

MgO	periclase
CaO	lime
SiO ₂	quartz
Mg ₂ SiO ₄	forsterite
Mg ₂ Si ₂ O ₆	enstatite
CaMgSi ₂ O ₆	diopside
CaSiO ₃	wollastonite
Ca ₇ Mg(SiO ₄) ₄	bredigite
Ca ₂ MgSi ₂ O ₇	åkermanite

To plot them on the MgO-SiO₂-CaO ternary, you need to separate out the oxide components in each formula. Periclase has one MgO and no CaO or SiO₂, so it plots at the MgO corner. Forsterite and enstatite plot along the bottom of the ternary. What about the minerals that plot in the middle?

Let's work through the example of åkermanite, Ca₂MgSi₂O₇. Its formula can be broken down in terms of oxide units:

- 2 CaO
- 1 MgO
- 2 SiO₂.

To plot this composition, we have to make the components add up to 100%, as we did for the two-component example above:

$$2 \text{ CaO} + 1 \text{ MgO} + 2 \text{ SiO}_2 = 5$$

$$\frac{100 \times 2}{5} = 40\% \text{ CaO,}$$

$$\frac{100 \times 1}{5} = 20\% \text{ MgO, and}$$

$$\frac{100 \times 2}{5} = 40\% \text{ SiO}_2.$$

To plot the line of compositions that are 40% CaO, count in four lines, or 40% worth, from the MgO-

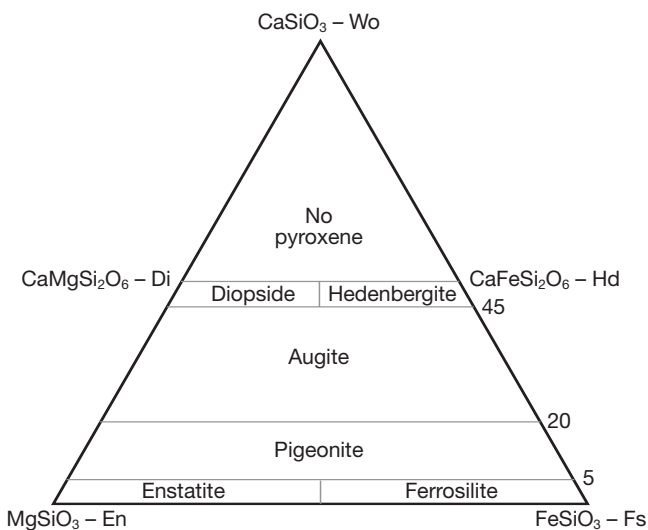


Figure 10.4. Ternary plot of the compositional space where pyroxenes (and pyroxenoids, which lie above the diopside-hedenbergite line) are represented. The different composition fields have mineral names associated with them as shown.

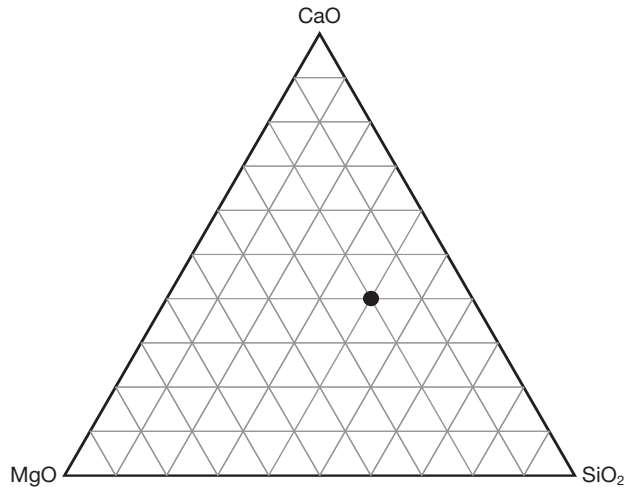


Figure 10.5. Ternary plot of the system MgO-SiO₂-CaO. The composition of åkermanite (Ca₂MgSi₂O₇) is calculated in the text and is CaO = 40%, MgO = 20%, and SiO₂ = 40%. These data are then plotted on the ternary diagram. Their point of intersection locates the composition of åkermanite in MgO-SiO₂-CaO space. (See the text for details on how to plot these data.)

SiO₂ edge of the plot, or you can count in six lines, or 60% worth, from the CaO corner. Now plot the line of compositions representing 20% MgO, and the intersection of those two lines will uniquely define our åkermanite. This example is plotted for you on Figure 10.5. You can even check to see if you got this correct by checking that the third oxide, SiO₂, plots where it should. For fun, try plotting the remaining Ca-Mg-Si minerals on the diagram yourself! The real power of these sorts of diagrams will be evident when you take igneous petrology. Petrologists will use the oxide weight of the rock to make such plots. In fact, they refer to the chemical analysis of a rock (mixture of minerals), often done by XRF or ICP, as a **whole-rock analysis**. From those chemical data, they'll do everything from deriving naming systems for the rocks based on their chemistry to helping explain how volcanic rock compositions change over the age of a magma system.

