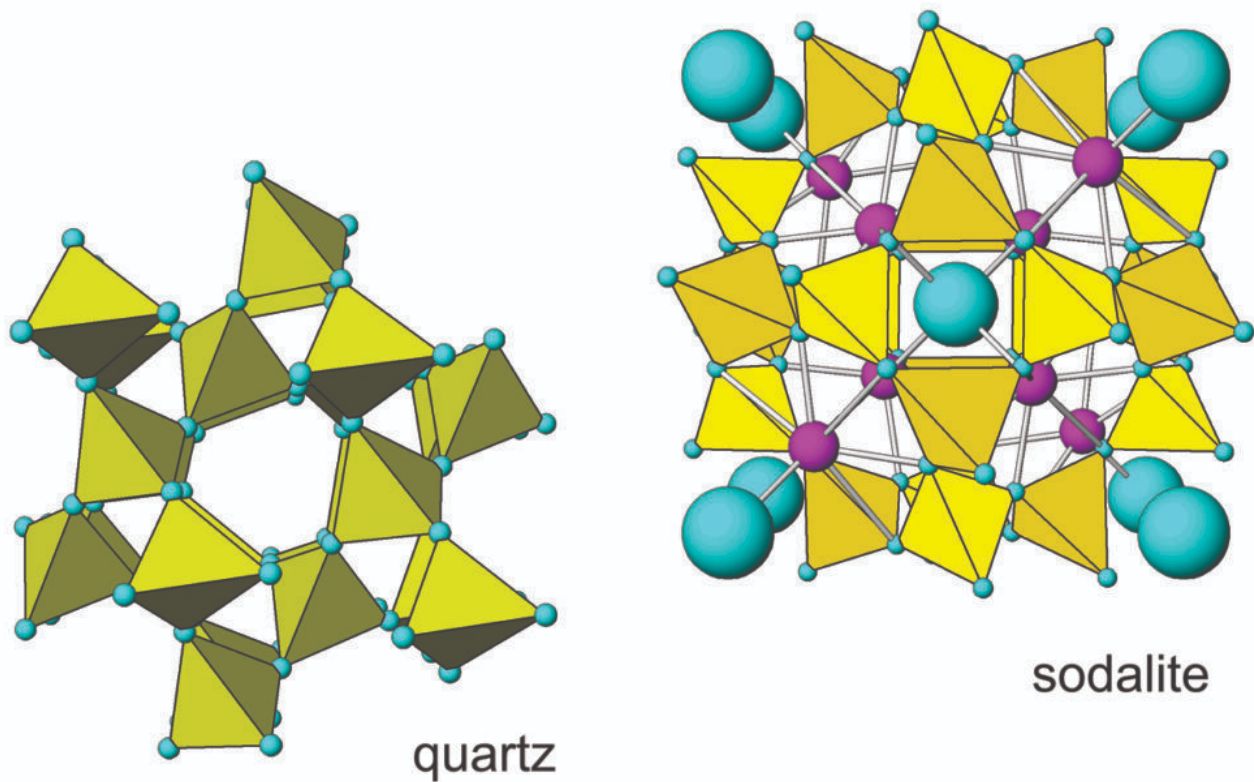


# 13 Crystal Structures



13.1 The atomic arrangements in quartz and sodalite

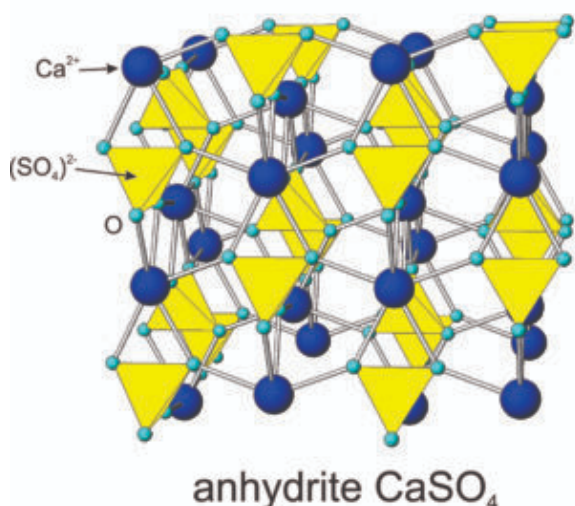
## 13 Atomic Structures

### 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 discovery 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 ( $\text{CaSO}_4$ ). This arrangement was first described by J.A. Wasastjerna in 1925, based on X-ray studies. Blue spheres are  $\text{Ca}^{+2}$  ions and yellow

tetrahedra are sulfate ( $\text{SO}_4$ )<sup>2-</sup> 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.

