 CHAPTER 5

CRYSTAL CHEMISTRY

Equilibrium reactions of carbonate and silicate minerals with aqueous solutions have been the center of attention in the last two chapters. We turn now to a closer examination of minerals themselves. Minerals, by definition, are naturally-occurring homogeneous solids, for the most part inorganically formed, with definite chemical compositions and specific arrangements of atoms. More than 3800 mineral species have been identified, but we limit discussion here to the crystal chemistry of the small number that are major constituents of rocks in the Earth’s crust. Only about a dozen kinds of minerals make up the greater part of common rocks, and these dozen are composed of only a small number of elements—only 8 (O, Si, Al, Fe, Mg, Ca, Na, K) out of the more than 100 elements that are known. These eight (Fig. 5-1) account for more than 99% of the mass of the Earth’s crust. The two mineral species quartz and feldspar make up almost two-thirds of the crustal volume. If pyroxenes, olivine, and hydrated silicates are added to these two, over 90% of the volume is included in the sum. The study of crystal chemistry is greatly simplified by the small number of elements and the small number of minerals that we need be concerned with in discussing most geological processes and geologic environments.

The mineral structures of most interest in geology are those of crystalline solids composed of ions. A few materials found in nature, for example diamond and sulfur, are constructed of un-ionized atoms. A few others, like asphalt, are best regarded as made up of molecules; in these the structure of the molecule itself may be complex and may largely determine the properties of the substance. But the rocks
and soils with which a geologist commonly deals are composed almost wholly of ionic solids, and it is the structure of these that will be the subject of our inquiry here.

5-1 STRUCTURE OF NaCl

A familiar crystalline solid, ordinary table salt, has an especially simple structure that will serve as a good starting point. Salt occurs in nature as the mineral halite, which has the composition of NaCl and is a major constituent of evaporite deposits.
The arrangement of ions in the structure of halite has a cubic pattern, as shown in Fig. 5-2. Note that Na⁺ ions alternate with Cl⁻, that every Na⁺ is surrounded by six Cl⁻ ions at the corners of an octahedron and every Cl⁻ by six Na⁺ ions. Figure 5-2(a) shows only the arrangement, not the sizes; actually the ions should be regarded as touching their nearest neighbors, so that the entire volume of the crystal is occupied except for spaces between the spheres, as illustrated in Fig. 5-2(b).

Now what are these objects called ions, which we write as Na⁺ and Cl⁻ and which we represent in diagrams as tiny spheres? In the familiar model, a simple ion like Na⁺ or Cl⁻ consists of a compact positive nucleus made up of protons and neutrons, surrounded by negative electrons. Both nucleus and electrons are tiny compared with their distance apart. The positive charge of Na⁺ means that its nucleus contains one positive charge (one proton) in excess of the number of surrounding electrons, and the negative charge of Cl⁻ means that it contains one electron in excess. All this is simple enough, but difficulties arise if we try to make the picture more definite by specifying the arrangement and movement of the electrons. For some purposes the electrons can be thought of as minute particles revolving around the nucleus in orbits, like planets around the sun, but this model is too simple to describe all aspects of electronic behavior. Actually the positions and motions of the electrons cannot be specified precisely; according to quantum theory,
we can only indicate the probability of finding electrons at particular places within an ion or atom. The region of probability for a given electron is described as its orbital, rather than an orbit. This gives us a rather fuzzy and elusive sort of unit out of which to build our crystalline structures.

Fortunately the deeper questions about the nature of the electron are not essential for considering the elementary relations of ions in crystals. The important thing here is to remember that an ion consists essentially of widely spaced electric charges, so that its boundaries are actually boundaries of electric fields. We cannot expect, then, that ions will behave entirely like rigid spheres, nor can we expect to assign precise values to their radii or volumes.

The size of an ion, despite the fact that it cannot be defined or measured with great exactness, is a useful concept in discussing crystal structures. Some idea of the magnitude of ionic sizes can be gained by a simple calculation. The molecular weight of sodium chloride tells us that 58.5 g of NaCl must contain $6.02 \times 10^{23}$ (Avogadro's number) molecules of NaCl, or $6.02 \times 10^{23}$ Na$^+$ ions and the same number of Cl$^-$ ions. The density of NaCl is 2.16 g/cm$^3$, so that these ions occupy a volume of 58.5/2.16, or about 27 cm$^3$. If we assume that the two ions have roughly the same size, the volume of a single ion would be

$$\frac{27}{2 \times 6.02 \times 10^{23}} = 22 \times 10^{-24} \text{ cm}^3.$$

The diameter of an ion would then be approximately the cube root of this figure or 2.8 $\times$ 10$^{-8}$ cm, and the radius 1.4 $\times$ 10$^{-8}$ cm (generally written 1.4 Å, = 1.4 angstroms). Actually the radii are not equal, Cl$^-$ having a radius of about 1.8 Å and Na$^+$ about 1.0 Å.

Better values of ionic sizes can be obtained by measurements of spacings of planes in crystal structures by means of x-rays, coupled with measurements of molar refractivities and with calculations from quantum mechanics. Methods of finding ionic sizes differ in detail, so that currently several sets of radii are available. Some of the differences are real, in that ionic radii for some purposes are defined differently, and therefore measured differently, than for other purposes. Some of the differences can be ascribed to experimental uncertainties and to differences in radii selected as standards. The discrepancies are mostly in the second decimal place and are not of great concern here.

The most widely used set of radii is given in Appendix VI, and values for some of the common ions are shown pictorially in Fig. 5-3. Most of the values shown are the so-called octahedral radii, calculated on the assumption that the ion has octahedral coordination—in other words, that its closest neighbors in crystal structures are six other ions at the corners of an octahedron, like the six Cl$^-$ ions around each Na$^+$ in the NaCl structure. For other types of coordination (for example, tetrahedral, as in quartz) the radii would be slightly different; thus the octahedral radius of aluminum is 0.54 Å and the tetrahedral radius about 0.41 Å. Octahedral coordination is the commonest type for the cations of geologic interest and is a good average between the extremes found in crystals, hence the octahedral radii are the most generally useful.
An arrangement like the NaCl structure of Fig. 5-2 represents, for these particular ions, the most stable possible pattern, i.e., the arrangement in which the forces between adjacent Na⁺ and Cl⁻ particles are a maximum, or for which the potential energy is a minimum. If we focus attention on the forces, we may speak of an ionic bond between Na⁺ and Cl⁻, and since NaCl is particularly stable, we would describe this bond as stronger than that, say, in a crystal of AgCl. Or if we think in terms of energy, we could say that the crystal energy—the amount of energy needed to tear apart a mol of NaCl into widely separated individual ions—of NaCl is larger than the crystal energy of AgCl.

The arrangement of ions in a crystal would be expected to have a close relation to some of the ordinary large-scale properties of the crystal, particularly its symmetry, cleavage, and effect on polarized light. The cubic pattern of ions in sodium chloride, for example, is reflected in the cubic habit of halite crystals, in the three mutually perpendicular planes of cleavage, and in the ability of light to traverse the crystal with the same speed in any direction. Historically these megascopic properties were studied in great detail long before anything was definitely known about the particles and the geometric patterns of crystal structures. It is one of the great triumphs of twentieth-century science that the inner structures elucidated by x-rays have been found to correlate with and to explain so elegantly the intricate relationships among geometric and optical properties discovered by nineteenth-century crystallographers.
5-2 OTHER IONIC SOLIDS

The pattern of ions in sodium chloride is very simple, and the correlation with elementary crystal properties is transparently obvious. Can we find similar patterns and similar correlations in other crystalline solids? To what extent can the properties of solids be related to geometric arrangements of ions treated simply as small, hard spheres?

