- and square-shaped symbols), but not 3-fold. The symmetries of the two patterns in Figure 13.11 are equivalent to the symmetries of a hexanet and a square net (Figures 11.23 and 11.27 in Chapter 11).

We call the arrangement of marbles in Figure 13.11*a* *hexagonal packing*. We call the pattern in Figure 13.11*b* *tetragonal packing* because of the obvious 4-fold symmetry. In hexagonal packing the marbles are closer together than in tetragonal packing. Because no other two-dimensional arrangement allows marbles to be closer together, we say the hexagonal arrangement is *closest packed*. Each marble touches six others, the maximum possible. In the tetragonal arrangement, each marble only touches four others.

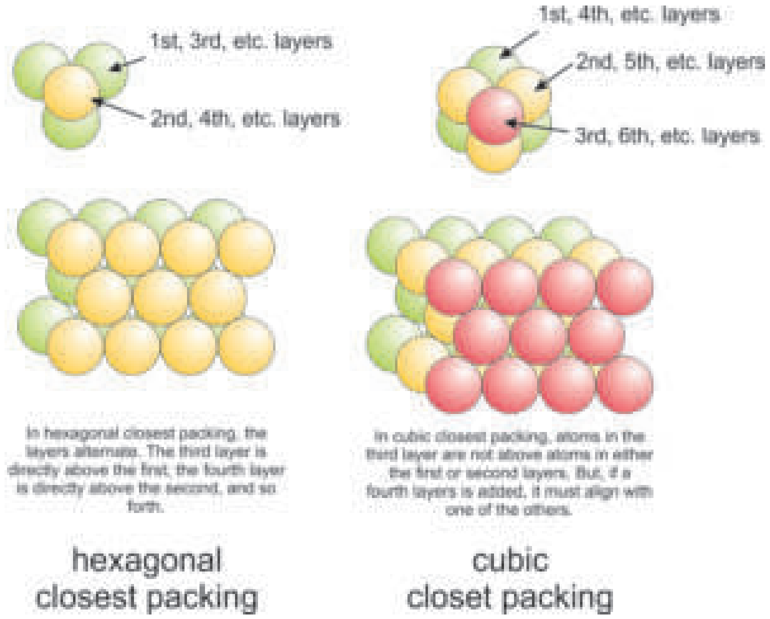
13.3.2 Packing in Three Dimensions

In three dimensions, marbles (or anions) can be closest packed in two ways. Both are equivalent to piling hexagonal packed sheets one above another. Three adjacent marbles in a hexagonal closest-packed sheet make a triangle. If we put another marble on top of them, it slips into the low spot above the center of the triangle, resulting in a tetrahedral structure composed of four marbles (Figure 13.12*a*). All four marbles touch each other, so the arrangement is closest packed. Alternatively, we could put three marbles on top of the first three, as shown in Figure 13.12*b*. This arrangement of marbles, too, is closest packed. Each marble is in contact with three in the adjacent layer but you may have to look closely to convince yourself that this is the case.



13.12 Closest packing in three dimensions

Figure 13.12*a* shows four marbles, or four cations, forming a tetrahedron. If an anion is between them, it will be in tetrahedral coordination. Figure 13.12*b* shows 6 marbles, or cations, forming an octahedron. If an anion is between them, it will be in octahedral coordination. The geometric shapes in the bottom of Figure 13.12 are different views of tetrahedra and octahedra created by joining the centers of the anions.



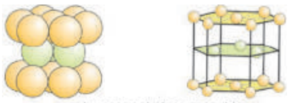
13.13 Hexagonal closest packing and cubic closest packing

Now consider an entire layer of hexagonal packed marbles. If we put another hexagonal packed layer on top, its marbles naturally fall into gaps produced by groups of three in the bottom layer. So the marbles in the second layer will not be directly above those in the first (Figure 13.13).

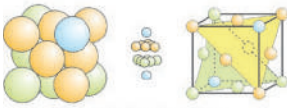
If we now place a third layer on top of the second, marbles will fill gaps as before. However, marbles in the third layer may or may not be directly above those in the first layer. There are two possibilities (Figure 13.13). If the third layer is above the first layer, we call the *structure hexagonal closest packed*. If the layer is not, we call it *cubic closest packed* (see Box 13-3, below). Although it may not be immediately obvious, if we add a fourth layer, its marbles must lie directly above those of another layer.

We can describe hexagonal closest packed (HCP) structures as having ABABAB layering because alternate layers are directly above each other. Cubic closest packed (CCP) structures have an ABCABCABC packing sequence; it takes three layers before they repeat. In both HCP and CCP, every marble (or anion) is in contact with 12 others.

● Box 13-3 Why Are Atomic Arrangements Called Hexagonal Closest Packed (HCP) and Cubic Closest Packed (CCP)?



a. hexagonal closest packing



b. cubic closest packing

c. body-centered cube

13.14 Three ways atoms can pack together

In two dimensions, closest-packed atoms are in hexagonal patterns. Each atom is surrounded by six others with no wasted space between. In 3D closest-packed structures, each atom is surrounded by 12 others with no wasted space between.

3D closest packed arrangements may be *hexagonal closest packed (HCP)* or *cubic closest packed (CCP)*. If HCP, atoms from alternating layers yield a unit cell with the shape of a hexagonal prism. If CCP, atoms from four layers combine to form a unit cell with the shape of a cube. The large drawings in Figure 13.14 show two different views of three structures. The drawings on the left show packing more clearly, but the drawings on the right (with much smaller atoms) do a better job of revealing atom locations.

Hexagonal closest packing involves two layers of atoms that alternate – even-numbered layers are directly above/below each other, and odd-numbered layers are directly above/below each other (but are offset with respect to the even-numbered layers). Figure 13.14*a* shows an example of an HCP arrangement. The bottom and top (orange) layers of seven atoms are identical; they are in a hexagonal pattern with an extra atom at the center. The middle layer (green) contains three touching atoms forming an equilateral triangle. The three nestle snugly above and below opening in the bottom and top layers.

The drawing of cubic closest packing (Figure 13.14*b*) is a bit more difficult to see. 14 atoms form a cubic unit cell. The arrangement contains three layers that repeat. The blue atom in the top right corner is in a layer by itself. Behind it, the six orange atoms form a closest packed triangle. Behind them, six green atoms also form a closest packed triangle, but with a different orientation. And, behind *them* is another single blue atom. So, the layers are sloping instead of horizontal or vertical. The inset shows the layers rotated to be horizontal.

Although the closest packing model is a convenient concept, most minerals do not have atoms in closest-packed arrangements. Some halide and sulfide minerals have nearly closest packed structures, but metal crystals are the best examples. Gold, silver and platinum are examples of native metals with cubic closest packing. Magnesium and zinc are examples of native metals with hexagonal closest packing. Native iron has atoms with a body-centered cubic arrangement (Figure 13.14*c*) with atoms at the corners and one in the center. This arrangement, however, is not closest packed.

13.3.3 Exceptions to Closest Packing

Johannes Kepler first broached the idea of atoms as touching spheres in 1611. William Barlow described the systematics of closest-packed structures more than 250 years later in 1883. For a long time, all structures were thought to have simple repetitive closest packing. It was not long after the Braggs’s X-ray studies led to the first crystal structure determination that scientists found exceptions.

In closest-packed structures, the arrangement of anions means that only tetrahedral and octahedral sites are present (Figure 13.12). We can use closest packing to describe metals, sulfides, halides, some oxides, and other structures in which all cations are in tetrahedral or octahedral coordination. Sphalerite (ZnS), halite (NaCl), and native metals gold, silver, platinum, and copper are all examples of cubic closest-packed minerals. Wurtzite (ZnS), magnesium metal, and zinc metal are hexagonal closest packed. Other mineral structures are, however, not truly closest packed. In general, dense minerals with few large cations are most closely packed.

Today we know that some minerals have complicated structures, and that many minerals have polyhedral frameworks that are not closest packed at all. Minerals containing alkali or alkaline earth elements cannot be closest packed because alkalis and alkaline earths are too large to fit in tetrahedral or octahedral sites. The closest-packed model also fails for other minerals, such as fluorite, CaF_2, in which small anions are between large cations, and for metals that have a body-centered cubic structure in which each atom contacts eight others.

13.4 Pauling’s Rules

In 1929, Linus Pauling summarized five general rules that apply to ionic structures. The rules, now called *Pauling’s Rules*, provide a convenient framework for examining some details of ionic structures (Box 13-4).

● Box 13-4 Pauling’s Rules

Rule 1. Radius Ratio Principle: Cation-anion distances are equal to the sum of their effective ionic radii, and cation coordination numbers are determined by the ratio of cation to anion radii.

Rule 2. Electrostatic Valency Principle: The strength of an ionic bond is equal to ionic charge divided by coordination number.

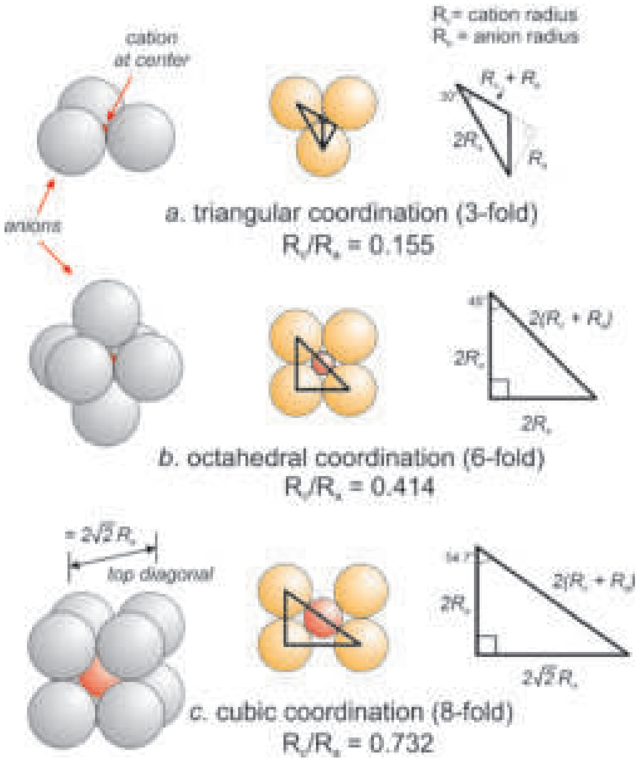
Rule 3. Sharing of edges or faces by coordinating polyhedra is inherently unstable.