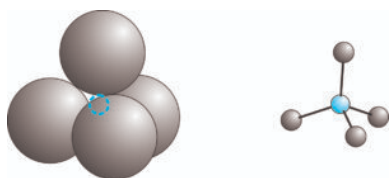
Pauling's chemical studies covered many fields, including both organic and inorganic chemistry. One of the first to interpret crystal structures using quantum mechanics, he was also a pioneer of X-ray diffraction. His studies of chemical bonding resulted in the publication of his book *The Nature of 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

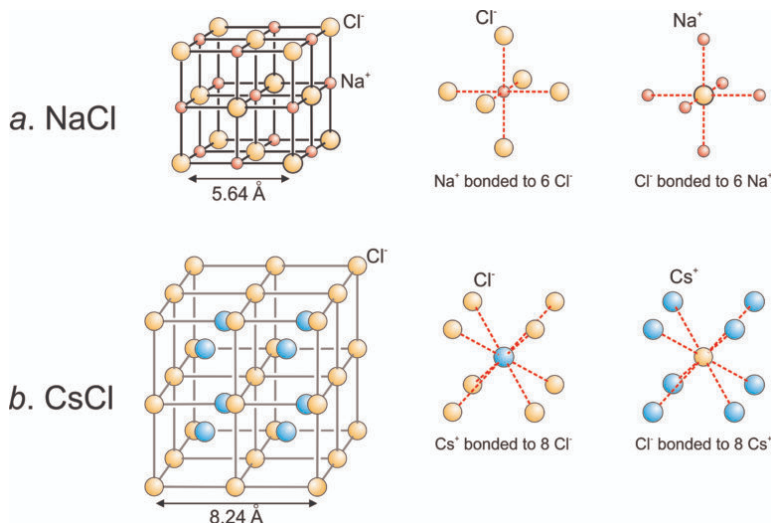
*Ionic crystals* are those composed of cations and anions held together primarily by ionic bonds. They have overall electrical neutrality, or else electrical current would flow until they obtained charge balance; so the total number of electrons in the structure is equal to the total number of protons. 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.

Consider the mineral halite, NaCl, which contains an equal number of Na and Cl atoms (Figure 13.5a). Mineralogists have determined its atomic arrangement through X-ray studies, finding that  $\text{Na}^+$  and  $\text{Cl}^-$  ions pack around each other in an alternating three-dimensional structure. As shown in the enlarged views, each  $\text{Na}^+$  bonds to six  $\text{Cl}^-$  and vice versa. Bonds around one ion are all equal length and at  $90^\circ$  to each other. Unit cells are therefore cubic, containing four  $\text{Na}^+$  and four  $\text{Cl}^-$  ions in a face-centered arrangement. Halite salt crystals, including the ones that come out of your salt shaker, are often perfect cubes.

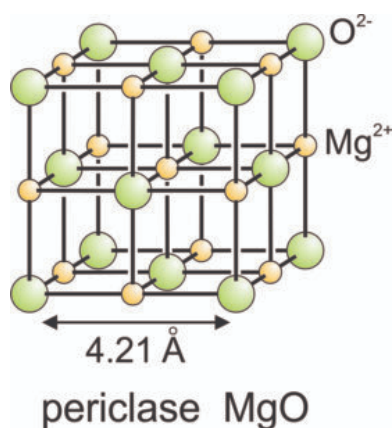
Besides halite (NaCl), other alkalis combine with chlorine to produce alkali chlorides. Figure 13.5b, for example, shows the atomic arrangement in CsCl. The arrangement, like halite's, is cubic. But in contrast with the halite structure, eight anions surround the alkali cation ( $\text{Cs}^+$ ). The difference is because  $\text{Cs}^+$  is larger than  $\text{Na}^+$ . It requires more room in the crystal structure.

Because there are equal numbers of  $\text{Cs}^+$  and  $\text{Cl}^-$  in CsCl, if eight anions surround every  $\text{Cs}^+$ , eight cations must surround every  $\text{Cl}^-$ , as shown in the enlarged views.



13.5 The atomic arrangements in NaCl and CsCl

The ionic bonds between alkalis and  $\text{Cl}^-$  are not terribly strong. They break easily when salts dissolve in water, releasing free alkalis and  $\text{Cl}^-$  ions. High solubility in water is characteristic of highly ionic crystals, especially those in which the ions only have charges of  $\pm 1$ . If concentrations of dissolved  $\text{Na}^+$  and  $\text{Cl}^-$  reach high enough levels, perhaps due to evaporation, halite may precipitate from solution.