We look first at compounds chemically similar to NaCl, consisting merely of an alkali metal joined to a halogen. These show a gratifying similarity, both in megascopic properties and in patterns of ions, except for a few salts of lithium, cesium, and fluorine. These three elements have ions of extreme sizes, small for lithium and fluorine and large for cesium; we might guess, therefore, that an explanation for the exceptions is somehow connected with different ionic volumes. The simplest assumption is that any given combination of ions will form a structure in which the ions are packed as close together as possible, since this would make the forces between them a maximum. The packing arrangement to secure this closest approach would necessarily depend on the relative sizes of the anions and the cations. On this assumption our problem becomes the purely geometric one of how to arrange spheres of different sizes so as to give the densest possible packing.

From solid geometry the following rules can be worked out for three-dimensional structures, which are illustrated in Fig. 5-4:

1. If the radius ratio (radius of cation divided by radius of anion) is unity, the pattern of closest packing has each ion surrounded by twelve ions of opposite charge that are located at the midpoint of the edges of a cube. This is the structure of cesium oxide (see Table 5-1).

2. If the radius ratio lies between 0.73 and 1, closest packing is secured when each ion has eight ions of opposite sign as closest neighbors that are located at the corners of a cube. This is often described as the cesium chloride structure, consistent with the radius ratio Cs⁺/Cl⁻ = 0.92.

3. If the radius ratio is between 0.41 and 0.73, the pattern of closest packing has each ion surrounded by six ions of opposite sign located at the corners of an octahedron. This is the sodium chloride structure (radius ratio for Na⁺/Cl⁻ = 0.56).

4. If the radius ratio is in the range 0.22 to 0.41, each cation can surround itself with only four anions located at the corners of a tetrahedron. This kind of structure is found in sphalerite, ZnS, with a ratio Zn²⁺/S²⁻ = 0.41, and is often called the sphalerite structure.

For a great many simple compounds these rules hold remarkably well, and crystal structures can be in large measure predicted from geometry.

A further word is needed about nomenclature. In sodium chloride structures, with a pattern of six ions around each ion of opposite sign, the cation is said to have a coordination number of 6, or to be 6-coordinated. The anion could equally well be regarded as having a coordination number of 6, but conventionally the term is more
<table>
<thead>
<tr>
<th>Radius ratio</th>
<th>Coordination number</th>
<th>Atomic structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>0.73–1</td>
<td>8</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>0.41–0.73</td>
<td>6</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>0.22–0.41</td>
<td>4</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>0.15–0.22</td>
<td>3</td>
<td><img src="image" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**FIGURE 5-4**
Relation between radius ratio, coordination number, and the geometric arrangement of anions (open spheres) about a central cation (solid spheres).

commonly applied to the cation. The six ions surrounding a central ion are arranged at the corners of an octahedron (see Fig. 5-4), so that the sodium chloride structure is often spoken of as octahedral. Similarly the cesium chloride structure may be referred to as cubic, and the cesium ion may be assigned a coordination number of 8. The sphalerite structure is tetrahedral, and the zinc ion in sphalerite is 4-coordinated. In mineral structures the commonest anion by far is $\text{O}^{2-}$, with an ionic radius of 1.40 Å; most of the common cations have radii in the range 0.60 to 1.10 Å, giving radius ratios with oxygen of 0.43 to 0.79; hence the most frequent coordination number in minerals is 6. This is why ionic radii are generally tabulated as octahedral radii rather than tetrahedral or cubic.
TABLE 5-1
Comparison of observed coordination numbers with numbers predicted from geometric radius ratios

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius ratio:</th>
<th>Coordination predicted from ratio</th>
<th>Observed coordination numbers</th>
<th>Theoretical limiting radius ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ionic radius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>radius of O$^{2-}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$^+$</td>
<td>1.19</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>1.08</td>
<td>12</td>
<td>8-12</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.98</td>
<td>8</td>
<td>8-12</td>
<td>1.00</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.84</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>0.73</td>
<td>8</td>
<td>6,8</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.71</td>
<td>6</td>
<td>6,8</td>
<td>0.73</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.56</td>
<td>6</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.51</td>
<td>6</td>
<td>6</td>
<td>0.41</td>
</tr>
<tr>
<td>AI$^{3+}$</td>
<td>0.38</td>
<td>4</td>
<td>4,6</td>
<td>0.22</td>
</tr>
<tr>
<td>S$^{2+}$</td>
<td>0.18</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

1 Data from Appendix VI. Radius of O$^{2-}$ assumed = 1.40 Å.

The same sort of geometric argument can be used to make predictions about the crystal structures of more complex compounds, and for many of these the predictions fit observed facts just as admirably as they do for simple ones.

Is crystallography, then, no more than an extension of solid geometry? The answer, of course, is "No." A great deal more than geometry is involved, but we have so far looked only at specially selected examples for which geometric reasoning works fairly well. In view of the complex electronic structure of ions, it is cause for wonder that the simple geometric model of ions as hard round spheres is actually so successful for a large number of substances.

The failure of geometric reasoning as a complete explanation is illustrated by Table 5-1, which shows a comparison between predicted and observed coordination numbers for several cations in compounds with oxygen. For cations whose radius ratios fall within the theoretical limits, like Sr$^{2+}$ and Mg$^{2+}$, the agreement of observed and predicted values is excellent. But cations like Ca$^{2+}$, Na$^{+}$, and Al$^{3+}$, whose ratios are close to the limiting figures, show variable coordination which the simple theory could not predict. A similar table for compounds containing sulfur would bring to light more serious discrepancies. Geometric reasoning breaks down also for complex anion groups like SO$_4^{2-}$, CO$_3^{2-}$, AsS$_3^{-}$; these groups show smaller interionic distances, and correspondingly greater stability, than would be expected from the sizes of the S$^{2-}$, C$^{4+}$, and As$^{3+}$ ions alone. Our next step must be to inquire into the reasons for these deviations from strict geometric rules.
5-3 COVALENT BONDS

The nature of the deviation from radius-ratio predictions may be illustrated with some compounds of calcium and cadmium. These two metals have ions of almost identical radius: 1.00 Å for Ca$^{2+}$ and 0.95 Å for Cd$^{2+}$. In their compounds with oxygen (ionic radius 1.40 Å) the interionic distances are 2.40 Å for CaO and 2.34 Å for CdO. There is nothing new here: the interionic distance for CdO is a trifle less than the sum of the radii, but the difference is hardly more than the uncertainty in the radii themselves. For the sulfides (ionic radius of S$^{2-}$ = 1.84 Å), however, the interionic distances are 2.80 Å for CaS and 2.51 Å for CdS. Obviously something is amiss. It looks as if the ions in cadmium sulfide are squashed against each other, so that the interionic distance is considerably less than the sum of the radii. The crystal structures suggest the same thing: both compounds would be expected to have the NaCl structure (radius ratios 0.54 and 0.52), but the prediction is fulfilled only for CaS; CdS has the sphalerite structure instead, showing that the ions are so deformed that only four rather than six can be grouped around an ion of opposite sign.

To describe the apparent deformation of ions in some crystal structures, we look at the nature of the bond between atoms. In compounds of simple ionic character like NaCl, the formation of a bond between two atoms (an ionic bond) involves the complete removal of the outermost electron from one atom (Na) and its incorporation into the structure of the other (Cl), giving the latter a negative charge and leaving a positive charge on Na. Compounds like CdS have bonds of a different sort, in that electrons are partly shared between the atoms rather than completely transferred from one atom to another. The shared electrons are commonly grouped in pairs, which may be thought of as occupying positions about halfway between the atoms.