Rule 4. Cations of high valence and small coordination number tend not to share anions with other cations.

Rule 5. Principle of Parsimony: The number of different components in a crystal tends to be small.

13.4.1 Pauling’s First Rule

Pauling’s first rule, sometimes called the *Radius Ratio Principle*, states that the distance between cations and anions can be calculated from their effective ionic radii, and that cation coordination number depends on the relative ratio of cation and surrounding anion radii. In essence, this rule says that very small cations will bond to only a few anions, while very large cations may bond to many anions. In other words, as the radius of the cation increases, so too will the coordination number.



13.15 Calculating radius rations for different coordinations

Figure 13.15*a* shows the limiting case when a cation just fits into the opening between three touching anions. Application of the Pythagorean theorem, which is a bit complicated, reveals that the ratio of cation radius to anion radius (R_c/R_a) = 0.155.

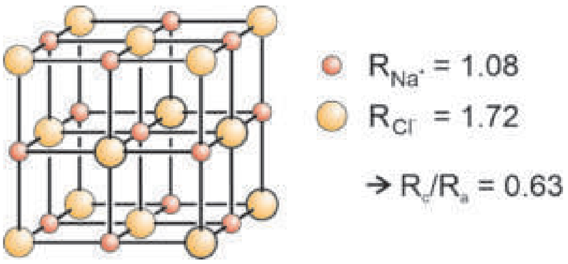
Figure 13.15*b* shows four touching anions with a cation between. If additional anions are directly above and below the cation, the cation is in perfect octahedral coordination. Application of the Pythagorean theorem to the right triangle reveals the ratio of cation radius to anion radius (R_c/R_a) to be 0.414. This value is the square root of 2 minus 1.

Figure 13.15*c* shows similar calculations for a cation in cubic coordination. (R_c/R_a) comes out to be 0.732. This value is the square root of 3 minus 1. We can make similar, though more complicated, calculations for cations in other coordinations. It should not be surprising, however, that the (R_c/R_a) value for perfect dodecahedral coordination is the square root of 4 minus 1 = 1. The pattern involving square roots is because the calculations all involve the Pythagorean theorem.

As coordination number increases, space between anions increases, and the size of the cation that fits increases. Pauling argued, therefore, that as R_c/R_a increases, cations will move from 2- or 3-fold to higher coordinations in atomic structures. He further argued that stretching a polyhedron to hold a cation larger than ideal might be possible. However, it was unlikely, he said, that a polyhedron would be stable if cations were smaller than ideal. In nature, the upper limits given for various coordinations are sometimes stretched; the lower ones are rarely violated. The table below summarizes the different limiting ratios for different coordinations.

R_c/R_a and Coordination of Cations

R_c/R_a	expected coordination	coordination number
<0.15	2-fold coordination	2
0.15 0.15– 0.22	perfect triangular coordination triangular coordination	3
0.22 0.22– 0.41	perfect tetrahedral coordination tetrahedral coordination	4
0.41 0.41– 0.73	perfect octahedral coordination octahedral coordination	6
0.73 0.73– 1.0	perfect cubic coordination cubic coordination	8



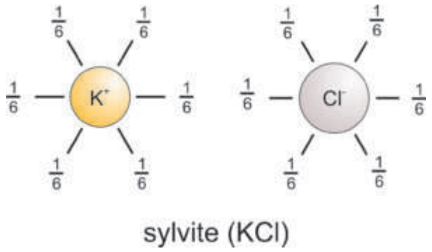
13.16 Halite with Na^+ and Cl^- in 6-fold (octahedral) coordination

As an example of application of Pauling's first rule, let's take another look at halite. The radii of Na^+ and Cl^- in octahedral coordination are 1.08Å and 1.72Å. The radius ratio, R_c/R_a, is 1.08/1.72 = 0.63. Thus we can expect the cation Na^+ to be in octahedral (6-fold) coordination, consistent with the model shown here in Figure 13.16 (and in Figure 13.5*a*). If Na^+ is in 6-fold coordination, Cl^- must be as well, since the structure contains an equal number of both.

For a video discussing coordination polyhedra and the coordinations of cations in olivine (an example of application of Pauling's Rule #1), click on the link below:

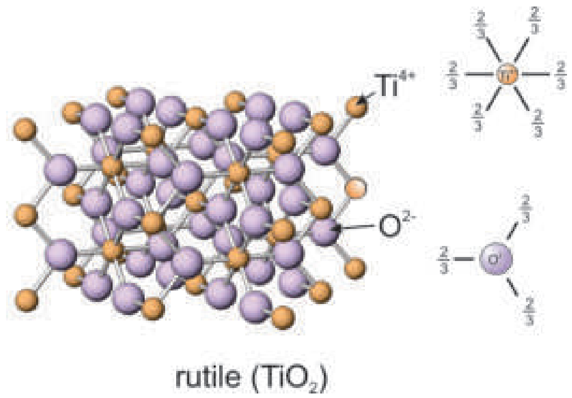
[▶️ Video 13-2: https://www.youtube.com/watch?v=hUmTK0hI5EA (8 minutes)](https://www.youtube.com/watch?v=hUmTK0hI5EA)

13.4.2 Pauling's Second Rule



13.17 Atoms in sylvite

Pauling’s second rule, sometimes called the *Electrostatic Valency Principle*, says that we can calculate the strength of a bond (its electrostatic valence) by dividing an ion’s valence by its C.N. Consequently, the sum of all bonds to an ion must be equal to the charge on the ion. In sylvite (KCl), six Cl^- bond to each K^+ and the strength of each bond is 1/6, total charge divided by number of bonds (Figure 13.17). The strength of each bond around Cl^- is 1/6 as well. Six bonds of charge 1/6 add up to 1, the charge on each ion.

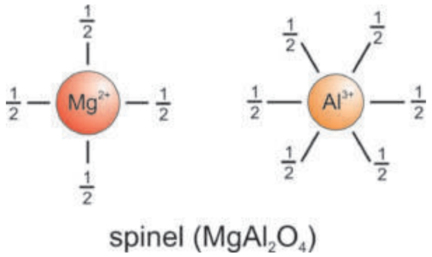


13.18 The atomic arrangement in rutile

We can use Pauling’s first two rules to analyze a more complicated mineral, rutile (TiO_2). In rutile, Ti-O bonds are the only bonds present (Figure 13.18). The radii of Ti^{4+} and O^{2-} are 0.69 Å and 1.32 Å. R_c/R_a is 0.52 and, as predicted by Rule 1, Ti^{4+} is in 6-fold (octahedral) coordination – shown in the enlarged coordination drawing in this figure. Each bond has a strength of 4/6 (total charge divided by number of bonds) = 2/3. Since each O^{2-} has a total charge of -2, it must be bonded to three Ti^{4+} to satisfy Rule 2, so O^{2-} is in triangular coordination (Figure 13.18).

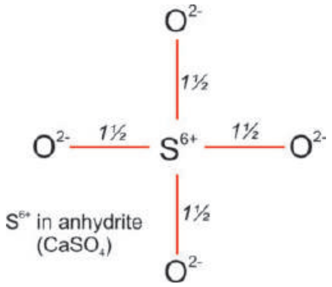
Although Pauling’s first two rules are useful guides to crystal structures, they have shortcomings. First, ionic radii vary with C.N. and valence, among other things. Sometimes radius-ratio calculations may be ambiguous because they require choosing a C.N. before we may make calculations (see Box 13-3). Second, bonds in minerals are rarely completely ionic, and ionic radius varies with the nature of the bond. Third, in cases where R_c/R_a is near a limiting value, we cannot be certain whether the higher or lower C.N. will prevail. Fourth, some coordination polyhedra, especially for high C.N.s, may be irregular in shape.

13.4.2.1 Isodesmic, Anisodesmic, and Mesodesmic Crystals



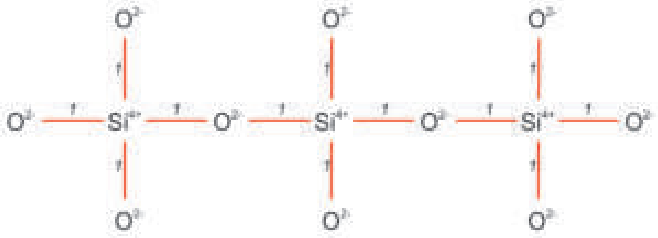
13.19 Bond strengths in spinel

Halite, sylvite, fluorite, and rutile are relatively simple minerals; they each contain one cation and one anion and, therefore, one kind of bond. Most minerals contain more than two elements and may have many kinds of bonds. We saw a model of spinel, $MgAl_2O_4$, in Figure 13.10. Spinel contains Mg-O and Al-O bonds. X-ray studies reveal that Mg^{2+} is in tetrahedral coordination and Al^{3+} is in octahedral coordination. Consequently, as shown in Figure 13.19,the strength of the bonds around Mg^{2+} is 2/4 = 1/2, and the strength of the bonds around Al^{3+} is 3/6 = 1/2. We call compounds such as spinel, in which all bonds have the same strength, *isodesmic*. They have the same bond lengths and properties (*e.g.*, cleavage and hardness) in all directions.



13.20 Bonds around S^{6+} in anhydrite

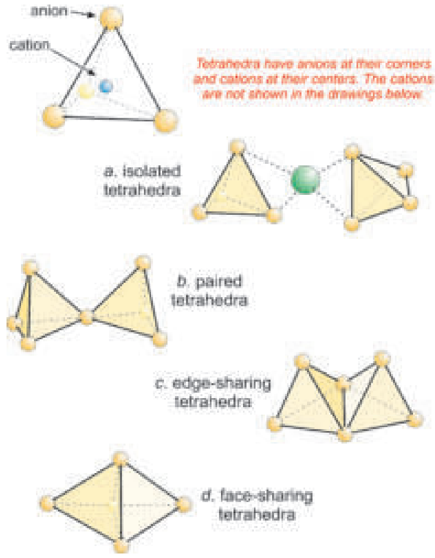
Figure 13.2 showed the atomic arrangement in anhydrite, $CaSO_4$. Anhydrite and other sulfates are examples of *anisodesmic* compounds. In sulfates, S^{6+} is in 4-fold coordination with O^{2-}. The strength of a sulfur-oxygen (S-O) bond (shown in red in Figure 13.20) is therefore 6/4 = 1½ (Figure 13.20). Because the strength of each S-O bond is greater than half the charge on coordinating oxygen, oxygen bonds to S^{6+} more tightly than to Ca^{2+}. Consequently, $(SO_4)^{2-}$ molecules are tight units within the crystal structure. All sulfates, carbonates, nitrates, and other anisodesmic compounds contain tightly bonded molecular ions. So, we can think of $(SO_4)^{2-}$, $(CO_3)^{2-}$, and $(NO_3)^{-}$ as single anionic units within crystals.