13.6 The atomic arrangement in periclase

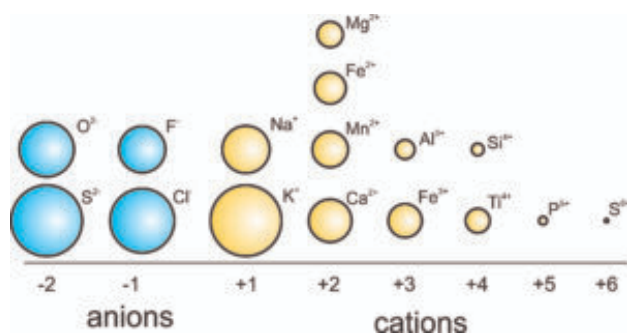
Other minerals have different atoms but have atomic structures and bonding similar to halite's; sylvite (KCl) and periclase (MgO) are both examples. In periclase (shown in Figure 13.6), however, the ions are divalent, having a charge of  $\pm 2$  (in contrast with the ions in halite and sylvite which 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 ( $\text{CO}_3^{2-}$ ), sulfate ( $\text{SO}_4^{2-}$ ), or phosphate ( $\text{PO}_4^{3-}$ ) are present instead of simple anions. These molecules alternate with cations just as  $\text{O}^{2-}$  and  $\text{Mg}^{2+}$  alternate in periclase. The molecular ions may not dissociate, even if a mineral dissolves in water, because covalent bonds hold them together. Calcite,  $\text{CaCO}_3$ , is a good example. In the calcite structure, carbonate groups and  $\text{Ca}^{2+}$  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  $\text{Ca}^{2+}$  and  $(\text{CO}_3)^{2-}$ , and sometimes  $(\text{HCO}_3)^{-}$ .

### 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 compares 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 ( $\text{MgO}$ ) shown in Figure 13.6. Through X-ray diffraction studies we have learned that the distance between the centers of the  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions is about 2.11 Å, so the sum of the effective ionic radii of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  is 2.11 Å. A standard value for the radius of  $\text{O}^{2-}$  is 1.32 Å, so this yields a radius of 0.79 Å for  $\text{Mg}^{2+}$  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  $\text{Mg}^{2+}$ , 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  $\text{R}_2\text{O}$ , 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  $\text{O}^{2-}$  is common to all alkali oxides, variations in bond length must be due to variations in the radii of the alkalis. If we assume  $\text{O}^{2-}$  has a

constant radius of  $1.32 \text{ \AA}$ , 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	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
at. no.	3	11	19	37	55
radius $\text{\AA}$	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	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$	$\text{Si}^{4+}$	$\text{P}^{5+}$	$\text{S}^{6+}$	$\text{S}^{2-}$	$\text{Cl}^-$	$\text{Ar}^0$
at. no.	11	12	13	14	15	16	16	17	18
radius $\text{\AA}$	1.18	0.79	0.55	0.41	0.25	0.20	1.72	1.70	—

The table above also includes two anions ( $\text{S}^{2-}$  and  $\text{Cl}^-$ ) 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 <sup>0</sup>	Mn <sup>2+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>	Mn <sup>6+</sup>	Mn <sup>7+</sup>
radius Å	1.12	0.97	0.70	0.62	0.35	0.34

Radii of Vanadium Atoms and Cations					
cation	Va <sup>0</sup>	Va <sup>2+</sup>	Va <sup>3+</sup>	Va <sup>4+</sup>	Va <sup>5+</sup>
radius Å	1.31	0.87	0.72	0.67	0.53

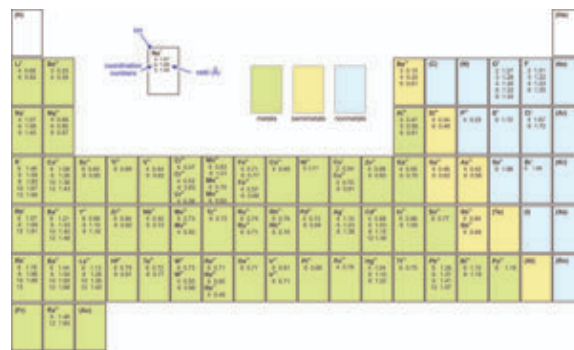
Box 13–2 contains a table with effective ionic radii for the most common ions. The table includes more than one value for most ions because radius varies depending on how an ion is bonded. For example, the radius of Na<sup>+</sup> is listed as 1.07, 1.08, and 1.40 Å; these difference reflect different numbers of bonds going to the cation. And the radii of Na<sup>+</sup> 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<sup>2+</sup> 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<sup>2-</sup> to calculate radii for cations bonded to oxygen. Depending on the kind of bonding and several other things, O<sup>2-</sup> 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

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.