Chemical bonds of this latter kind, consisting of electron pairs held jointly between adjacent atoms, go by the name of covalent (or homopolar) bonds. Compounds with covalent bonds differ from ionic compounds, as a rule, in their slight solubilities in water and in their failure to conduct an electric current when melted. The formation of covalent bonds may lead to very stable molecules with little attraction for one another (for example, Cl$_2$, CH$_4$, SO$_2$), in which case the compounds have low melting and boiling points and form solids with little strength or hardness. Alternatively such bonds may give continuous three-dimensional structures in which atoms are linked to others on all sides, as in diamond; in this case the substances have high melting points and exceptional hardness.

The ionic bonds in crystalline NaCl and the covalent bonds in Cl$_2$ or diamond are extreme types. In most substances the bonds are neither purely ionic nor purely covalent, but have an intermediate character; in other words, the electron pair between adjacent atoms may be regarded as somewhat displaced toward one of the atoms, but still attached to both. In crude symbols, with : representing the electron pair,

\[
\begin{align*}
\text{Na} & : \text{Cl} & \text{H} & : \text{Cl} & \text{Cl} & : \text{Cl} \\
\text{ionic bond, NaCl} & \text{polar bond, HCl} & \text{covalent bond, Cl}_2
\end{align*}
\]
Bonds of intermediate type are called polar-covalent or simply polar, the term polar meaning that one end of such a bond is relatively more positive than the other. The partial separation of charge may give polar molecules (like HCl), or it may be compensated by oppositely directed bonds in the same molecule (for example, CCl₄). Water is an interesting case: although we might expect the polarity of the two bonds to compensate each other (H-O-H), the molecule is not linear but bent, as we noted before [Fig. 2-5(a)]. The four electron pairs around the oxygen nucleus are approximately at the corners of a tetrahedron; the angle between the O-H bonds is 104.5°, close to the theoretical tetrahedral angle 109°28'. Because of the bending, one side of the molecule has a net negative charge and the other side a positive charge.

Many polar compounds are soluble in water, but they generally do not dissociate appreciably (for example, sugar and alcohol). Some polar compounds, however, react with water to produce ions:

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]  \hspace{1cm} (5-1)

This is a more accurate picture of the reaction we usually symbolize as \( \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \) (Sec. 2-2).

Bonds in minerals, which cover the whole range from ionic to covalent, may be described as having so much "ionic character" or "covalent character." In CaS, for example, the bond is largely ionic, whereas the bond in CdS has considerable covalent character. The geometric radius-ratio rules of the last section apply strictly only to ionic compounds, and show increasing deviations as bonds become more covalent. Fortunately the bonds in many common minerals are sufficiently ionic that the rules hold fairly well, and the effects of covalency can be treated as minor corrections. In other words, to answer a question posed several paragraphs back, mineralogical crystallography can indeed be regarded as largely an exercise in solid geometry, but with many complications arising from the partial covalent character of bonds.

The bonds in radicals like \( \text{SO}_4^{2-} \) and \( \text{CO}_3^{2-} \) are largely covalent and particularly strong, so that these groups are stable and remain intact through many chemical reactions. In the structures of crystals, such groups are so compact that to a first approximation they may be regarded as simple anionic units. For example, the structure of calcite may be pictured as a distorted NaCl structure, the \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) ions playing the roles of \( \text{Na}^+ \) and \( \text{Cl}^- \).

5-4 ELECTRONEGATIVITY

So far the discussion of bond type has been entirely qualitative. We have merely noted that bonds in some minerals have a partly covalent character, so that predictions about crystal structures from the radius-ratio rules are not wholly accurate. Obviously it would be desirable to make the concept quantitative—to express the amount of covalent character by numbers, and to relate these numbers to other properties of elements so that the covalent character of a given bond could be predicted. This program has proved difficult to carry out in detail, but several
semiempirical schemes have been suggested by which the amount of covalent character can at least be estimated.

The most successful of these schemes is based on a concept called electronegativity. The general, qualitative meaning of this word is familiar from elementary chemistry: chlorine is an electronegative element because it readily forms negative ions in solution; sodium is an electropositive element because it forms positive ions; and copper is more electronegative (or less electropositive) than iron because Cu\(^{2+}\) will take electrons away from iron metal. The electronegativity of an element is clearly related to its ionization potential (for cations) and its electron affinity (for anions), but the relationship is not simple. Two examples of sets of numbers expressing electronegativity are given in Appendix VI and in abbreviated form in Table 5-2. One set (columns headed “Electronegativity”) consists of values calculated by Pauling (1960) from bond strengths as measured by heats of formation, with an arbitrary range from 0.7 for Cs to 4.0 for F. The other set (Percent ionic character) is based on electronegativities estimated by Povarennykh (1956) from ionization potentials and electron affinities; the numbers are not electronegativities as such, but percentages of ionic character of bonds with oxygen calculated from the electronegativities by Smith (1963).

Appendix VI gives an alphabetical listing for easy reference, but Table 5-2 is arranged so as to bring out more clearly the relations of the two sets of numbers with each other and with chemical properties of the elements. From Pauling’s numbers we can generalize that a bond formed between any two atoms in the table is almost purely covalent if the electronegativities are similar, and largely ionic if the electronegativities are very different. Note, for example, that the electronegativity difference for NaCl is 2.1, for CaS 1.5, for CuS 0.5, and for CS\(_2\) 0.0, in agreement with the increasing covalent character of the bonds in this series of compounds. Smith’s percentages express similar electronegativity differences for compounds of

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**TABLE 5-2**

Partial list of electronegativities and percentages of ionic character of bonds with oxygen

<table>
<thead>
<tr>
<th>Ion</th>
<th>Electronegativity</th>
<th>% Ionic character</th>
<th>Ion</th>
<th>Electronegativity</th>
<th>% Ionic character</th>
<th>Ion</th>
<th>Electronegativity</th>
<th>% Ionic character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>0.7</td>
<td>89</td>
<td>Mg(^{2+})</td>
<td>1.5</td>
<td>72</td>
<td>Si(^{4+})</td>
<td>1.8</td>
<td>48</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>0.8</td>
<td>87</td>
<td>Zn(^{2+})</td>
<td>1.7</td>
<td>63</td>
<td>Cl(^{3+})</td>
<td>2.5</td>
<td>23</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>0.9</td>
<td>83</td>
<td>Sn(^{2+})</td>
<td>1.8</td>
<td>73</td>
<td>F(^{3+})</td>
<td>2.1</td>
<td>35</td>
</tr>
<tr>
<td>Li(^{+})</td>
<td>1.0</td>
<td>82</td>
<td>Pb(^{2+})</td>
<td>1.8</td>
<td>72</td>
<td>N(^{5+})</td>
<td>3.0</td>
<td>9</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>0.9</td>
<td>84</td>
<td>Fe(^{2+})</td>
<td>1.8</td>
<td>69</td>
<td>Se</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.0</td>
<td>79</td>
<td>Fe(^{3+})</td>
<td>1.9</td>
<td>54</td>
<td>S</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1.2</td>
<td>71</td>
<td>Ag(^{+})</td>
<td>1.9</td>
<td>71</td>
<td>O</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Be(^{3+})</td>
<td>1.5</td>
<td>63</td>
<td>Cu(^{+})</td>
<td>1.9</td>
<td>71</td>
<td>I</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>1.5</td>
<td>60</td>
<td>Cu(^{2+})</td>
<td>2.0</td>
<td>57</td>
<td>Cl</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>B(^{3+})</td>
<td>2.0</td>
<td>43</td>
<td>Au(^{+})</td>
<td>2.4</td>
<td>62</td>
<td>F</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Data from Appendix VI.
each cation with oxygen; thus the bonds Na-O, Ca-O, Cu-O, C-O have, respectively, 83, 79, 57, and 23% ionic character. In general, as would be expected, Pauling's numbers are low and Smith's high for the active metals at the left side of Table 5-2, and Pauling's are high and Smith's low for the nonmetals at the right side. Since the two sets of numbers represent two different ways of calculating electronegativity, however, the agreement is far from perfect. Discrepancies are particularly evident among the metals from the middle of the periodic system (transition metals) shown in the center of Table 5-2; as a single example, Pauling's numbers would make the Sn-O bond less ionic than the Zn-O bond, while Smith's numbers make it more ionic.