13.21 Mesodesmic bonds joining silicon and oxygen ions

Silicate minerals belong to a special group of compounds that are *mesodesmic*. If a bond distribution is mesodesmic, cation-anion bond strength equals exactly half the charge on the anions. In silicates, Si^{4+} is in tetrahedral coordination and each Si-O bond (shown red in Figure 13.21) has a strength of 1, exactly half the charge of O^{2-}. Consequently, oxygen may coordinate to another cation just as strongly as to its coordinating Si^{4+}. In many silicates, the “other” cation is another Si^{4+}. For example in Figure 13.21, pairs of Si^{4+} share an oxygen producing chains of Si^{4+} alternating with O^{2-}. This is why silica tetrahedra can polymerize to form pairs, chains, sheets, or networks. It also helps explain why many silicate minerals are quite hard; the Si-O bonds are very strong.

13.4.3 Pauling’s Third Rule



13.22 Silicon tetrahedra and sharing of anions

In all crystals, anions bond to more than one cation. For example, Figure 13.22 shows several ways silica tetrahedra might be associated in an atomic structure. In Figure 13.22*a*, tetrahedra do not share any common oxygen. They are isolated tetrahedra linked by bonds to a cation between them. In 13.22*b*, a pair of tetrahedra share one oxygen (called a *bridging oxygen*). Bonding of these two sorts commonly holds crystal structures together.

In Figure 13.22*c*, adjacent tetrahedra share an edge (two oxygen). In Figure 13.22*d*, they share a face (three oxygen). We can see that as the structure progresses from Figure 13.22*a* to 13.22*d*, Si^{4+} in the centers of the tetrahedra get closer together. Yet, because the Si^{4+} are all positively charged, we expect them to repel each other. This is the essence of Pauling's third rule. The third rule is that coordinating polyhedra become less stable when they share edges and are extremely unstable if they share faces. Instability results because if polyhedra share edges or faces, cations in the centers of the polyhedra are too close together. The instability is especially important for cations of high charge, high C.N., or in cases when R_c/R_a is near limiting values.

Although this discussion of Pauling's third rule is focused on tetrahedra, the same principles apply to octahedra and other polyhedra. Edge- and even sometimes face-sharing, however is more common in larger polyhedra than in tetrahedra because there is more room for cations to stay apart.

13.4.4 Pauling's Fourth Rule

Pauling's fourth rule is an extension of his third, stating that small cations with high charges do not share anions easily with other cations. This is another consequence of the fact that highly charged cations will repel each other. For example, all silicate minerals contain Si^{4+} tetrahedra. Yet in all the many known silicate minerals, none contains $(SiO_4)^{4-}$ polyhedra that share edges or faces because that would bring Si^{4+} cations too close together.

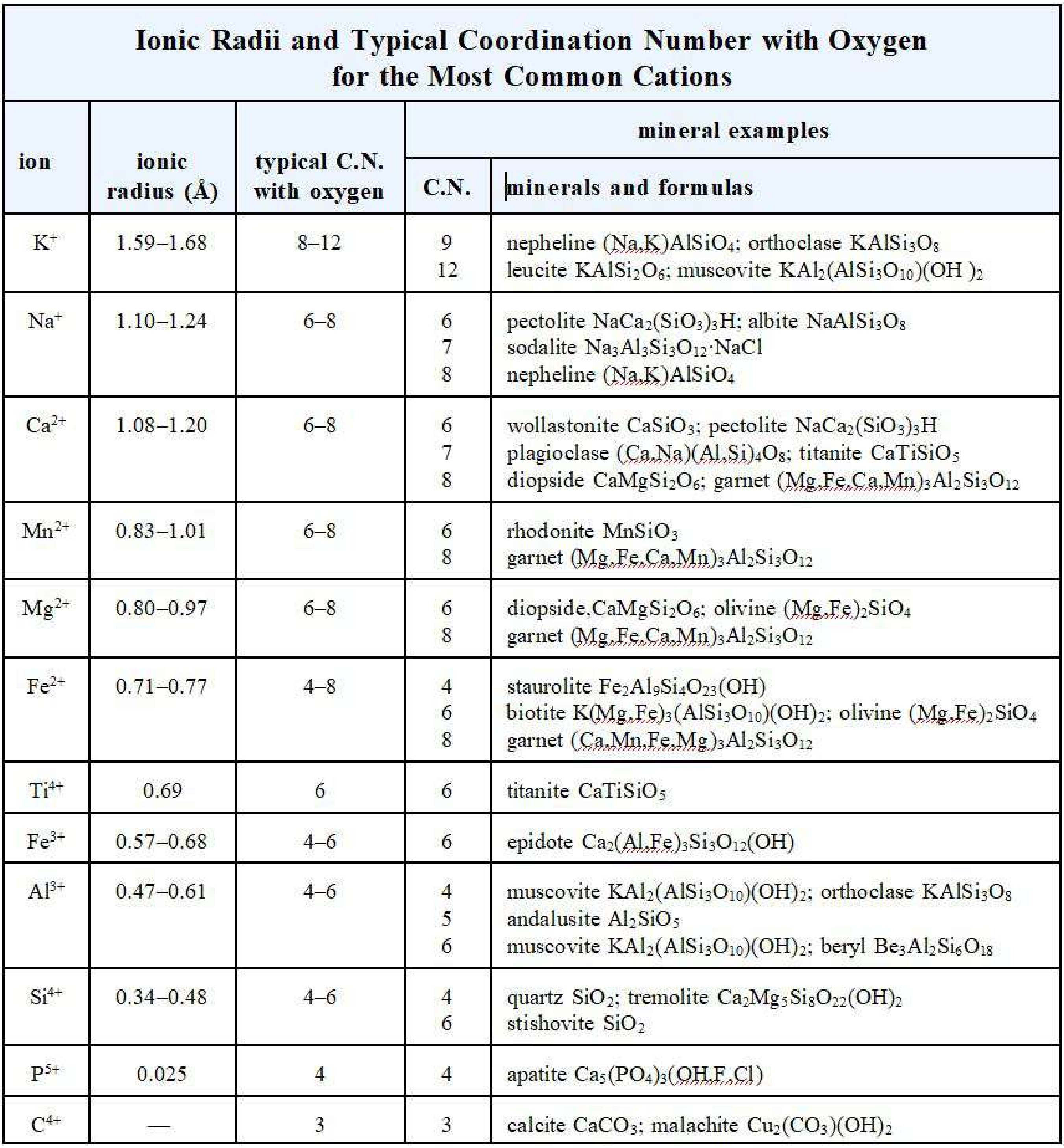
13.4.5 Pauling's Fifth Rule

We call Pauling's last rule the *principle of parsimony*. It states that atomic structures tend to be composed of only a few distinct components. This means that atomic structures are relatively simple and ordered. They normally contain a few types of bonds and only a few types of cation or anion sites. While a mix of ions on a particular site is possible, the mix is limited and controlled. This rule is, in large part, because chemical systems try to minimize energy. The lowest energy arrangements are preferred and much more common than any other possible configurations.

13.5 Oxygen and Other Common Elements

Oxygen is the most abundant element in Earth's crust, accounting for about 60 wt. %. It is not surprising, then, that O^{2-} is the most common anion in minerals. The ionic radius of oxygen varies from about 1.27 Å to 1.34 Å, depending on its coordination number.

The most abundant crustal cations include Si^{4+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ca^{2+}, and K^{+}. The table below lists the typical coordinations for each (with oxygen) and gives example minerals. A range of radius values is given for each cation because cation radius varies slightly with structure and coordination. The C.N.s in this table are, for the most part, consistent with Pauling's first rule.



Ionic Radii and Typical Coordination Number with Oxygen for the Most Common Cations

ion	ionic radius (Å)	typical C.N. with oxygen	mineral examples	
			C.N.	minerals and formulas
K^+	1.59–1.68	8–12	9 12	nepheline $(Na,K)AlSiO_4$; orthoclase $KAlSi_3O_8$ leucite $KAlSi_2O_6$; muscovite $KAl_2(AlSi_3O_{10})(OH)_2$
Na^+	1.10–1.24	6–8	6 7 8	pectolite $NaCa_2(SiO_3)_3H$; albite $NaAlSi_3O_8$ sodalite $Na_3Al_3Si_3O_{12}\cdot NaCl$ nepheline $(Na,K)AlSiO_4$
Ca^{2+}	1.08–1.20	6–8	6 7 8	wollastonite $CaSiO_3$; pectolite $NaCa_2(SiO_3)_3H$ plagioclase $(Ca,Na)(Al,Si)_4O_8$; titanite $CaTiSiO_5$ diopside $CaMgSi_2O_6$; garnet $(Mg,Fe,Ca,Mn)_3Al_2Si_3O_{12}$
Mn^{2+}	0.83–1.01	6–8	6 8	rhodonite $MnSiO_3$ garnet $(Mg,Fe,Ca,Mn)_3Al_2Si_3O_{12}$
Mg^{2+}	0.80–0.97	6–8	6 8	diopside,$CaMgSi_2O_6$; olivine $(Mg,Fe)_2SiO_4$ garnet $(Mg,Fe,Ca,Mn)_3Al_2Si_3O_{12}$
Fe^{2+}	0.71–0.77	4–8	4 6 8	staurolite $Fe_2Al_9Si_4O_{23}(OH)$ biotite $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$; olivine $(Mg,Fe)_2SiO_4$ garnet $(Ca,Mn,Fe,Mg)_3Al_2Si_3O_{12}$
Ti^{4+}	0.69	6	6	titanite $CaTiSiO_5$
Fe^{3+}	0.57–0.68	4–6	6	epidote $Ca_2(Al,Fe)_3Si_3O_{12}(OH)$
Al^{3+}	0.47–0.61	4–6	4 5 6	muscovite $KAl_2(AlSi_3O_{10})(OH)_2$; orthoclase $KAlSi_3O_8$ andalusite Al_2SiO_5 muscovite $KAl_2(AlSi_3O_{10})(OH)_2$; beryl $Be_3Al_2Si_6O_{18}$
Si^{4+}	0.34–0.48	4–6	4 6	quartz SiO_2; tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$ stishovite SiO_2
P^{5+}	0.025	4	4	apatite $Ca_5(PO_4)_3(OH,F,Cl)$
C^{4+}	—	3	3	calcite $CaCO_3$; malachite $Cu_2(CO_3)(OH)_2$

Cation size increases from the bottom of the table to the top, and coordination number increases too. Small cations such as C^{4+} and B^{3+} can have triangular coordination. Si^{4+} is nearly exclusively tetrahedral, while Al^{3+} may be either tetrahedral or octahedral. Although radius ratios predict only 6-fold coordination for Fe^{3+}, in natural crystals Fe^{3+} can be either tetrahedral or octahedral. Other elements can be in octahedral coordination as well. The alkalis and the alkaline earths are the only elements that normally can be in cubic or dodecahedral coordination.