13.8 Effective ionic radii for ions in different coordinations

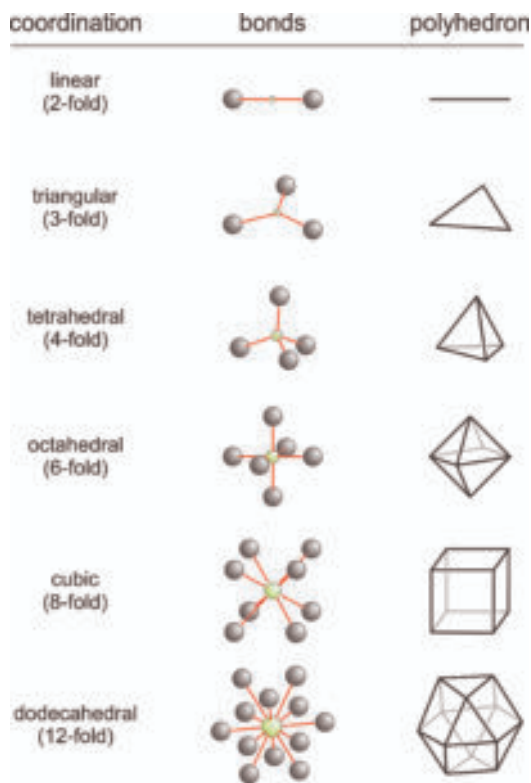
Most of the elements listed in Figure 13.8 have several different values of ionic radius listed. The first number in every entry is the coordination number. The second number (for cations) is the effective ionic radius in coordination with  $O^{2-}$  having a radius of 1.32 Å. Values for elements in 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

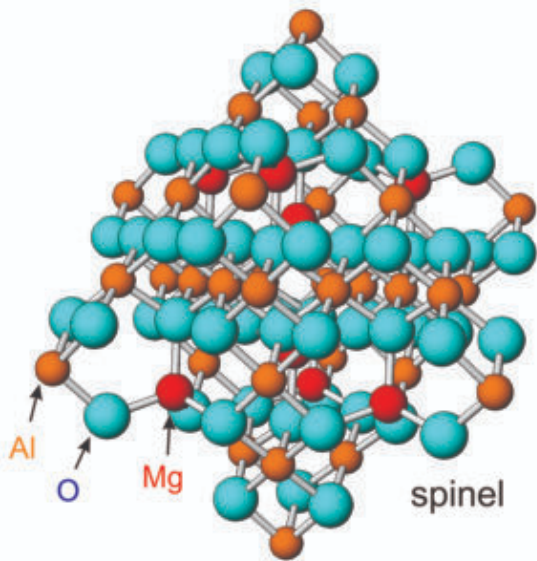
Figure 13.4 showed one way a group of identical anions may pack around a single cation. The cation was in 4-fold coordination, but there are other possibilities, shown here in Figure 13.9. In this figure, because only one cation and one kind of anion are involved, all bond distances (in red) are the 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,  $\text{MgAl}_2\text{O}_4$ . 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.

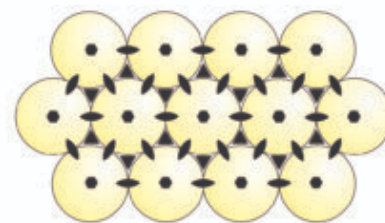
An ionic model, although incorrect in detail, works for many sulfides too, even though bonding in them has little ionic character. No matter the kind of bonding, (wholly or partially) positively charged ions alternate with (wholly or partially) negatively charged ions. Because ionic bonds are easier to analyze, and because they explain most mineral properties, we will stick with them for the rest of this chapter.

## 13.3 Closest Packing

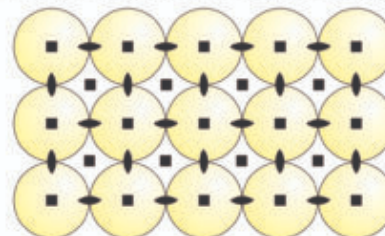
### 13.3.1 Closest Packing in Two Dimensions

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 13.11a 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 13.11b 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).

a. hexagonal (closest) packing



b. tetragonal (not closest) packing

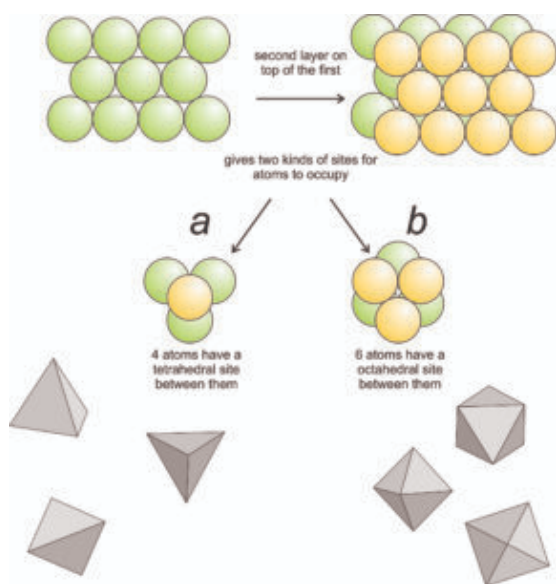


13.11 Packing of ions in 2D

We call the arrangement of marbles in Figure 13.11a *hexagonal packing*. We call the pattern in Figure 13.11b *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 13.12a). 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 13.12b. 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 13.12a shows four marbles, or four cations, forming a tetrahedron. If an anion is between them, it will be in tetrahedral coordination. Figure 13.12b 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.

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

*13.13 Hexagonal closest packing and cubic closest packing*

(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)?