It is a general rule, illustrated by these two sets of numbers and also by several alternative sets that have been proposed as a measure of electronegativity, that numbers can be made to express very nicely the chemical properties of elements at the ends of the periods in the periodic table (Table 5-3), but that unresolvable difficulties arise in trying to express the subtle and complicated relationships among the transition metals in the interior of the table. Electronegativity is a useful concept, but it cannot be depended on for wholly accurate predictions about character of bonding and coordination numbers in all kinds of compounds.

5-5 GENERAL RULES ABOUT BOND TYPE

The ionic radii and electronegativities in Appendix VI permit the formulation of a few useful rules about chemical bonds:

1. For a given cation and two different anions, the bond with the larger anion is more covalent (MgS is more covalent than MgO).
2. For a given anion and two different cations, the bond with the smaller cation is more covalent (MgO is more covalent than BaO).
3. For ions of similar size and different charge, the one with the highest charge forms the most covalent bonds (Ca-O is more covalent than Na-O in Na₂O).
4. Ions of metals in the middle of the long periods of the periodic table form more covalent bonds with anions than do ions of similar size and charge in the first two or three groups of the table (CdS is more covalent than CaS, and FeO is more covalent than MgO).

These rules have many exceptions, but they often help in making qualitative predictions about crystal structures and about the distribution of rare elements in geochemical materials.

Such rules, it should be emphasized once again, are based on a crude model of electron-pair bonds linking spherical, somewhat deformable ions. The number of exceptions to the rules is a measure of the crudity of the model. Considerable refinement in predictions is possible by calculating bond energies and bond angles from quantum mechanics (see, for example, Fyfe, 1964), but for most purposes in geochemical arguments the simpler picture is adequate.
Covalent and ionic bonds are the only bond types of much interest in geology, but one other kind needs brief mention. The metallic bond, characteristic of all metals, is formed typically in substances whose atoms do not have sufficient valence electrons to fill completely a given stable shell of 8, either by sharing or by transfer. In this case the electrons may be pictured as largely free to wander from atom to atom, hence capable of moving along a metal under the influence of an electric potential difference. Some of the sulfide minerals, especially those with metallic luster, contain partly free electrons and so exhibit to some degree the characteristics of the metallic bond.

5-6 SILICATE STRUCTURES

The crystal structures of most interest in geology are also the most complicated—the structures of the multitudinous compounds called silicates.

We note first that the element silicon is a nonmetal of intermediate electronegativity, that it has an oxidation number of 4 and also a coordination number of 4, and that therefore the fundamental unit of silicate structures ought to be the anion SiO$_4^{4-}$, in which the silicon ion is surrounded by four oxygen ions at the corners of a tetrahedron. This expectation is borne out in nature, for silicon practically always occurs in SiO$_4$ tetrahedra. A few silicate minerals contain this group in the form of simple ions; for example, the common mineral olivine (Mg$_2$SiO$_4$) has a structure consisting of alternate Mg$^{2+}$ and SiO$_4^{4-}$ ions, much as magnesite consists of alternating Mg$^{2+}$ and CO$_3^{2-}$ ions. In such compounds silicon acts like a typical nonmetal, and its structural chemistry is no more complicated than that of sulfur or phosphorus or the carbon of carbonates. But compared with these other nonmetals, silicon displays astonishing versatility, for its simple ionic compounds are only the first step of an elaborate structural chemistry that includes rings, chains, sheets, and solid frameworks of interconnected silicon–oxygen groups. Why should this particular nonmetal form compounds of such enormous variety?

For an answer we recall that silicon, although a nonmetal, has properties in some measure intermediate between those of nonmetals and metals. A more metallic element like aluminum or magnesium would form a structure with oxygen in which metal ions and oxygen ions are linked together in a strong three-dimensional framework. Silicon exhibits this kind of behavior in quartz and the other silica minerals (tridymite, cristobalite, coesite, stishovite): here silicon remains at the center of SiO$_4$ tetrahedra, but each oxygen ion is linked with an adjacent silicon ion (Fig. 5-5). A more nonmetallic element like carbon or sulfur would form a volatile oxide consisting of self-contained molecules (like CO$_2$ or SO$_2$) having only slight attraction for one another, and would also form ionic compounds with metals in whose structure the nonmetal is part of a compact anion (like CO$_3^{2-}$ or SO$_4^{2-}$). Silicon forms no volatile oxide, but it does follow the behavior of nonmetals, as we saw in the last paragraph, by entering structures like that of olivine in the form of simple anions. Thus the behavior of silicon straddles the roles of metal and nonmetal. It forms not only structures typical of the extremes, but intermediate structures in which it is part of large silicon–oxygen units that are at
the same time anions and more or less continuous frameworks. This dual capacity of silicon, the ability to play the role of metal or nonmetal or anything in between, accounts for the diversity of silicate structures.

This explanation is largely in terms of chemical properties. We could say the same thing in more structural language by noting that the size of the Si$^{4+}$ ion is intermediate between that of the smallest common metal ions (Ti$^{4+}$ and Al$^{3+}$) and the largest divalent nonmetal ions (P$^{5+}$, S$^{6+}$). If the silicon ion were smaller, it could polarize oxygen ions more effectively, deforming them to fit around it in a compact, self-contained molecules or anions. If it were larger, its attraction for oxygen ions would be less, so that Si$^{4+}$ and O$^{2-}$ would simply be independent units in a framework like that of metal oxide crystals. The in-between size gives silicon the ability to perform either function in a crystal structure.

In silicates, then, the silicon ions occur always surrounded by oxygen ions at the corners of a tetrahedron. The tetrahedral groups may be independent anions, or they may be linked together in a variety of ways. The linkage simply means that one or more oxygens in a given tetrahedron are also part of adjacent tetrahedra. The possible varieties of structure permitted by these linkages are illustrated in Fig. 5-5 and described below:

**Independent tetrahedral groups (nesosilicates).** Silicon–oxygen tetrahedra as independent anions; the most familiar example is olivine.

**Multiple tetrahedral groups (sorosilicates).** Two to six tetrahedra linked together to form larger independent anions. A typical example is hemimorphite, Zn$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O.

**Ring structures of linked tetrahedra (cyclosilicates).** The commonest example is beryl, Be$_2$Al$_2$Si$_6$O$_{18}$, with rings consisting of six tetrahedra.

**Chain structures (inosilicates).** Tetrahedra linked to form linear chains of indefinite length. Two kinds of chains are found: single chains with a silicon–oxygen ratio of 1:3, characteristic of the pyroxenes, and cross-linked double chains with a silicon–oxygen ratio of 4:11, characteristic of the amphiboles. The chains are bonded to one another by metal ions.