When contradictions between nature and radius ratios occur, it is usually for cations in highly irregularly shaped sites. For example, the aluminum in andalusite is in both 5-fold and 6-fold coordination, some magnesium in anthophyllite is in 7-fold coordination, and the potassium in microcline is in 10-fold coordination. We have not considered 5-fold and 7-fold coordination in this chapter because no regular polyhedra have five or seven vertices – and application of Pauling’s first rule is problematic.

Sometimes we wish to show cation coordination in a mineral formula. Traditionally, this has been done using superscript Roman numerals. For example, we may write andalusite’s formula as $Al^{V}Al^{VI}SiO_5$ to remind us of the unusual aluminum coordination. We may write magnetite’s as $Fe^{IV}Fe^{VI}{}_2O_4$ to show that iron occupies two differently coordinated sites. Many crystallographers and chemists today use Arabic numerals in square brackets instead of Roman numerals to show coordination numbers.

13.6 Silicate Structures in General

In Chapter 6 we discussed silicate mineral structures. Here we take another look at silicate structures in light of Pauling’s rules and other crystal-chemical principles. Because oxygen and silicon are the two most abundant elements in the Earth’s crust, and because the (SiO_4) tetrahedron is such a stable complex, silicate minerals are extremely stable and abundant in crustal rocks and sediments. They dominate igneous and metamorphic rocks, and also many sedimentary rocks. An individual SiO_4 tetrahedron has a charge of -4. Because minerals must be charge balanced, silicon tetrahedra in crystals must share oxygen ions, or must bond to other cations.

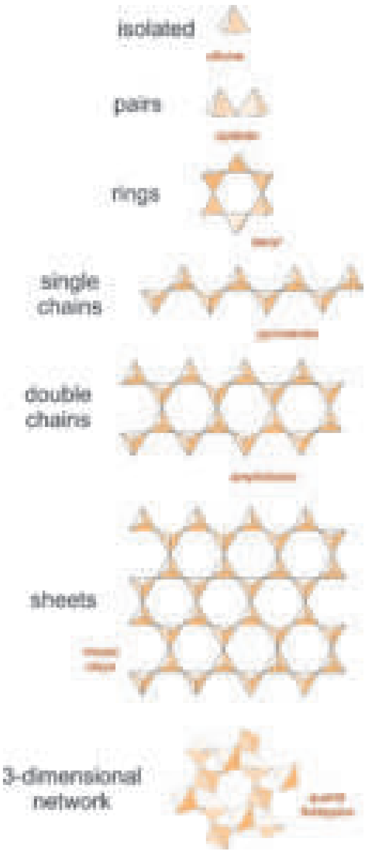
As we have seen previously, sharing of oxygen between tetrahedra is a form of polymerization. Quartz and tridymite (SiO_2), for example, are highly polymerized. In most of the SiO_2 polymorphs, two $(SiO_4)^{4-}$ tetrahedra share each oxygen atom (see Figure 6.25 in Chapter 6). The strength of each Si-O bond is 1; each Si^{4+} bonds to four oxygen, and each O^{2-} to two silicon, so charge balance is maintained and the overall formula is SiO_2.

Polymerization is absent in some silicates, such as olivine, $(Mg,Fe)_2SiO_4$ (see Figure 6.94 in Chapter 6). Instead, cations link individual silicon tetrahedra. In many silicates, a combination of oxygen sharing between tetrahedra, and the presence of additional cations, leads to charge balance. The more oxygen sharing, the fewer additional cations needed.

In still other silicates, Al^{3+} replaces some tetrahedral $Si^{4+.}$ Consequently, more additional cations must be present to maintain charge balance. In albite, for example, Al^{3+} replaces one-fourth of the tetrahedral Si^{4+}. Na^+ ions between tetrahedra maintain charge balance. Albite’s formula is $NaAlSi_3O_8$, which we may write $Na(AlSi_3)O_8$ to emphasize that both Al^{3+} and Si^{4+} occupy the same structural sites. In anorthite, another feldspar, Al^{3+} replaces half the Si^{4+}, resulting in the formula $Ca(Al_2Si_2)O_8$. Besides feldspars, tetrahedral aluminum is common in micas, amphiboles, and, to a lesser extent, in pyroxenes.

The feldspars and other minerals, in which tetrahedra form a 3D network, contain large atomic sites that can hold large cations including Na^+, K^+, and Ca^{2+}. Most crystal structures are more closely packed and large cations will not fit. This explains why rocks rich in alkali and alkali-earth elements always contain feldspar or, less commonly, feldspathoid minerals.

13.6.1 Silicate Classification



13.23 Some ways that silicon tetrahedra may polymerize

The orderly way silica (or alumina) tetrahedra polymerize leads naturally to the division of silicate minerals into the subclasses introduced in Chapter 1 and Chapter 2, and discussed in Chapter 6. Figure 13.23 is the same as Figure 6.24 – it shows the different kinds of polymerization in different subclasses. The table below lists examples of minerals in each subclass.

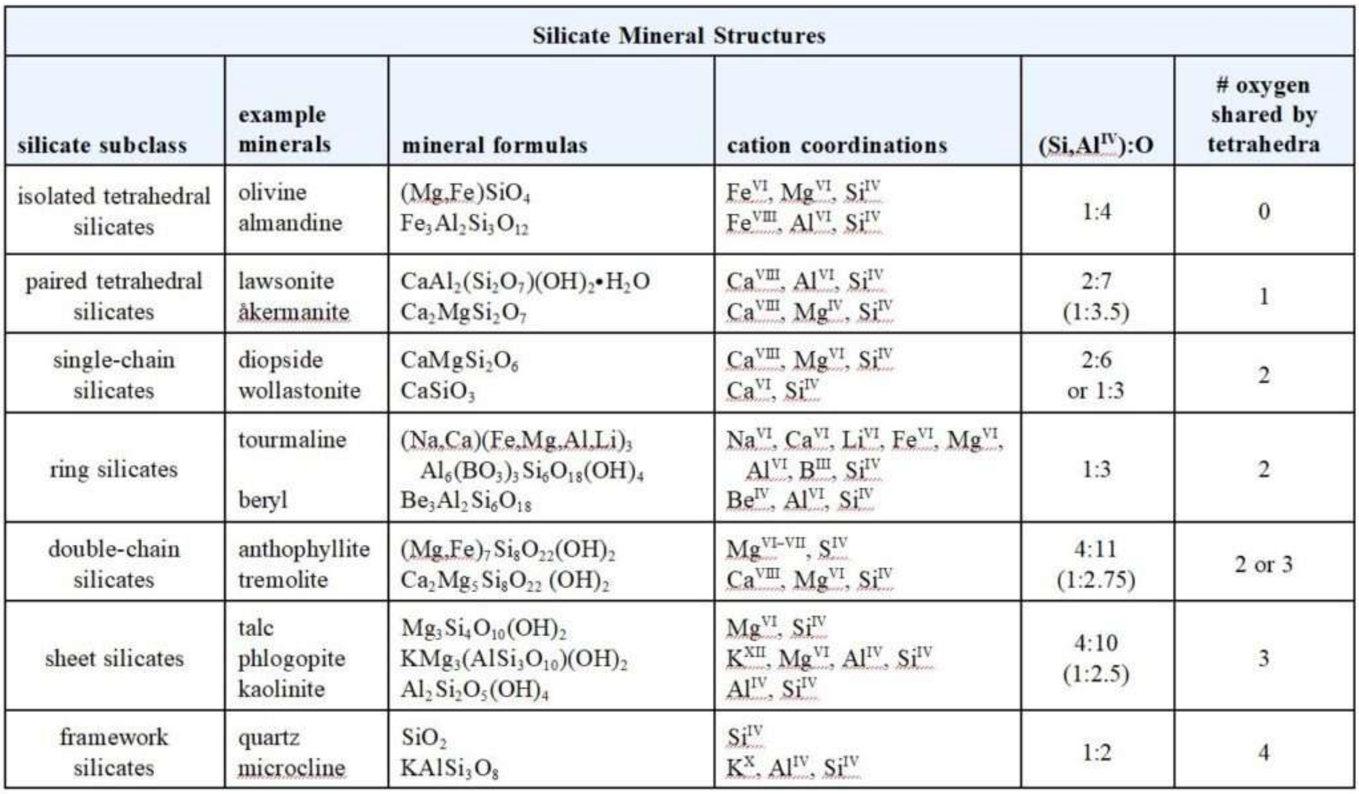
We call silicates such as olivine, in which tetrahedra share no O^{2-}, *island silicates* or *isolated tetrahedral silicates* (also called *nesosilicates* or *orthosilicates*). Silicates in which pairs of tetrahedra share oxygen are *paired tetrahedral silicates* (*sorosilicates*). If two oxygen on each tetrahedron link to other tetrahedra, we get *single-chain silicates* (*inosilicates*) or *ring silicates* (*cyclosilicates*). If some oxygen are shared between two tetrahedra, and some between three, we get *double-chain silicates* (also considered *inosilicates*). If three oxygen on each tetrahedron link to other tetrahedra to form tetrahedral planes, we get *sheet silicates* (also called *layered silicates* or *phyllosilicates*), and if all oxygen are shared between tetrahedra we get *framework silicates* (also called *network silicates* or *tectosilicates*). The ratio of Si:O, then, indicates silicate subclass because different ratios result from different amounts of oxygen sharing.

In minerals containing tetrahedral aluminum, the ratio of (Al^{IV} + Si^{IV}):O, which we can abbreviate T:O, reflects the silicate subclass. But if the only tetrahedral cation is silicon, island silicates are often characterized by SiO_4 in their formulas, paired tetrahedral silicates by Si_2O_7, single-chain silicates by SiO_3 or Si_2O_6, ring silicates by Si_6O_{18}, double-chain silicates by Si_4O_{11}, sheet silicates by Si_2O_5 or Si_4O_{10}, and framework silicates by SiO_2.