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.

*13.14 Three ways atoms can pack together*



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 13.14a 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 openings in the bottom and top layers.

The drawing of cubic closest packing (Figure 13.14b) 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 13.14c) 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,  $\text{CaF}_2$ , 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.

Figure 13.15a 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 13.15b 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.

13.15 Calculating radius ratios for different coordinations

Figure 13.15c 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.

<b><math>R_c/R_a</math> and Coordination of Cations</b>		
<b><math>R_c/R_a</math></b>	<b>expected coordination</b>	<b>coordination number</b>
<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

As an example of application of Pauling's first rule, let's take another look at halite. The radii of  $\text{Na}^+$  and  $\text{Cl}^-$  in octahedral coordination are 1.08 Å and 1.72 Å. The radius ratio,  $R_c/R_a$ , is  $1.08/1.72 = 0.63$ . Thus we can expect the cation  $\text{Na}^+$  to be in octahedral (6-fold) coordination, consistent with the model shown here in Figure 13.16 (and in Figure 13.5a). If  $\text{Na}^+$  is in 6-fold coordination,  $\text{Cl}^-$  must be as well, since the structure contains an equal number of both.

13.16 Halite with  $\text{Na}^+$  and  $\text{Cl}^-$  in 6-fold (octahedral) coordination

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:

blank  Video 13-2: <https://www.youtube.com/watch?v=hUmTKOhI5EA> (8 minutes)

### 13.4.2 Pauling's Second Rule

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 ( $\text{KCl}$ ), six  $\text{Cl}^-$  bond to each  $\text{K}^+$  and the strength of each bond is  $1/6$ , total charge divided by number of bonds

13.17 Atoms in sylvite

(Figure 13.17). The strength of each bond around  $\text{Cl}^-$  is  $1/6$  as well. Six bonds of charge  $1/6$  add up to 1, the charge on each ion.

We can use Pauling's first two rules to analyze a more complicated mineral, rutile ( $\text{TiO}_2$ ). In rutile, Ti-O bonds are the only bonds present (Figure 13.18). The radii of  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  are 0.69 Å and 1.32 Å.  $R_c/R_a$  is 0.52 and, as predicted by Rule 1,  $\text{Ti}^{4+}$  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  $\text{O}^{2-}$  has a

13.18 The atomic arrangement in rutile

total charge of  $-2$ , it must be bonded to three  $\text{Ti}^{4+}$  to satisfy Rule 2, so  $\text{O}^{2-}$  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,  $\text{MgAl}_2\text{O}_4$ , in Figure 13.10. Spinel contains Mg-O and Al-O bonds. X-ray studies reveal that  $\text{Mg}^{2+}$  is in tetrahedral coordination and  $\text{Al}^{3+}$  is in octahedral coordination. Consequently, as

shown in Figure 13.19, the strength of the bonds around  $\text{Mg}^{2+}$  is  $2/4 = 1/2$ , and the strength of the bonds around  $\text{Al}^{3+}$  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  $\text{S}^{6+}$  in anhydrite

Figure 13.2 showed the atomic arrangement in anhydrite,  $\text{CaSO}_4$ . Anhydrite and other sulfates are examples of *anisodesmic* compounds. In sulfates,  $\text{S}^{6+}$  is in 4-fold coordination with  $\text{O}^{2-}$ . The strength of a sulfur-oxygen (S-O) bond (shown in red in Figure 13.20) is therefore  $6/4 = 1\frac{1}{2}$  (Figure 13.20). Because the strength of each S-O bond is greater than half the charge on coordinating oxygen, oxygen bonds to  $\text{S}^{6+}$  more tightly than to  $\text{Ca}^{2+}$ . Consequently,  $(\text{SO}_4)^{2-}$  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  $(\text{SO}_4)^{2-}$ ,  $(\text{CO}_3)^{2-}$ , and  $(\text{NO}_3)^-$  as single anionic units within crystals.

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,  $\text{Si}^{4+}$  is in tetrahedral coordination and each Si-O

*13.21 Mesodesmic bonds joining silicon and oxygen ions*

bond (shown red in Figure 13.21) has a strength of 1, exactly half the charge of  $\text{O}^{2-}$ . Consequently, oxygen may coordinate to another cation just as strongly as to its coordinating  $\text{Si}^{4+}$ . In many silicates, some of the “other” cations are another  $\text{Si}^{4+}$ . For example in Figure 13.21, pairs of  $\text{Si}^{4+}$  share an oxygen producing chains of  $\text{Si}^{4+}$  alternating with  $\text{O}^{2-}$ . Mesodesmic bonding 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

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 13.22a, tetrahedra do not share any common oxygen. They are isolated tetrahedra linked by bonds to a cation between them. In 13.22b, a pair of tetrahedra share one oxygen (called a *bridging oxygen*). Bonding of these two sorts commonly holds crystal structures together.