**Sheet structures (phylosilicates or layer silicates).** Three oxygens of each tetrahedron are linked with adjacent tetrahedra, forming flat sheets of indefinite extent. In effect this is the double-chain inosilicate structure extended in two dimensions instead of one. The silicon–oxygen ratio is 2:5. This structure is found in the micas and clay minerals; the sheet structures with a hexagonal pattern are reflected in the perfect basal cleavage and pseudohexagonal habit of these minerals.

**Framework structures (tectosilicates).** Three-dimensional networks, each tetrahedron sharing all its oxygens with adjacent tetrahedra, thus giving a structure with a silicon–oxygen ratio of 1:2. Quartz and the other silica minerals are good examples (Fig. 5-5). Other minerals may have this structure provided that some of the silicon ions are replaced by ions of lower charge; the commonest substitution is Al$^{3+}$ for Si$^{4+}$, giving a negative charge to the framework which is balanced by positive metal ions. The feldspars and zeolites are familiar examples of this kind of structure.
<table>
<thead>
<tr>
<th>Classification</th>
<th>Structural arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nesosilicates:</td>
<td>Independent tetrahedra</td>
</tr>
<tr>
<td></td>
<td>$(\text{SiO}_4)^{4-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image1.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Sorosilicates:</td>
<td>Two tetrahedra sharing</td>
</tr>
<tr>
<td></td>
<td>one oxygen</td>
</tr>
<tr>
<td></td>
<td>$(\text{Si}_2\text{O}_7)^{6-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>Cyclosilicates:</td>
<td>Closed rings of</td>
</tr>
<tr>
<td></td>
<td>tetrahedra, each sharing</td>
</tr>
<tr>
<td></td>
<td>two oxygens</td>
</tr>
<tr>
<td></td>
<td>$(\text{Si}_3\text{O}_8)^{6-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image3.png" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$(\text{Si}<em>4\text{O}</em>{12})^{6-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$(\text{Si}<em>6\text{O}</em>{18})^{6-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image5.png" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td><img src="image6.png" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>0 1 2 3 Angstrom units</td>
</tr>
<tr>
<td>Inosilicates:</td>
<td>Continuous chains</td>
</tr>
<tr>
<td></td>
<td>of tetrahedra</td>
</tr>
<tr>
<td></td>
<td>Single chain, each</td>
</tr>
<tr>
<td></td>
<td>tetrahedron sharing</td>
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<tr>
<td></td>
<td>two oxygens</td>
</tr>
<tr>
<td></td>
<td>$(\text{SiO}_3)^{2-}$</td>
</tr>
<tr>
<td></td>
<td><img src="image7.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**FIGURE 5-5**
Structural characteristics of the silicates. (Reprinted by permission from Berry et al., 1983.)
5-7 POLYMORPHISM

Two substances are *isomorphous* if they have similar crystal structures but different chemical formulas, *polymorphous* if they have similar formulas but different structures. Calcite and aragonite, for example, are polymorphs of CaCO₃; α-quartz, β-quartz, tridymite, and cristobalite are polymorphs of SiO₂; andalusite,
kyanite, and sillimanite are polymorphs of Al₂SiO₅. If a compound is known in only two crystalline modifications, it is often called *dimorphous* rather than polymorphous; thus pyrite is a dimorph of marcasite.

From a structural standpoint, polymorphism means that the ions making up a compound can be arranged in two or more different patterns. For example, rubidium ion, Rb⁺, with an ionic radius intermediate between the radii of Cs⁺ and Na⁺, forms a chloride (RbCl) with the 8-coordinated cesium chloride structure at high pressures and the more open 6-coordinated structure of sodium chloride at ordinary pressures. Another example is the series of carbonates MgCO₃, CaCO₃, SrCO₃, BaCO₃, arranged in the order of increasing size of the cation; the compounds of the large ions Sr²⁺ and Ba²⁺ show the aragonite structure and that of the small ions Mg²⁺ the calcite structure, and only CaCO₃ with its cation of intermediate size is capable of crystallizing in either structure.

Polymorphism, however, is much more complicated than such a simple rule would indicate. Ideally we can refer it to geometry, but the factors influencing the geometry are numerous and inadequately understood. Temperature, of course, is one such factor, and pressure is another; in general, a particular structure is stable only over a certain range of temperature and pressure. Rhombic sulfur, for example, is stable at temperatures below 96°C, monoclinic above; and the temperature of the change, or *transition temperature*, is raised if the pressure is increased. Speaking still in generalities, we can say that high-temperature polymorphs have more open structures with higher symmetry than their low-temperature equivalents, and that high-pressure polymorphs have more closely packed structures with higher coordination numbers than low-pressure forms. The form in which a substance crystallizes, however, may be changed by impurities, even though these are sometimes present in very minor amounts. The form also depends on rate of crystallization: high-temperature forms sometimes appear in low-temperature environments, apparently because crystallization took place so rapidly that arrangement of ions into the more stable and more ordered arrangement of the low-temperature polymorph was impossible. Cristobalite, for example, although stable only at temperatures above 1470°C, is commonly found encrusting cavities in lava which could not have been at temperatures over a few hundred degrees, either because it contains enough impurities to modify its stability range profoundly or because it crystallized very rapidly.

The influence of temperature and pressure on polymorph stability is illustrated by the three forms of aluminum silicate, Al₂SiO₅, shown in Fig. 5-6. The lines representing solid–solid transformations for the reactions kyanite ⇌ andalusite, kyanite ⇌ sillimanite, and andalusite ⇌ sillimanite were derived from carefully conducted experiments. There are large uncertainties in the positions of the lines for these reactions because of difficulties in establishing equilibrium in laboratory experiments on reactions that involve only solids. Nevertheless, these three minerals are common constituents of metamorphic rocks, and the relative positions of their transformations provide one means of estimating pressure and temperature conditions of metamorphic processes.
FIGURE 5-6
Pressure and temperature stabilities of Al$_2$SiO$_5$ polymorphs kyanite, sillimanite, and andalusite. Solid lines represent equilibrium for the solid-solid transformations as deduced from experimental observations reported by Bohlen, S. R., A. Montana, and D. M. Kerrick: "Precise determinations of the equilibria kyanite–sillimanite and kyanite–andalusite and a revised triple point for Al$_2$SiO$_5$ polymorphs," *American Mineralogist*, vol. 76, pp. 677–680, 1991. The dashed lines are those reported by Holdaway, M. J., and B. Mukhopadhyay: "A reevaluation of the stability relations of andalusite: thermochemical data and phase diagram for the aluminum silicates," *American Mineralogist*, vol. 78, pp. 298–315, 1993. The "triple point" shows the pressure and temperature where the three polymorphs are in equilibrium. Experimental values of pressure and temperature for the triple point obtained by others are indicated by the solid symbols.