13.6.2 Chemical Trends

The chemistries of silicates correlate, in a general way, with the subclass to which they belong (table below). This correlation reflects silicon:oxygen ratios, and it also reflects the way in which silica polymerization controls the number and nature of cation sites between anions. There are many variables, but we can make some generalizations. Isolated tetrahedral silicates and chain silicates include minerals rich in Fe^{2+} and Mg^{2+}, but framework silicates do not. The three-dimensional polymerization of framework silicates generally lacks sufficient anionic charge and the small crystallographic sites necessary for small highly charged cations. Even if Al^{3+} substitutes for Si^{4+}, little charge is left over to allow other cations to be present. So small, highly charged cations are absent from framework silicates.

For opposite reasons, Na^{+} and K^{+} enjoy highly polymerized structures because of the large sites that easily accommodate monovalent cations. The alkalis are absent from island silicates and uncommon in chain silicates.



Silicate Mineral Structures

silicate subclass	example minerals	mineral formulas	cation coordinations	$(Si,Al^{IV}):O$	# oxygen shared by tetrahedra
isolated tetrahedral silicates	olivine almandine	$(Mg,Fe)SiO_4$ $Fe_3Al_2Si_3O_{12}$	Fe^{VI}, Mg^{VI}, Si^{IV} Fe^{VIII}, Al^{VI}, Si^{IV}	1:4	0
paired tetrahedral silicates	lawsonite åkermanite	$CaAl_2(Si_2O_7)(OH)_2{\bullet}H_2O$ $Ca_2MgSi_2O_7$	Ca^{VIII}, Al^{VI}, Si^{IV} Ca^{VIII}, Mg^{IV}, Si^{IV}	2:7 (1:3.5)	1
single-chain silicates	diopside wollastonite	$CaMgSi_2O_6$ $CaSiO_3$	Ca^{VIII}, Mg^{VI}, Si^{IV} Ca^{VI}, Si^{IV}	2:6 or 1:3	2
ring silicates	tourmaline beryl	$(Na,Ca)(Fe,Mg,Al,Li)_3$ $Al_6(BO_3)_3Si_6O_{18}(OH)_4$ $Be_3Al_2Si_6O_{18}$	Na^{VI}, Ca^{VI}, Li^{VI}, Fe^{VI}, Mg^{VI}, Al^{VI}, B^{III}, Si^{IV} Be^{IV}, Al^{VI}, Si^{IV}	1:3	2
double-chain silicates	anthophyllite tremolite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$ $Ca_2Mg_5Si_8O_{22}(OH)_2$	Mg^{VI-VII}, S^{IV} Ca^{VIII}, Mg^{VI}, Si^{IV}	4:11 (1:2.75)	2 or 3
sheet silicates	talc phlogopite kaolinite	$Mg_3Si_4O_{10}(OH)_2$ $KMg_3(AlSi_3O_{10})(OH)_2$ $Al_2Si_2O_5(OH)_4$	Mg^{VI}, Si^{IV} K^{XII}, Mg^{VI}, Al^{IV}, Si^{IV} Al^{IV}, Si^{IV}	4:10 (1:2.5)	3
framework silicates	quartz microcline	SiO_2 $KAlSi_3O_8$	Si^{IV} K^{X}, Al^{IV}, Si^{IV}	1:2	4

13.6.3 Complex Atomic Arrangements

Silicate crystal structures may be complex. Many silicates contain anions or anionic groups other than O^{2-}. Muscovite, for example, contains $(OH)^{-}$ and has the formula $KAl_2(AlSi_3O_{10})(OH)_2$. Other silicates, such as kyanite, and titanite, $CaTi(SiO_4)O$, contain O^{2-} ions unassociated with the $(SiO_4)^{4-}$ tetrahedra. In muscovite and many other minerals, aluminum is in both tetrahedral and octahedral coordination. Still other silicates do not fit neatly into a subclass. Zoisite, $Ca_2Al_3O(SiO_4)(Si_2O_7)(OH)$, contains both isolated tetrahedra and paired tetrahedra. (It also contains oxygen not in tetrahedra.) Some mineralogy texts and reference books separate elements and include extra parentheses in mineral formulas (as has been done in this paragraph) to emphasize the nature of the atomic arrangement, but often we omit such niceties for brevity. In shorter form, we can write muscovite's formula as $KAl_3Si_3O_{10}(OH)_2$; kyanite's becomes Al_2SiO_5; titanite's becomes $CaTiSiO_5$; and zoisite's becomes $Ca_2Al_3Si_3O_{12}(OH)$. While being shorter and, perhaps, easier to write, these formulas give little hint of crystal structure.

13.6.4 Elemental Substitutions in Silicates

While quartz is usually 99.9% SiO2, most minerals have variable chemistries due to elemental substitutions. Consistent with Pauling's rules, the nature and extent of substitutions depend primarily on ionic size and charge and on the nature of atomic bonding in a mineral's structure. Because silicate minerals are dominantly ionic, the nature of bonding is relatively constant; size and ionic charge control most substitutions. Figure 13.7 showed the relative sizes and charges of the most common elements in silicate minerals. Elements of similar size and charge may occupy similar sites in crystal structures without causing distortion or charge imbalance. As an example, Ca^{2+}, Mn^{2+}, Fe^{2+}, and Mg^{2+} substitute for each other in many silicates (and other minerals), including garnets and pyroxenes.

The extent to which elements may substitute for each other is often limited. Natural garnets may have any composition described by the formula $(Ca,Mn,Fe,Mg)_3Al_2Si_3O_{12}$. In contrast, the substitution of Ca^{2+} for Mn^{2+}, Fe^{2+}, or Mg^{2+} in pyroxenes is limited at all but the highest temperatures (due to the large size of Ca^{2+} compared with the other ions). Consequently, a miscibility gap is found between orthopyroxene and clinopyroxene. A similar gap exists in the Ca-Mn-Fe-Mg carbonate system.

Similarity in size and charge allows K^+ and Na^+ to substitute for each other in feldspars, amphiboles, and other minerals. Fe^{3+} and Al^{3+} replace each other in minerals such as garnet and spinel. These are both examples of *simple substitutions*. In a simple substitution the substituting ion has the same charge as the one it replaces. Sometimes simple substitutions are described using equations such as $Fe^{2+} = Mg^{2+}$ or $Fe^{3+} = Al^{3+}$.

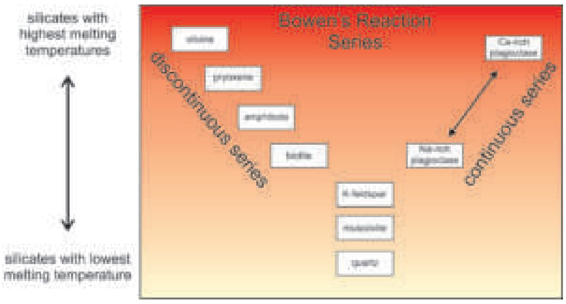
Other elemental substitutions are more complex. For example, Ca^{2+} may replace Na^+ in feldspar. To maintain charge balance, Al^{3+} replaces Si^{4+} at the same time, and we describe the *coupled substitution* as $Ca^{2+}Al^{3+} = Na^+Si^{4+}$ or just CaAl = NaSi. This substitution relates the feldspar end member anorthite ($CaAl_2Si_2O_8$) to albite ($NaAlSi_3O_8$) and occurs in other minerals too. Ions related by coupled substitutions never have charge differences greater than 1.

Anions, too, may substitute for each other in minerals. In micas and amphiboles, for example, F^- or Cl^- may replace $(OH)^-$. More complex substitutions in micas involve the replacement of $(OH)^-$ by O^{2-}, which requires some compensatory substitution to maintain charge balance. In scapolite and a few other minerals, $(CO_3)^{2-}$ or $(SO_4)^{2-}$ may replace Cl^-. To add further complexity, in some minerals, substitutions involve vacancies. For example, in hornblende, □ Si = KAl is a common substitution. The □ symbol shows a vacancy. The table below lists some of the more common and most important elemental substitutions.

Some Typical Elemental Substitutions	
possible substitutions	**example minerals**
$Na^{+} = K^{+}$	alkali feldspar, hornblende, micas
$Ca^{2+} = Mg^{2+} = Fe^{2+} = Mn^{2+}$	pyroxenes, amphiboles, micas, garnet, carbonates
$F^{-} = Cl^{-} = OH^{-}$	amphiboles, micas, apatite
$Fe^{3+} = Al^{3+}$	garnet, spinels
$Ca^{2+}Al^{3+} = Na^{+}Si^{4+}$	plagioclase, hornblende
$Al^{3+}Al^{3+} = (Mg,Fe)^{2+}Si^{4+}$	pyroxenes, amphiboles, micas
$\square Si^{4+} = K^{+}Al^{3+}$	hornblende
$O^{2-} = (OH)^{-}$ plus other substitution to keep charge balance	biotite, titanite

While the elemental substitutions listed above occur in many minerals, including many nonsilicates, they do not necessarily occur in all. Generally, limited substitution is because ions vary in size, and some atomic sites can accommodate larger or smaller ions than other. For example, there is only very minor substitution of Fe^{3+} for Al^{3+} in corundum, but unlimited substitution of Fe^{3+} for Al^{3+} takes place in garnet. Complete solid solution exists between andradite ($Ca_3Fe_2Si_3O_{12}$) and grossular ($Ca_3Al_2Si_3O_{12}$). Similarly, periclase is always close to end member MgO, rarely forming significant solid solution with FeO or with MnO. Nonetheless, the substitutions listed are common, occur in more than one mineral class, and explain most of the mineral end members discussed in earlier chapters in this book. A glance back to Chapters 6 and 7, for example, will show that elemental substitutions, including the nature and extent of solvi, are about the same in pyroxenes, amphiboles, and carbonates. Major substitutions for all are $Ca^{2+} = Mg^{2+} = Fe^{2+} = Mn^{2+}$.

13.6.5 Melting and Weathering Relationships



13.24 Bowen’s Reaction Series

In Chapter 6, we talked about the melting temperatures of minerals. Figure 13.23 is based on Figure 6.17 (Chapter 6). It depicts Bowen’s reaction series and compares melting temperatures of most common igneous minerals. Quartz has the lowest melting temperature, K$^-$feldspar the second lowest, followed by muscovite, biotite, amphiboles, pyroxenes, and finally olivine.