In Figure 13.22c, adjacent tetrahedra share an edge (two oxygen). In Figure 13.22d, they share a face (three oxygen). We can see that as the structure progresses from Figure 13.22a to 13.22d,  $\text{Si}^{4+}$  in the centers of the tetrahedra get closer together. Yet, because the  $\text{Si}^{4+}$  are all positively charged, we expect

*13.22 Silicon tetrahedra and sharing of anions*

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  $\text{Si}^{4+}$  tetrahedra. Yet in all the many known silicate minerals, none contains  $(\text{SiO}_4)^{4-}$  polyhedra that share edges or faces because that would bring  $\text{Si}^{4+}$  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.

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, consequently, 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  $\text{Al}^{\text{V}}\text{Al}^{\text{VI}}\text{SiO}_5$  to remind us of the unusual aluminum coordination. We may write magnetite's as  $\text{Fe}^{\text{IV}}\text{Fe}^{\text{VI}}_2\text{O}_4$  to show that iron occupies two differently coordinated sites. Today, however, many crystallographers and chemists 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  $(\text{SiO}_4)$  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  $\text{SiO}_4$  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 ( $\text{SiO}_2$ ), for example, are highly polymerized. In most of the  $\text{SiO}_2$  polymorphs, two  $(\text{SiO}_4)^{4-}$  tetrahedra share every oxygen atom (see [Figure 6.25](#) in Chapter 6). The strength of each Si-O bond is 1; each  $\text{Si}^{4+}$  bonds to four oxygen, and each  $\text{O}^{2-}$  to two silicon, so charge balance is maintained and the overall formula is  $\text{SiO}_2$ .

Polymerization is absent in some silicates, such as olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$  (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,  $\text{Al}^{3+}$  replaces some tetrahedral  $\text{Si}^{4+}$ . Consequently, more additional cations must be present to maintain charge balance. In albite, for example,  $\text{Al}^{3+}$  replaces one-fourth of the tetrahedral  $\text{Si}^{4+}$ .  $\text{Na}^+$  ions between tetrahedra maintain charge balance. Albite's formula is  $\text{NaAlSi}_3\text{O}_8$ , which we may write  $\text{Na}(\text{AlSi}_3)\text{O}_8$  to emphasize that both  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  occupy the same structural sites. In anorthite, another feldspar,  $\text{Al}^{3+}$  replaces half the  $\text{Si}^{4+}$ , resulting in the formula  $\text{Ca}(\text{Al}_2\text{Si}_2)\text{O}_8$ . 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  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ . 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

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. A table below lists examples of minerals in each subclass.

We call silicates such as olivine, in which tetrahedra share no  $\text{O}^{2-}$ , *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



13.23 Some ways that silicon tetrahedra may polymerize

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  $(\text{Al}^{\text{IV}} + \text{Si}^{\text{IV}}):\text{O}$ , which we can abbreviate T:O, reflects the silicate subclass. But if the only tetrahedral cation is silicon, island silicates are often characterized by  $\text{SiO}_4$  in their formulas, paired tetrahedral silicates by  $\text{Si}_2\text{O}_7$ , single-chain silicates by  $\text{SiO}_3$  or  $\text{Si}_2\text{O}_6$ , ring silicates by  $\text{Si}_6\text{O}_{18}$ , double-chain silicates by  $\text{Si}_4\text{O}_{11}$ , sheet silicates by  $\text{Si}_2\text{O}_5$  or  $\text{Si}_4\text{O}_{10}$ , and framework silicates by  $\text{SiO}_2$ .

## 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  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$ , 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  $\text{Al}^{3+}$  substitutes for  $\text{Si}^{4+}$ , 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,  $\text{Na}^+$  and  $\text{K}^+$  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.

### 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% SiO<sub>2</sub>, 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<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, and Mg<sup>2+</sup> 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)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>. In contrast, the substitution of Ca<sup>2+</sup> for Mn<sup>2+</sup>, Fe<sup>2+</sup>, or Mg<sup>2+</sup> in pyroxenes is limited at all but the highest temperatures (due to the large size of Ca<sup>2+</sup> 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<sup>+</sup> and Na<sup>+</sup> to substitute for each other in feldspars, amphiboles, and other minerals. Fe<sup>3+</sup> and Al<sup>3+</sup> 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<sup>2+</sup> = Mg<sup>2+</sup> or Fe<sup>3+</sup> = Al<sup>3+</sup>.