5-8 ISOMORPHISM AND SUBSTITUTIONAL ORDER–DISORDER

The formula of olivine is customarily written (Mg,Fe)$_2$SiO$_4$. This means that olivine contains both magnesium and iron, that the ratio of the two metals is variable from one specimen to another but the ratio of total metal to silicon (in atoms or gram-atoms) remains constant, and that magnesium ordinarily is present in greater amount than iron. For this mineral all ratios of magnesium to iron are possible, and the two end members Mg$_2$SiO$_4$ (forsterite) and Fe$_2$SiO$_4$ (fayalite) have a similar crystal form and crystal structure. This relationship is described as *isomorphism*, and olivine is said to be an *isomorphous mixture* of its two end members. Alternatively olivine may be called a *solid solution* of fayalite and forsterite, the term referring to the fact that this solid resembles a liquid solution in that it remains homogeneous when its components are varied over a certain range of compositions. Still another way of describing the relationship of the two metals is to say that Mg$^{2+}$ substitutes for Fe$^{2+}$ in the crystal structure.
Isomorphism is a very common phenomenon, and its explanation seems obvious: when two compounds differ in only a single constituent and when the two kinds of ions that play the role of this constituent have similar sizes, we might expect that the two could substitute for one another in crystallographic sites. Thus the ions Mg$^{2+}$ and Fe$^{2+}$ have roughly the same radii (0.72 Å and 0.78 Å, respectively), and the olivine structure can accommodate either or both. A similar isomorphous relationship between magnesium and iron is common in other silicate minerals; many of the pyroxenes [for example, diopsidehedenbergite, Ca(Mg,Fe)Si$_2$O$_6$] and amphiboles [for example, actinolite, Ca$_3$(Mg,Fe)$_2$(Si$_4$O$_{11}$)$_2$(OH)$_2$] are familiar examples.

But it does not follow that all pairs of magnesium and iron compounds are isomorphous. Very little magnesium is found in pyrite (FeS$_2$), and very little iron in epsomite, MgSO$_4$$\cdot$7H$_2$O, for example. We might guess that the slight difference in ionic size prevents isomorphism in these compounds, or alternatively we recall that iron (a transition metal in the middle of the first long period of the periodic system) should form bonds of more covalent character than magnesium (near the beginning of a period), so that despite the similarity in size the ions can play somewhat different roles in crystal structures. As a general rule, ionic size is the most important determinant of isomorphism, but similarity of bond character is another major factor.

In olivine the two metals can substitute for one another in any proportions; in other words, the two end members of the solid solution are completely miscible. More commonly the amount of substitution is limited, especially if the difference in ionic size between two ions is greater than about 15%. For example, K-feldspar generally has a little Na$^+$ substituting for K$^+$, but the sizes are so different (radii 1.02 Å and 1.38 Å, respectively) that only a little can be accommodated without altering the crystal structure. In general, the extent of substitution of one ion for another depends on the properties of the ions and the nature of the crystal framework; it also depends on temperature, since at high temperature the added thermal energy serves to increase the vibratory motion of ions, expanding the structure and making it more tolerant of foreign particles. To continue with the feldspar example, increasing amounts of sodium substitute for potassium as the temperature rises, until at about 650°C the two compounds KAlSi$_3$O$_8$ and NaAlSi$_3$O$_8$ become isomorphous and form a complete solid-solution series. On cooling, the isomorphous mixture separates (or exsolves) into two phases—the familiar perthite and antiperthite intergrowths of K-rich and Na-rich feldspars. This relationship is shown in the phase diagram of Fig. 5-7. The solid line in the figure, showing temperatures and compositions where Na-rich and K-rich feldspars coexist as two separate phases, is called a solvus.

The actual-location of the solvus in Fig. 5-7 is uncertain because of slowness of reaction rates in laboratory experiments and because of complications arising from exchanges of Al and Si in the crystal structure. For other common minerals that exhibit unmixing of high-temperature solid solutions (e.g., Ca–Mg carbonates, calcite and dolomite; pyroxenes, Ca-rich and Ca-poor pyroxenes; and ternary feldspars, K-feldspar and plagioclase) experimental difficulties are less serious. For
these minerals the solvi have been accurately determined, thus permitting compositions of coexisting mineral pairs to be used in estimating the temperature of equilibration during geologic processes.

The alkali feldspars provide an example of a more complicated kind of substitutional relationship. The two ions $\text{Al}^{3+}$ and $\text{Si}^{4+}$ occupy four tetrahedral sites in the feldspar structure that differ slightly in size and nearest neighbor configuration. In feldspars formed at relatively low temperatures, $\text{Al}^{3+}$ ions occupy one kind of site and three $\text{Si}^{4+}$ ions the other three, with the sizes of the ions well adapted to the differing properties of the sites. At higher temperatures, say in K-feldspar formed by rapid cooling of magma, the distribution of ions is more random, some $\text{Si}^{4+}$ occupying sites better adapted to $\text{Al}^{3+}$ and some $\text{Al}^{3+}$ in sites appropriate for $\text{Si}^{4+}$. The low-temperature distribution is said to be ordered, the high-temperature distribution disordered. A disordered distribution is typical of K-feldspar in volcanic rocks, where the random pattern was frozen in by rapid quenching of the lava; this is the feldspar called high-sanidine. In contrast, K-feldspars formed in slow-cooling plutons, such as granite, are highly ordered with $\text{Al}$ partitioned into the largest and most distorted tetrahedral sites, producing the ordered feldspar called maximum microcline.

Similarly, in pyroxenes the cations $\text{Mg}^{2+}$ and $\text{Fe}^{2+}$ are systematically partitioned between two distinct octahedral sites, designated M1 and M2. The M2 site is slightly larger than the M1 site and thus can accommodate large cations. In an ordered distribution of the two cations, then, we would expect to find the larger cation ($\text{Fe}^{2+}$) concentrated in the M2 sites and the smaller cations ($\text{Mg}^{2+}$) in M1. At higher temperatures we would expect increasing disorder between the two sites. Expectations like this can be summarized by writing the formula for orthopyroxene in the form:

$$(\text{Mg,Fe}^{2+})^{\text{M1}}(\text{Fe}^{2+},\text{Mg})^{\text{M2}}\text{Si}_2\text{O}_6,$$  \hspace{1cm} (5-2)
which indicates that the composition of the mineral is variable, with Fe$^{2+}$ exchanging for Mg$^{2+}$, and that for any specified composition Mg$^{2+}$ is preferentially partitioned into the M1 site and Fe$^{2+}$ into M2. These relations are confirmed by the data shown in Fig. 5-8, data obtained by spectroscopic analysis of orthopyroxenes that had been heated at temperatures between 500° and 800°C for several weeks. Clearly the upper curve in the figure shows only small amounts of Fe$^{2+}$ in M1 sites for the relatively ordered structure at 500°C, and a steady increase as temperature rises toward the state of complete disorder indicated by the straight diagonal line.

The curves in Fig. 5-8 are called distribution isotherms. They represent equilibrium partitioning of Fe$^{2+}$ and Mg$^{2+}$ between the two types of octahedral sites, which can be described by the intracrystalline reaction,

\[
\text{Fe}_{M2}^{2+} + \text{Mg}_{M1}^{2+} \rightleftharpoons \text{Fe}_{M1}^{2+} + \text{Mg}_{M2}^{2+}.
\]  

This reaction represents a state of homogeneous equilibrium in pyroxene, and is analogous to chemical reactions we used in Chapter 2 to describe homogeneous equilibrium among ions and complexes in an aqueous solution. One might expect that the isotherms in Fig. 5-8 would provide a basis for predicting the temperature of pyroxene formation by plotting measured site distributions of igneous and metamorphic pyroxenes on the figure. With the exception of rapidly cooled volcanic rocks, temperatures estimated by this technique are unreasonably low relative to those computed using other methods, such as the intercrystalline partitioning of cations discussed below. It turns out that the state of atomic ordering in a mineral may change after formation of the mineral. This change is a complex function of intracrystalline reaction kinetics and of cooling rates. In principle, if the reaction kinetics are understood, the degree of atomic ordering in a mineral may be used to predict cooling rates of igneous and metamorphic rocks.