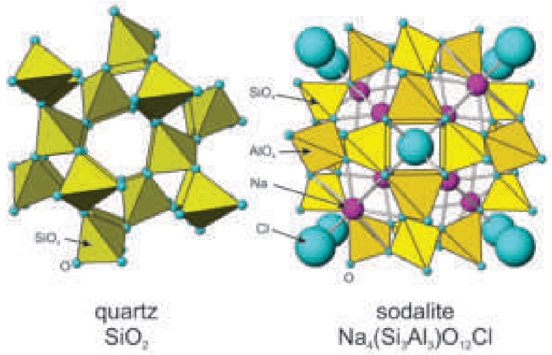
Bowen’s reaction series is based on melting temperatures determined by laboratory experiments, but it mirrors the degree to which silicate minerals are polymerized (which is also a reflection of how much silica they contain). Quartz, feldspars, and other framework silicates are highly polymerized, and they melt at the lowest temperatures. Muscovite, biotite, and other sheet silicates are less polymerized, and melt at higher temperatures. Amphiboles (double chain silicates) and pyroxenes (single chain silicates) are still less polymerized, and melt at even higher temperatures. Olivine and other island silicates are not polymerized at all, and melt at the highest temperatures.

Why does the polymerization affect melting temperatures? The answer lies not so much with the nature of the minerals, but with the nature of the melt they create. Magmas, just like minerals, contain polymers when silicon and oxygen form chains in the melt. Magmas richest in silicon and oxygen are more polymerized, and have lower Gibbs free energy. In a sense, magmas that are highly polymerized form at lower temperatures than those that are less polymerized because fewer bonds need to be broken to create the melt. So, silica-rich magmas, and silica-rich minerals, melt at lower temperatures than those that are silica-poor.

In Chapter 7, we pointed out that the order in which silicate minerals weather is opposite the order in which they melt. Those minerals that melt at lowest temperature are most resistant to weathering. This phenomenon, too, is partly a result of how much silica is in the different silicate minerals. Minerals rich in silica are more tightly bonded (and thus more resistant to weathering) because they contain more $(SiO_4)^{4-}$ anion molecules and because the valence of ionic bonds is generally greater than in minerals poorer in silica. Because of stronger bonds, they are less easily attacked by water and other weathering agents.

13.7 Structures of the Basic Silicate Subclasses

13.7.1 Framework Silicates



quartz
SiO_2

sodalite
$Na_4(Si_3Al_3)O_{12}Cl$

13.25 The atomic

arrangements in two framework silicates

Framework silicates consist of a three-dimensional polymerized network of Si or (Si,Al) tetrahedra. Figure 13.25 shows two examples: quartz and sodalite. Quartz is a hexagonal mineral and sodalite is cubic; these symmetries are apparent in Figure 13.25. Most framework silicates, however, have less symmetry.

Quartz is the most common framework silicate. In quartz and several other SiO_2 polymorphs, oxygen links each silicon tetrahedron to four others. Different SiO_2 polymorphs have different arrangements of tetrahedra; some contain 4-, 6-, or 8-membered loops, and some contain channels. See Box 4-2 and Chapter 6 (Section 6.4.1) for further discussion of the different polymorphs.

The two photos below (Figures 13.26 and 13.27) show a monstrous 260-kg quartz crystal from Brazil, and amethyst from Mexico. Other photos of quartz were in Chapters 1, 3, and 6: Figure 1.8, Figure 3.44, Figure 3.61, Figure 6.26, and Figure 6.27.

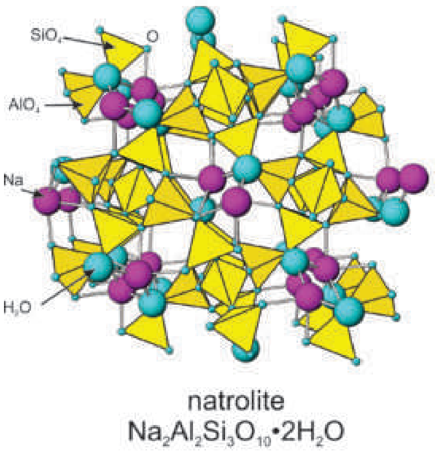
13.26 A 260 kg quartz crystal from Minas Gerais, Brazil

13.27 Amethyst (quartz) from Veracruz, Mexico. The largest crystal is 5.8 cm long.

In sodalite, all the feldspars, and a number of other framework silicates, tetrahedral Al^{3+} replaces some Si^{4+}. This leads to a charge deficiency. However, three-dimensional (SiO_4) polymerization creates holes between tetrahedra. The openings, sometimes irregular, can accommodate alkalis, alkali earths, and other large cations to make up the missing charge. In sodalite, Na^+ occupies the large site. The sodalite structure also contains Cl^- anions between tetrahedra.

In orthoclase and other feldspars, K^+, Na^+, or Ca^{2+} occupy large distorted sites with coordinations of 6 to 9, depending on the feldspar. In other framework silicates, including some feldspathoids (for example, analcime) and zeolites, the openings between silica tetrahedra are large enough to hold molecular water.

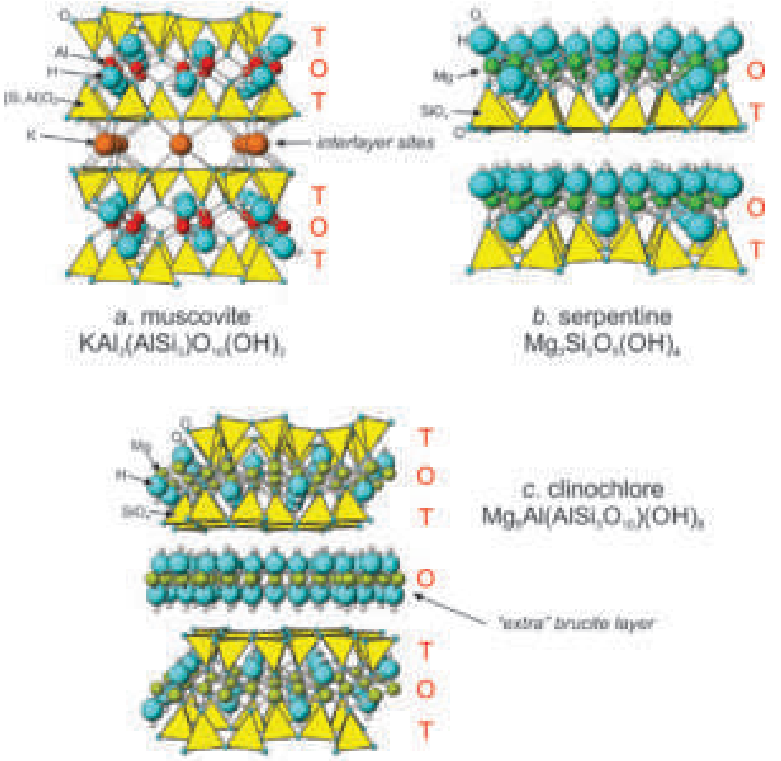
Figure 13.28 shows the atomic arrangement in natrolite, one of the more common zeolites. Blue spheres show H_2O molecules. Because of their many channels and cage-like openings, zeolites are used as molecular sieves and as absorbents in many applications. The photo in Figure 13.29 shows an example of natrolite from central France. Figure 7.56 (Chapter 7) shows a photo of chabazite, another zeolite species.



13.28 The atomic arrangement in natrolite, one of the most common zeolites

13.29 Natrolite crystals on basalt from the Puy de Dôme, central France. The specimen is 5.3 cm tall.

13.7.2 Sheet Silicates



a. muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$

b. serpentine $Mg_3Si_2O_5(OH)_4$

c. clinochlore $Mg_5Al(AlSi_3O_{10})(OH)_8$

13.30 The atomic arrangements in three sheet silicates

Sheet silicates are planar structures containing several different kinds of layers. One consequence is that sheet silicates can accommodate cations of all sizes. Tetrahedral layers (labeled T in Figure 13.30) consist mostly of SiO_4 tetrahedra, sometimes with lesser amounts of AlO_4 tetrahedra. Octahedral layers (O) contain divalent and trivalent cations (*e.g.*, Fe^{2+}, Mg^{2+}, Al^{3+}) in 6-fold coordination.

We call the octahedral layers *gibbsite-like layers* if they contain Al^{3+} and *brucite-like layers* if they contain Mg^{2+} or Fe^{2+} – because the structures of the layers resemble the structures of the minerals gibbsite and brucite. Besides tetrahedral and octahedral layers, micas have interlayer sites containing alkalis or alkali earth cations, most commonly K^+, Na^+, Li^+, or Ca^{2+}.

Figure 13.30*a* shows the atomic arrangement in muscovite, the most common of the sheet silicates. The structure of muscovite, and of all the other micas, consists of sequences of TOT-alkali-TOT-alkali, repeating many times. The thickness of one repeat sequence is about 10 Å.

Some sheet silicates, like muscovite, are *dioctahedral*, meaning they contain two Al^{3+} cations for every four tetrahedra. Other sheet silicates, including biotite, $K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$, contain three divalent cations for every four tetrahedra. They are *trioctahedral*. Thus, the arrangement of atoms in biotite is identical to that in muscovite, except that three Mg^{2+} or Fe^{2+} replace every two Al^{3+} in octahedral sites. In both muscovite and biotite, one of every four tetrahedra contains Al^{3+} instead of Si^{4+}. An interlayer K^+ provides the missing charge. Pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, and talc, $Mg_3Si_4O_{10}(OH)_2$, have structures identical to muscovite and biotite except that the K^+ layer is absent. Consequently, all tetrahedra are SiO4.

Tetrahedral (T) and octahedral (O) layers may stack in various ways. In the micas, pyrophyllite, and talc, tetrahedral layers are above and below octahedral layers, producing TOT *sandwiches*. In serpentine, $Mg_3Si_2O_5(OH)_4$, and kaolinite $Al_2Si_2O_5(OH)_4$, T- and O-layers alternate. The arrangement is a little like *open-face sandwiches* with TO sandwiches piled on top of each other. For example, Figure 13.30*b* shows the atomic arrangement in serpentine, a trioctahedral sheet silicate. Layers of SiO_4 tetrahedra alternate with layers of Mg octahedra in brucite-like layers. Kaolinite (dioctahedral) has a similar structure except that two Al^{3+} (gibbsite-like layers) replace every three Mg^{2+} (brucite-like layers). The layers in serpentine and kaolinite repeat about every 7 Å.