Other elemental substitutions are more complex. For example, Ca<sup>2+</sup> may replace Na<sup>+</sup> in feldspar. To maintain charge balance, Al<sup>3+</sup> replaces Si<sup>4+</sup> at the same time, and we describe the *coupled substitution* as Ca<sup>2+</sup>Al<sup>3+</sup> = Na<sup>+</sup>Si<sup>4+</sup> or just CaAl = NaSi. This substitution relates the feldspar end member anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) to albite (NaAlSi<sub>3</sub>O<sub>8</sub>) 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<sup>–</sup> or Cl<sup>–</sup> may replace (OH)<sup>–</sup>. More complex substitutions in micas involve the replacement of (OH)<sup>–</sup> by O<sup>2–</sup>, which requires some compensatory substitution to maintain charge balance. In scapolite and a few other minerals, (CO<sub>3</sub>)<sup>2–</sup> or (SO<sub>4</sub>)<sup>2–</sup> may replace Cl<sup>–</sup>. To add further complexity, in some minerals, substitutions involve vacancies.

For example, in hornblende,  $\square \text{Si} = \text{KAl}$  is a common substitution. The  $\square$  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
$\text{Na}^+ = \text{K}^+$	alkali feldspar, hornblende, micas
$\text{Ca}^{2+} = \text{Mg}^{2+} = \text{Fe}^{2+} = \text{Mn}^{2+}$	pyroxenes, amphiboles, micas, garnet, carbonates
$\text{F}^- = \text{Cl}^- = \text{OH}^-$	amphiboles, micas, apatite
$\text{Fe}^{3+} = \text{Al}^{3+}$	garnet, spinels
$\text{Ca}^{2+}\text{Al}^{3+} = \text{Na}^+\text{Si}^{4+}$	plagioclase, hornblende
$\text{Al}^{3+}\text{Al}^{3+} = (\text{Mg,Fe})^{2+}\text{Si}^{4+}$	pyroxenes, amphiboles, micas
$\square\text{Si}^{4+} = \text{K}^+\text{Al}^{3+}$	hornblende
$\text{O}^{2-} = (\text{OH})^-$ 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  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  in corundum, but unlimited substitution of  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  takes place in garnet. Complete solid solution exists between andradite ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ) and grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ). Similarly, periclase is always close to end member  $\text{MgO}$ , rarely forming significant solid solution with  $\text{FeO}$  or with  $\text{MnO}$ . 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  $\text{Ca}^{2+} = \text{Mg}^{2+} = \text{Fe}^{2+} = \text{Mn}^{2+}$ .

## 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 13.24 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<sup>+</sup> 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  $(\text{SiO}_4)^{4-}$  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

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.

*13.25 The atomic arrangements in two framework silicates*

Quartz is the most common framework silicate.

In quartz and several other  $\text{SiO}_2$  polymorphs, oxygen links each silicon tetrahedron to four others. Different  $\text{SiO}_2$  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  $\text{Al}^{3+}$  replaces some  $\text{Si}^{4+}$ . This leads to a charge deficiency. However, three-dimensional ( $\text{SiO}_4$ ) 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,  $\text{Na}^+$  occupies the large site. The sodalite structure also contains  $\text{Cl}^-$  anions between tetrahedra.

In orthoclase and other feldspars,  $\text{K}^+$ ,  $\text{Na}^+$ , or  $\text{Ca}^{2+}$  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  $\text{H}_2\text{O}$  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

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  $\text{SiO}_4$  tetrahedra, sometimes with lesser amounts of  $\text{AlO}_4$  tetrahedra. Octahedral layers (O) contain divalent and trivalent cations (*e.g.*,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) in 6-fold coordination.

We call the octahedral layers *gibbsite layers* if they contain  $\text{Al}^{3+}$  and *brucite layers* if they contain  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  – because the structures of the layers resemble the structures of the

13.30 The atomic arrangements in three sheet silicates

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 13.30a 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 (Si,Al) 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  $Al^{3+}$  cations in the 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  $SiO_4$ .

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 13.30b shows the atomic arrangement in serpentine, a trioctahedral sheet silicate. Layers of  $SiO_4$  tetrahedra alternate with layers of Mg octahedra in brucite layers. Kaolinite (dioctahedral) has a similar structure except that two  $Al^{3+}$  (gibbsite layers) replace every three  $Mg^{2+}$  (brucite layers). The layers in serpentine and kaolinite repeat about every 7 Å.

Figure 13.30c shows the atomic arrangement of 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 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 slightly 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)

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 13.34c and 13.34d. 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

13.34 View down the *c* axis in diopside and wollastonite

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 ( $\text{Ca}_2\text{Si}_2\text{O}_6$ ), rhodonite ( $\text{Mn}_2\text{Si}_2\text{O}_6$ ), bustamite ( $\text{CaMnSi}_2\text{O}_6$ ), and pectolite ( $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ ). 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 13.34a). 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 ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in diopside) between chains, creating a three-dimensional structure. In single chain silicates, cations are exclusively tetrahedral or octahedral. Consequently,  $\text{K}^+$  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 13.34a), are larger than the other two (the green *M1 sites*). In diopside and other calcic pyroxenes, the large M2 site contains