**FiguRE 5-8**
Distribution of Fe$^{2+}$ and Mg$^{2+}$ in the octahedral M1 and M2 sites in orthopyroxene. Symbols represent measured average site occupancies at various temperatures. (Reprinted by permission from Saxena, S., and G. Ghose: "Mg$^{2+}$-Fe$^{2+}$ order–disorder and the thermodynamics of the orthopyroxene crystalline solution," *American Mineralogist*, vol. 56, pp. 532–559, 1971, Fig. 1, p. 535.) For reference, the solid diagonal line shows site occupancies for a completely disordered arrangement of octahedral cations. Dashed diagonal lines are constant compositions of orthopyroxene (mol fraction of Fe$_{SiO_3}$), ranging from enstatite at the lower left to ferrosilite in the upper right.
The equilibrium intracrystalline partitioning of elements between lattice sites in a mineral, as shown in Fig. 5-8, can also be applied to intercrystalline partitioning of cations between minerals of different structures. As an example, we consider partitioning of Fe$^{2+}$ and Mg$^{2+}$ between the nesosilicate garnet [represented by the end members Fe$_3$Al$_2$Si$_3$O$_{12}$ (almandine) and Mg$_3$Al$_2$Si$_3$O$_{12}$ (pyrope)] and the phyllosilicate biotite [KFe$_3$AlSi$_3$O$_{10}$(OH)$_2$ (annite) and KMg$_3$AlSi$_3$O$_{12}$(OH)$_2$ (phlogopite)]. This is a mineral assemblage commonly formed during amphibolite facies metamorphism of pelitic rocks. The intercrystalline exchange reaction is,

$$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 \rightleftharpoons \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2.$$  \hspace{1cm} (5-4)

The partitioning represented by this reaction has been experimentally determined at temperatures between 550$^\circ$ and 800$^\circ$C, and the change in extent of partitioning with temperature makes it possible to determine temperatures of equilibration during metamorphism from measured compositions of garnet and biotite. Values of the distribution coefficient ($K_D$) for this reaction, defined as

$$K_D = \frac{X_{\text{Fe}_{\text{g}}-\text{bi}} X_{\text{Mg}_{\text{g}}-\text{bi}}}{X_{\text{Fe}_{\text{bi}}-\text{bi}} X_{\text{Mg}_{\text{bi}}-\text{bi}}}$$  \hspace{1cm} (5-5)

(where $X_{\text{Mg}_{\text{g}}-\text{bi}}$ means the mol fraction of the Mg end member of garnet, etc.), are computed from experiments where garnet and biotite were allowed to equilibrate at temperatures over 550$^\circ$C. These values are shown in Fig. 5-9. The distribution coefficient, like the concentration constant presented in Sec. 1-8 and the solubility product discussed in Chapter 2, is equal to the thermodynamic equilibrium constant [$K_{(5-5)}$] only if the activities of the mineral components ($a_i$) are equal to the mol fractions of the end member components ($X_i$).

**FIGURE 5-9**
Temperature dependence of the distribution coefficient for the intracrystalline partitioning of Fe$^{2+}$ and Mg$^{2+}$ between garnet and biotite. Symbols represent experimental partition coefficients ($K_D$) computed using Eq. (5-5) for the compositions of garnet and biotite equilibrated in laboratory experiments at 2.07 kbar. The line is fitted to the experimental data, as represented by Eq. (5-6). (Reprinted by permission from Ferry, J. M., and F. S. Spear: "Experimental calibration of the partitioning of Fe and Mg between biotite and garnet." Contributions to Mineralogy and Petrology, vol. 66, pp. 113-117, 1978.)
The curve in Fig. 5-9 was drawn to fit the experimental data, and is represented by the equation,

\[ T = \frac{2109}{0.782 - \ln K_D} - 273, \]  

(5-6)

where \( T \) is in degrees kelvin. This equation allows temperature to be estimated from measured compositions of coexisting garnet and biotite in metamorphic rocks. A word of caution is appropriate, however, in that temperature calculated from Eq. (5-6) will be dependent on pressure and on the possible substitution of other minor components in the garnet and biotite solid solutions, as well as on the extent to which equilibrium partitioning of Fe\(^{2+}\) and Mg\(^{2+}\) was attained during metamorphism. Geothermometers like this are probably accurate to plus or minus 50°C.

5-9 THE PERIODIC LAW

The classification of the elements according to the periodic law has been mentioned several times in this chapter, and will appear frequently hereafter. It is time to give this basic generalization of chemistry a more formal introduction, and especially to indicate its strong relation to the chemistry of crystals.

Based originally on chemical properties of the elements as observed in ordinary laboratory reactions, especially on the property of valence, Mendeleev's (1869) classification has proved also to be an expression of regularities in the arrangement of electrons in atomic structures. Its importance in chemistry has increased through the years, and it is scarcely less important in geochemistry. Already we have noted the relevance of an element's position in Mendeleev's table to its electronegativity and to the kinds of bonds it forms with other elements, hence to the sorts of crystal structure into which its atoms will fit most readily. This is only the beginning of the many applications we shall consider in later chapters.

In the usual expression of the periodic law as shown in Table 5-3, the horizontal sequences of elements are the rows or periods of the table and the vertical sequences are the columns or groups. The number under the symbol for each element is the atomic number, which is equal to the total number of electrons in the neutral atom (and also to the total number of positive charges in the atomic nucleus). For the main-group elements (those at either side of the table), the Roman numerals at the top of the columns indicate the number of electrons in the outer shells of the atoms, or the valence electrons, the electrons which are shared or transferred during the formation of chemical bonds and which therefore are most important in determining the chemical behavior of an element. These same numbers are also used as designations of element groups: thus the elements N, P, As, Sb, Bi belong to Group V and have atoms containing 5 valence electrons.

The principal relationships of the main-group elements are clear immediately. Exclusive of the inert gases (which form a group at the extreme right), active metals stand at the left and active nonmetals at the right side of the table. Within each row properties show a gradual change with increasing atomic number, metallic activity...
decreasing and nonmetallic activity increasing. Down each column is a similar but less pronounced change toward elements of increasing metallic character. This means that the most active metals of all are in the lower left corner and the most active nonmetals in the upper right. Ionic radii also change in fairly regular fashion across the rows and down the columns of the table: generally in each row the biggest ions appear at the beginning and end, and in each column the biggest ions are at the bottom. Thus the largest metallic ions appear in the lower left corner, and the largest nonmetallic (negatively charged) ions in the lower right.

Relationships among the transition metals in the middle of the table are more complex. These elements have atoms with 1, 2, or 3 valence electrons, and with 8 to 18 electrons in the shell below the valence shell. Since the number of valence electrons is small, the elements are all metals. Many of them can assume several oxidation states in their compounds, because some electrons in the second shell of their atoms ("d" electrons) have nearly the same energy as the outer electrons and can act as additional valence electrons. Some of these elements have faint relationships with main-group elements, as indicated by the Roman numerals designating A and B "subgroups." In general, however, these elements show less regularity in their properties than elements in the main groups, and their properties are less readily predictable from their position in the table.

The lanthanide, or rare-earth, elements and the actinide elements, which form part of the transition group but for convenience are shown at the bottom of the table, present still further complications. All the rare-earth elements and most of the actinides have atoms with 3 valence electrons and 8 electrons in the shell below the valence shell. Each atom differs from the one preceding it by 1 electron in the third shell ("f" electrons), two shells below the valence shell. Since the outer electron structures are so similar, the elements in each of the two groups show very similar chemical properties, so similar that the elements are difficult to separate in the laboratory and generally occur intimately associated in nature. This generalization is less true for the actinides than for the rare earths, because some of the former have higher stable oxidation states (additional electrons coming from the shell under the valence shell) which make their separation easier.