Figure 13.30*c* shows clinochlore, one of the more common chlorite minerals. Figure 6.69 (Chapter 6) showed a photo of clinochlore. Unlike micas, in chlorites, additional brucite layers (octahedral) separate the TOT sandwiches. And in other sheet silicates the stacking may be even more complex. Clay minerals, in particular, have complicated multilayered structures involving interlayers of H_2O. The repeat distance for layers in clinochlore is about 14 Å; in other clay minerals may it be 16 Å or greater.

Individual tetrahedral or octahedral layers in sheet silicates have 3-fold or 6-fold symmetry. So, if the different layers piled up aligned, crystals would be trigonal or hexagonal. However, the layers are sightly offset and 3-fold and 6-fold symmetry does not persist in 3D. Most sheet silicates are monoclinic or triclinic. Micas (and other sheet silicates) have several different polymorphs, related by the way in which TOT and TO sheets stack with respect to each other. The minerals also commonly twin, but the subtle distinctions between polymorphs and the twinning are difficult to detect without detailed X-ray or transmission electron microscope studies.

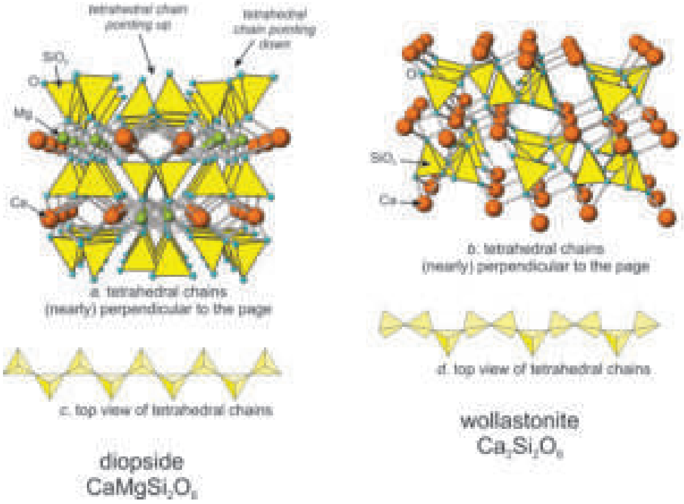
The photos below show muscovite, antigorite (a variety of serpentine), and margarite (a Ca-bearing mica). Photos of several other varieties of micas are in Chapters 6:Figure 6.61, Figure 6.62, Figure 6.63, Figure 6.64, Figure 6.65, and Figure 6.66. Other photos of serpentine can be seen in Figures 8.72, 8.73, and 8.74 (Chapter 8).

13.31 Muscovite from Minas Gerais, Brazil. The specimen is 11 cm tall.

13.32 Antigorite (serpentine) from the Shetland Islands. The specimen is 11 cm wide.

13.33 Silver-pink margarite from Chester, Massachusetts

13.7.3 Single Chain Silicates (Pyroxenes and Pyroxenoids)



13.34 View down the c axis in diopside and wollastonite

Figure 13.34 shows atomic arrangement in diopside, a pyroxene, and wollastonite, a pyroxenoid. In Chapter 6 we saw that pyroxenes and pyroxenoids contain chains of silica tetrahedra (see Figure 6.70). The chains are parallel to the c axes of the minerals In the Figure here (13.34), the view in drawings *a* (diopside) and *b* (wollastonite) is down the chain direction. Drawings *c* (diopside) and *d* (wollastonite) are top views of the chains.

Pyroxenes and pyroxenoids are both single-chain silicates. The main difference between them is subtle but can be seen by comparing Figures 13.34*c* and 13.34*d*. In pyroxenes the tetrahedra zigzag back and forth along the chain direction. In pyroxenoids, the pattern is more irregular. Pyroxenoids vary, but in wollastonite, the tetrahedral pattern repeats after three tetrahedra. As discussed in Chapter 6, pyroxenes may be orthorhombic or monoclinic. Twinning, both simple and complex, is common for both groups of minerals.

Pyroxenoids, which are triclinic, are much less common than pyroxenes. Although similar to pyroxenes, pyroxenoid atomic arrangements contain more large octahedral sites. The most common members of this group include wollastonite ($Ca_2Si_2O_6$), rhodonite ($Mn_2Si_2O_6$), bustamite ($CaMnSi_2O_6$), and pectolite ($NaCa_2Si_3O_8(OH)$). Because pyroxenoids are generally rare and their structures are difficult to depict, we will focus on pyroxenes for the rest of this discussion.

In pyroxenes, tetrahedra making up a chain all point the same direction (either up or down in Figure 13.34*a*). And tetrahedra in adjacent chains point in opposite directions. In the diopside figure, for example, chains of tetrahedra pointing up have chains to their left or right that are pointing down. Similarly, chains pointing down have chains on either side pointing up.

The oxygen anions at the top of chains pointing up (and at the bottom chains pointing down) are called *apical oxygens* because they are at the apices of tetrahedra. These oxygen bond to octahedral cations (Ca^{2+} and Mg^{2+} in diopside) between chains, creating a three-dimensional structure. In single chain silicates, cations are exclusively tetrahedral or octahedral. Consequently, K^+ and other large cations cannot be present.

Pyroxenes and pyroxenoids contain four octahedral sites between apical oxygen. Two of the sites, called the *M2 sites* (shown in orange in Figure 13.34*a*), are larger than the other two (the *M1 sites*). In diopside and other calcic pyroxenes, the large M2 site contains Ca^{2+} and the M1 site contains smaller cations. These other cations are commonly Fe^{2+}, Mg^{2+} or other cations of similar size and charge. The large M2 site in pyroxenes has a strong affinity for $Ca^{2+,}$ and the smaller site does not. Pyroxenes with M2 filled (or mostly filled) with Ca^{2+} are very stable compared with pyroxenes having a mix of different cations on that site. Consequently, a large miscibility gap (discussed in Chapter 6) separates calcic pyroxenes from those that are Ca-poor.

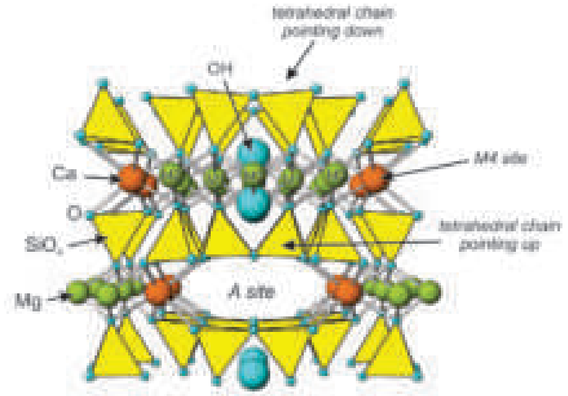
Besides the elements already discussed, pyroxenes may contain significant amounts of Na^{+}, Mn^{2+}, Ti^{4+}, Fe^{3+}, and Al^{3+}. Some pyroxenes contain significant amounts of octahedral Al^{3+} in their M sites. If so, Al^{3+} also substitutes for Si^{4+} in tetrahedral sites so there is not too much cation charge. This is a coupled substitution, described as $Al^{3+}Al^{3+} = (Mg,Fe)^{2+}Si^{4+}$ earlier in this chapter. We call it a *tschermak substitution*, named after 19th century Austrian mineralogist Gustav Tschermak. Other coupled substitutions are common in pyroxenes. For example, spodumene, $LiAlSi_2O_6$, is an important pyroxene in some pegmatites. It is related to diopside by the coupled substitution $Li^{+}Al^{3+} = Ca^{2+}Mg^{2+}$.

Diopside, shown in Figure 13.35 below, has relatively simple chemistry. The only major cations it contains, besides Si^{4+}, are Ca^{2+} and Mg^{2+}. Other pyroxenes may contain many different elements. Perhaps the most common pyroxene species is augite (Figure 13.36), a dark green to black pyroxene that typifies mafic and some other igneous rocks. A simplified formula for augite is $(Na,Ca)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$. The parentheses (from left to right) group elements that occupy the large octahedral site, the smaller octahedral site, and the tetrahedral site. Chapter 6 contains additional photos of pyroxenes: jadeite (Figure 6.73), spodumene (Figure 6.74), enstatite (Figure 6.76), diopside (Figure 6.77), and augite (Figure 6.78).

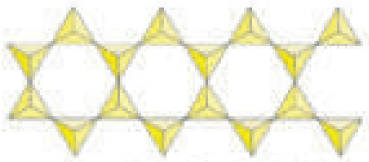
13.35 Diopside crystals on calcite. From Badkhshan, Afghanistan.

13.36 Augite from Millard County, Utah. The specimen is 4.6 cm tall.

13.7.4 Double Chain Silicates (Amphiboles)



a. tetrahedral chains (nearly) perpendicular to the page



b. top view of tetrahedral chains

tremolite
$Ca_2Mg_5Si_8O_{22}(OH)_2$

13.37 View down the c axis in tremolite

Figure 13.37 shows atomic arrangement in tremolite, an amphibole. Drawing *a* is a view down the chain direction (c axis). Drawing *b* shows a top view of the double tetrahedral chain. The tetrahedra generally contain Si^{4+} and sometimes lesser amounts of Al^{3+}.

Like the pyroxenes, chains in amphiboles point up and down. But in contrast with pyroxenes, amphiboles are double-chain silicates with four different-sized octahedral sites (and seven octahedral sites in all) between apical oxygens. In Figure 13.37, we labeled the sites M1 through M4. Because they contain four different octahedral sites, each characterized by slightly different bonding, amphiboles generally have more complicated chemistries than pyroxenes. Nonetheless, the two mineral structures share many characteristics.

In amphiboles, the two M4 sites (orange) are larger than the other octahedral sites and may hold Ca^{2+} or Na^{+}. Any of the octahedral sites may contain Mg^{2+}, Fe^{2+}, Al^{3+}, sometimes Ti^{4+}, and other cations of similar size and charge. Like the pyroxenes, amphiboles may be orthorhombic or monoclinic. Twinning, both simple and complex, is common in amphiboles.

Tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$ has relatively simple chemistry, similar to that of diopside. But, we can see a large hole just below the center of the tremolite model in Figure 13.37*a*. This site, called the *A site*, is vacant in tremolite and other calcic amphiboles. It has 10-12 fold coordination. In hornblende, the most common amphibole, this large interlayer site usually contains K^+ (somewhat like the K^+ between layers in micas) and sometimes Na^+. So, unlike pyroxenes, amphiboles can accommodate large cations.