$\text{Ca}^{2+}$  and the M1 site contains smaller cations. These other cations are commonly  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$  or other cations of similar size and charge. The large M2 site in pyroxenes has a strong affinity for  $\text{Ca}^{2+}$ , and the smaller site does not. Pyroxenes with M2 filled (or mostly filled) with  $\text{Ca}^{2+}$  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  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ . Some pyroxenes contain significant amounts of octahedral  $\text{Al}^{3+}$  in their M sites. If so,  $\text{Al}^{3+}$  also substitutes for  $\text{Si}^{4+}$  in tetrahedral sites so there is not too much cation charge. This is a coupled substitution, described as  $\text{Al}^{3+}\text{Al}^{3+} = (\text{Mg,Fe})^{2+}\text{Si}^{4+}$  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,  $\text{LiAlSi}_2\text{O}_6$ , is an important pyroxene in some pegmatites. It is related to diopside by the coupled substitution  $\text{Li}^+\text{Al}^{3+} = \text{Ca}^{2+}\text{Mg}^{2+}$ .

Diopside, shown in Figure 13.35 below, has relatively simple chemistry. The only major cations it contains, besides  $\text{Si}^{4+}$ , are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . 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  $(\text{Na,Ca})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6$ . 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 Badakhshan, Afghanistan.*

*13.36 Augite from Millard County, Utah. The specimen is 4.6 cm tall.*

### 13.7.4 Double Chain Silicates (Amphiboles)

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  $\text{Si}^{4+}$  and sometimes lesser amounts of  $\text{Al}^{3+}$ .

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.

*13.37 View down the *c* axis in tremolite*

In amphiboles, the two M4 sites (orange) are larger than the other octahedral sites and may hold  $\text{Ca}^{2+}$  or  $\text{Na}^+$ . Any of the octahedral sites may contain  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ , sometimes  $\text{Ti}^{4+}$ , 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,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  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 13.37a. 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 some  $\text{K}^+$  (somewhat like the  $\text{K}^+$  between layers in micas) and sometimes  $\text{Na}^+$ . So, unlike pyroxenes, amphiboles can accommodate large cations.

Hornblende chemistry is highly variable; we might write a simplified formula as  $(\text{K},\text{Na})_{0-1}(\text{Ca},\text{Na},\text{Mg})_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Si},\text{Al})_8\text{O}_{22}(\text{OH})_2$ . 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  $\text{K}^+$  and  $\text{Na}^+$ .

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,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$  and cordierite,  $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$ , contain rings but they also contain tetrahedra joined in other ways. In tourmaline, 6-membered rings bond to octahedral  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Al}^{3+}$ , and to triangular  $(\text{BO}_3)^-$  groups.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  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

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  $\text{Si}_2\text{O}_7$  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  $\text{SiO}_4$  and  $\text{Si}_2\text{O}_7$  groups. Figure 13.42 shows the atomic arrangement in zoisite. Both paired  $\text{SiO}_4$  tetrahedra and isolated  $\text{SiO}_4$  tetrahedra are present. The structure also contains  $\text{AlO}_6$  octahedra (red); some of the Al-octahedra share edges.  $\text{Ca}^{2+}$  (orange) occupies large octahedral sites between silicon tetrahedra and aluminum octahedra.

#### 13.42 The atomic arrangement in zoisite

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

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.

13.46 The atomic arrangements in some isolated tetrahedral silicates

Titanite (Figure 13.46a) contains octahedral  $\text{Ca}^{2+}$  alternating with  $(\text{SiO}_4)^{4-}$  tetrahedra and  $(\text{TiO}_6)^{8-}$  octahedra. In olivine, divalent octahedral cations (usually  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$ ), occupying two slightly different-sized sites,

link independent silicon  $(\text{SiO}_4)^{4-}$  tetrahedra (Figure 13.46b). In monticellite,  $\text{CaMgSiO}_4$  (a member of the olivine group), the larger octahedral site contains  $\text{Ca}^{2+}$ . The garnet structure (Figure 13.46c) contains  $(\text{SiO}_4)^{4-}$  tetrahedra sharing oxygen with distorted octahedral and cubic sites. The octahedral site normally contains  $\text{Al}^{3+}$ , but sometimes by  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$ .  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , and sometimes  $\text{Mn}^{2+}$  occupy the cubic site.

The island silicate group contains many important minerals besides titanite, olivine, and garnet. These include zircon ( $\text{ZrSiO}_4$ ), andalusite ( $\text{Al}_2\text{SiO}_5$ ), kyanite ( $\text{Al}_2\text{SiO}_5$ ), sillimanite ( $\text{Al}_2\text{SiO}_5$ ), topaz ( $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ ), and staurolite ( $\text{Fe}_2\text{Al}_9(\text{SiO}_4)_4(\text{O},\text{OH})_2$ ). 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 Peninsula, 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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13.51 Monticellite with calcite, dakotamatrix.com

13.52 Andalusite crystals, irocks.com

Video 13-1: Ionic radii, Keith Putirka, YouTube

Video 13-2: Polyhedra in olivine, Keith Putirka, YouTube



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