The importance of the table for crystal chemistry lies in the information it gives about the ability of rare elements to substitute for abundant elements in mineral structures. This is a complex subject that we will explore in more detail later (Chap. 20). For the moment we look only at what the table can tell us about the ability of rare metals to replace major ones in the silicate minerals that make up the bulk of most ordinary rocks.

As we have noted, the really abundant metallic constituents of silicates are limited to six: Na, K, Ca, Mg, Fe, and Al, which exist as ions linked through oxygen to Si. Other metals appear in silicate structures chiefly as ions substituting in minor amounts for one or more of this group. The position of a rare metal in the periodic table generally makes possible a good guess as to which of the abundant metals it can most easily replace, and as to the probable extent of the replacement.

Note that the six abundant ions all belong to Groups IA, IIA, and IIIA, except for Fe; this element is part of the group probably just because of its extreme overall
abundance in the Earth's materials. Rare metals whose ions readily substitute for the major ones likewise in large part belong to these same three groups, with some additions from Group IIIB. These are all, or nearly all, elements that are strongly electropositive and form bonds with oxygen of mostly ionic character. Specific substitutions depend chiefly on ionic size, and can be grouped according to size ranges of the major ions:

- Ions that replace K\(^+\), with radii well over 1.1 Å
- Ions that replace Na\(^+\) and Ca\(^{2+}\), with radii 0.9–1.1 Å
- Ions that replace Mg\(^{2+}\) and Fe\(^{3+}\), with radii 0.7–0.9 Å
- Ions that replace Al\(^{3+}\), with radii less than 0.7 Å

As we have noted before, substitution of one ion for another is generally limited if their sizes differ by more than 15%, and if their numbers of valence electrons differ by more than one unit.

We expect, then, that rubidium (ionic radius 1.52 Å) and barium (1.35 Å) would be found as minor constituents of potassium minerals (radius of K\(^+\), 1.38 Å), that lithium (0.76 Å) might replace magnesium, that yttrium and the rare earths (radii 0.86–1.01 Å) would substitute for calcium more extensively than for sodium, that gallium (0.62 Å) might be found in aluminum minerals, and so on. Predictions like this are not always valid, because in particular cases substitution of ions may be influenced by other factors, but generally they are borne out by silicate analyses.

Thus many of the rare elements found in silicate rocks, as well as the major elements, appear in the groups labeled IA, IIA, IIIA, and IIIB of Mendeleev's table. This clustering of elements simply reflects the fact that the properties of these elements make possible extensive substitution in silicate structures. Many other elements, notably those in Groups IVB, VB, VIB, and VIIB, are also found as common trace constituents of silicate rocks, but for different reasons that we will look into later on.

This brief look at the relation of mineral structures to one part of the periodic table is intended only as an introduction to a set of ideas that constitutes a large part of geochemistry. We shall hear much more about the table and its capacity to bring order into crystal chemistry in later chapters.

**SUMMARY**

The minerals that compose ordinary rocks are a small number cut of several thousands that are known, and these common minerals in turn are made up of only a few abundant elements. The less common minerals and rarer elements are of great interest, and we shall have much to say about them later, but the rocks and soils that occupy most of the geologist's attention are built from surprisingly few constituents.

In most minerals the building blocks are ions, and the ions are put together in the geometrically regular structures called crystals. The patterns in these structures are determined by the sizes of the ions and the nature of the bonds formed between
them. The patterns can change with temperature and pressure, since the ions are in vibratory motion and accommodate their geometric arrangements to the space available. In silicate minerals the patterns are especially complex, ranging from isolated SiO$_4$ groups to rings, chains, and three-dimensional networks of these groups.

For some chemical compositions more than one crystal structure is possible, and each polymorphous structure is stable over a particular range of temperature and pressure. Conversely, some structures can have different chemical compositions, since ions of different elements can occupy the same position in a crystal lattice provided their sizes and bonding properties are sufficiently similar. The substitution of one ion for another may range up to complete replacement, in which case the two structures are said to be isomorphous, or to form a complete solid-solution series. More commonly the substitution is only partial, its extent depending delicately on temperature and pressure. Analysis of the amount of substitution therefore provides a means of estimating temperatures (and sometimes pressures) of mineral formation. We shall find this technique particularly useful in discussions of metamorphic reactions and ore formation.

The ability of crystal structures to accommodate small amounts of foreign ions will also be important when we look into the geologic behavior of the rarer elements, since these often substitute for the ions of more abundant elements in common minerals rather than forming minerals of their own. Substitution of rare-element ions for the more abundant ions can be to a large extent predicted from their position in the periodic table of the elements.

**PROBLEMS**

1. Why does the zinc ion, Zn$^{2+}$, in many of its compounds show tetrahedral coordination, although its ionic radius is similar to that of ions like Mg$^{2+}$ which show only octahedral coordination?

2. Why is the radius of Fe$^{3+}$ smaller than the radius of Fe$^{2+}$? Would you expect, as a general rule, that the more highly charged ions of a multivalent element would have smaller radii than the ions of lower charge? Why?

3. The following substitutions are uncommon in minerals. Inspect each one, to see whether its infrequency of occurrence conforms to the general rules of isomorphous substitution:

- Li$^+$ for Na$^+$
- C$^{4+}$ for Si$^{4+}$
- Cd$^{2+}$ for Na$^+$
- Cu$^+$ for Na$^+$
- Sc$^{3+}$ for Li$^+$
- Cl$^-$ for F$^-$

4. Why are intergrowth textures (perthite and antiperthite) common in alkali feldspars (albite and orthoclase) but not in the plagioclase feldspars?

5. A possible method of estimating the temperature of formation of sulfide veins is based on a determination of the iron content of sphalerite. Assuming that iron was present in excess in the solutions from which sphalerite crystallized, would you expect the iron content of sphalerite to be greater at high temperature or low? Why?

6. In each of the following pairs, choose the one in which the chemical bond would have more covalent character:

- KCl and KI
- Li$_2$S and C$_8$S
- BaCl$_2$ and HgCl$_2$
- KCl and BaCl$_2$
- Cu$_2$O and Cu$_2$S
- B$_2$O$_3$ and Al$_2$O$_3$
7. Describe in general terms the crystal structure of diopside, forsterite, analcite, muscovite, tremolite.
8. Why do we not find a variety of complex carbonate minerals with structures analogous to silicate structures?
9. If a cation can show more than one type of coordination, would you expect the higher coordination to be found in minerals formed at high temperatures or at low temperatures? Why? A good example is $\text{Al}^{3+}$, which shows 4-coordination in orthoclase, $\text{KAlSi}_{3}\text{O}_{8}$, and 6-coordination in kaolinite, $\text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4}$.
10. Consider a series of cations having the same electronic structure, for example, the series: $\text{Na}^+$, $\text{Mg}^{2+}$, . . . , $\text{Cl}^{-}$. Do ionic radii show a regular change through this sequence? Can you suggest a reason for the pattern of change?

REFERENCES AND SUGGESTIONS FOR FURTHER READING

Smith, F. G.: *Physical Geochemistry*, Addison-Wesley, Reading, Massachusetts, 1963. Chapter 2 is an excellent brief account of the development of ideas about coordination and chemical bonding. It includes a table of electronegativities as estimated by Povarennykh and percentages of ionic character of bonds in oxides and sulfides as calculated from the electronegativities by Smith.
INTRODUCTION
TO
GEOCHEMISTRY

THIRD EDITION

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