Hornblende chemistry is highly variable; we might write a simplified formula as $(K,Na)_{0-1}(Ca,Na,Mg)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$. The parentheses (from left to right in this formula) group elements that occupy the A site, the large octahedral site (M4), the smaller octahedral sites (M1 through M3), and the tetrahedral site. The subscript 0-1 tells us that the A site may not be fully occupied by K^+ and Na^+.

The photos below show two examples of amphiboles. Additional photos of amphiboles are in Chapter 6: anthophyllite (Figure 6.83), actinolite (Figure 6.84), and hornblende (Figure 6.86).

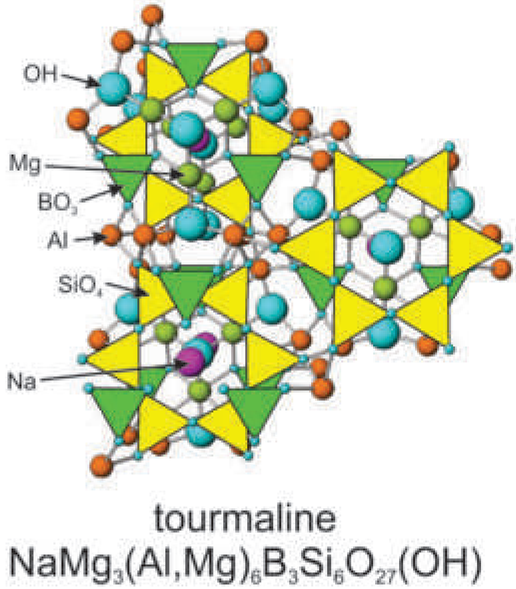
13.38 Tremolite from Campolungo, Switzerland. The sample is 14 cm across.

13.39 Hornblende from near Parry Sound, Ontario, Canada. The specimen is 6 cm tall.

13.7.5 Ring Silicates

Tourmaline is the only common mineral in which all tetrahedra link to form independent 6-member rings (Figure 13.40). Other minerals, including beryl, $Be_3Al_2Si_6O_{18}$ and cordierite, $(Mg,Fe)_2Al_4Si_5O_{18}$, contain rings but they also contain tetrahedra joined in other ways. In tourmaline, 6-membered rings bond to octahedral Fe^{2+}, Mg^{2+}, or Al^{3+}, and to triangular $(BO_3)^-$ groups.

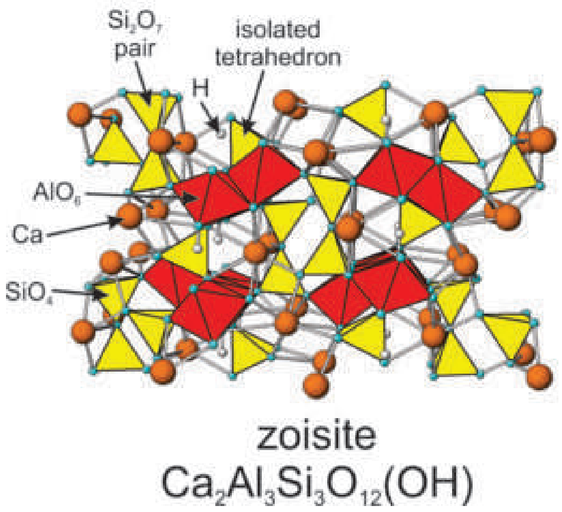
Ca^{2+}, Na^+, and K^+ occupy large sites centered in the rings and coordinated to the borate groups and silica tetrahedra. Thus, tourmaline contains several different kinds of sites and may incorporate just about any element in its structure. And tourmaline comes in many different colors because of its highly variable chemistry. The photo below (Figure 13.41) shows a black variety called *schorl*. Figure 6.90 (Chapter 6) shows a different example of schorl. Tourmaline is one of the few minerals that commonly exhibits color zonation. See Figure 4.13 (Chapter 4) and 6.22 (Chapter 6) for examples. So, tourmaline is a popular and valuable gemstone.



13.40 The atomic arrangement in tourmaline

13.41 Tourmaline crystals from Minas Gerais, Brazil. The specimen is 8 cm tall.

13.7.6 Paired Tetrahedral Silicates



13.42 The atomic arrangement in zoisite

Lawsonite, a rare mineral found in blueschists, and the melilite minerals åkermanite and gehlenite (also rare) are perhaps the best examples of paired tetrahedral silicates. The paired tetrahedra result in Si_2O_7 groups. Other minerals, commonly grouped with lawsonite and the melilites, contain some paired and some unpaired tetrahedra. Zoisite, vesuvianite, and epidote, for example, contain both SiO_4 and

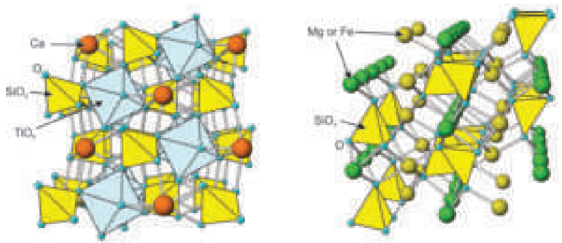
Si_2O_7 groups. Figure 13.42 shows the atomic arrangement in zoisite. Both paired SiO_4 tetrahedra and isolated SiO_4 tetrahedra are present. The structure also contains AlO_6 octahedra (red); some of the Al-octahedra share edges. Ca^{2+} (orange) occupies large octahedral sites between silicon tetrahedra and aluminum octahedra.

Figure 13.43 shows lawsonite from the blueschist terrane of northern California. Lawsonite is similar in many ways to a high-pressure form of anorthite. The photo in Figure 13.44 is gehlenite from near Bolzano, Italy. Figure 13.45 is a gemmy blue variety of zoisite called *tanzanite*. The raw stone in the top of photo is an imperfect orthorhombic prism; a cut and polished tanzanite gemstone is in the bottom of the photo.

Additional photos of paired tetrahedral silicates are in Chapter 6 and Ch 8: epidote (Figure 6.91), tanzanite (Figure 6.92), lawsonite (Figure 6.93), and a spectacular photo of green zoisite with red corundum and black hornblende (Figure 8.1).

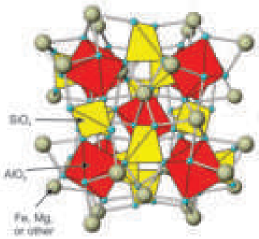
 13.43 Crystals of lawsonite from Mendocino County, California	 13.44 Cubes of gehlenite from Monte Monzoni, Italy	 13.45 Zoisite from the Merelani Hills, Tanzania. The polished gemstone is about 0.5 cm wide.

13.7.7 Isolated Tetrahedral Silicates



a. titanite
$CaTiSiO_5$

b. olivine
$(Mg,Fe)_2SiO_4$



c. garnet
$(Fe,Mg,Ca,Mn)_3Al_2Si_3O_{12}$

13.46 The atomic arrangements in some isolated tetrahedral silicates

Mineralogists often call isolated tetrahedral silicates *island silicates* because tetrahedra do not share oxygen. Island silicates contain tetrahedral and octahedral sites, and no sites large enough to hold alkalis and other large cations. Figure 13.46 shows atomic arrangements in some examples: titanite, olivine, and garnet.

Titanite (Figure 13.46*a*). contains octahedral Ca^{2+} alternating with $(SiO_4)^{4-}$ tetrahedra and $(TiO_6)^{8-}$ octahedra. In olivine, divalent octahedral cations (usually Fe^{2+} or Mg^{2+}), occupying two slightly different-sized sites, link independent silicon $(SiO_4)^{4-}$ tetrahedra (Figure 13.46*b*). In monticellite, $CaMgSiO_4$ (a member of the olivine group), the larger octahedral site contains Ca^{2+}. The garnet structure (Figure 13.46*c*) contains $(SiO_4)^{4-}$ tetrahedra sharing oxygen with distorted octahedral and cubic sites. The octahedral site normally contains Al^{3+}, but sometimes by Fe^{3+} or Cr^{3+}. Ca^{2+}, Mg^{2+}, Fe^{2+}, and sometimes Mn^{2+} occupy the cubic site.

The island silicate group contains many important minerals besides titanite, olivine, and garnet. These include zircon ($ZrSiO_4$), andalusite (Al_2SiO_5), kyanite (Al_2SiO_5), sillimanite (Al_2SiO_5), topaz ($Al_2SiO_4(F,OH)_2$), and staurolite ($Fe_2Al_9(SiO_4)_4(O,OH)_2$). Photos below show some examples.

13.47 Green titanite crystals on K-feldspar from near Meknes, Morocco

13.48 Brown zircon crystal from Pakistan. The specimen is 6 cm wide.

13.49 Topaz from northern Pakistan. The crystal is about 3 cm long.

13.50 Twinned staurolite from the Kola Penninsula, Russia

13.51 Brown monticellite with blue calcite from Crestmore, California

13.52 Andalusite crystals with classic dark *chiastolite* crosses caused by graphite inclusions

Other photos of island silicates can be found in Chapters 3, 4, 6, 8, and 10: olivine (Figures 6.1 and 6.20), garnet (Figures 3.6, 8.10, 8.21, 8.23, 8.30, 8.44, and 10.48), kyanite (Figures 8.46, and 8.51), and staurolite (Figures 4.40, and 8.45).

13.8 Structures and Chemistry of Nonsilicates

Having discussed silicate structures, we could go on and discuss structures in other mineral groups. However, unless we wanted to go into great detail, such a discussion would not be particularly fruitful for several reasons. First, because silicate structures are largely ionic, they are simpler and more regular than those of most other mineral groups. And in our discussion of silicate structures, we ignored or glossed over some complications that become very important in other kinds of minerals. Second, for some mineral groups we cannot make meaningful generalizations or categorize structures in a useful way. For example, the sulfide minerals involve structures that are covalent or metallic, or both. Sulfur may have any of several valences, and sulfide structures involve many different coordination polyhedra, layers, clusters, and other complex structural units. Thus, generalizations made about structure types will inevitably be too detailed or not detailed enough for different purposes. So, instead of worrying about the details of structure and chemistry of all mineral groups, we note that the same principles that apply to silicates also apply to other minerals.

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Video 13-2: Polyhedra in olivine, Keith Putirka, YouTube