Compositional Variation in Minerals

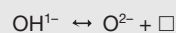
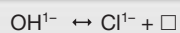
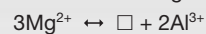
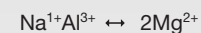
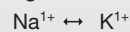
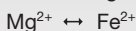
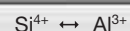
Another concept follows from the above discussion, and is useful in describing mineral compositions. This is the realization that minerals have variable compositions, and usually deviate (sometimes, significantly) from their ideal, published formulas. While this often tends to frustrate students, as well as professional scientists outside the fields of mineralogy and geology, we

must realize we are dealing with natural systems, and these systems often contain small amounts of many other elements. As we discussed in Chapters 1, 3 and 6, cations will occupy sites in minerals if their sizes and charges are appropriate. So if multiple elements with similar sizes and charges are “available” for incorporation into the structure when a mineral is crystallizing, they are likely to substitute for each other, and create compositions that are intermediate between ideal formulas. Some common examples of these substitutions are given in Table 10.10. Simple substitutions involve one-for-one replacement of one element by another element. These include Fe^{2+} for Mg^{2+} , F^{1-} for Cl^{1-} , Al^{3+} for Fe^{3+} , Na^{1+} for Ca^{2+} , etc. as shown in Table 10.10.

One of the most important and common substitutions in silicate minerals is Al^{3+} for Si^{4+} . However, charge balance is not maintained in this substitution, so it can only occur when the Al^{3+} -for- Si^{4+} substitution is charge-compensated by another substitution elsewhere in the mineral. For example, in the plagioclase feldspars, the loss of charge from the Al^{3+} -for- Si^{4+} substitution is charge balanced by substitution of Ca^{2+} for Na^{1+} . Another method of charge balancing is for a cation to be added somewhere in the structure. For instance, K^{1+} can be incorporated into the (previously vacant) interlayer site of a sheet silicate when one Al^{3+} substitutes for one Si^{4+} in the tetrahedral layer. Understanding these substitutions will help you not only understand why mineral compositions vary, but it will also help you to understand the systematics of mineral chemistries.

Table 10.10.

Examples of common substitutions that occur naturally in many minerals. (Many more substitutions can occur, but we are limiting them here to the major elements in the Earth’s crust plus Cl, F, and H. Also the symbol “□” is used to represent a vacancy in the structure (i.e., a crystallography site that is empty).)



Assigning Cations to Structural Sites

We began this chapter by pointing out that there are two parts to writing the chemical formula for a mineral: (1) determining the chemical composition of the mineral in terms of the atoms in its formula, which we termed apfu, and (2) being able to place these atoms in the correct sites (e.g., bonded in an appropriately sized coordination polyhedral). We’ll now take a more thorough look at the second of these issues.

Site occupancy questions set the study of minerals and crystalline materials apart from the study of chemistry of liquids, gases, or non-crystalline materials (i.e., this is really the guts of mineralogy)! So far, you should have learned that cations with different sizes fit in varying types of coordination polyhedra (you will recall that as size increases, so does coordination number). If a mineral has cations with vastly different sizes (i.e., big Ca^{2+} vs. tiny Si^{4+} in a garnet), it should be clear which sites they would occupy. If we think about similarly-sized cations (i.e., Mg^{2+} and Fe^{2+} in sheet or chain silicates or Si^{4+} and Al^{3+} in a framework silicate), it might be more difficult to determine site occupancy. As we are about to learn, site occupancy can be difficult to determine, and may require integration of *chemical* (e.g., compositional data obtained from EPMA), *structural* (e.g., size of coordination polyhedral obtained by X-ray diffraction), and *spectroscopic* (e.g., oxidation state of state of Fe from Mössbauer spectroscopy) information.

Fortunately, this problem can be greatly simplified through an understanding of mineral structures. A general overview of site occupancy will show the similarities of sites in many minerals and demonstrate that many site assignments can be made based on structural knowledge and good old-fashioned mineralogical common sense. The following discussion presents a simplified version of where to put cations in common rock-forming minerals. We encourage you, however, to consider each mineral group more carefully by consulting the discussion of nomenclature for each one, as presented in Chapters 21–23.

Garnets and olivines. As a first example, consider the site assignments for the garnet mineral andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$. There are three cations with sizes of $\text{Ca}^{2+} > \text{Fe}^{3+} > \text{Si}^{4+}$. Now take a look at the structure drawing of a garnet (Figure 10.6). Notice there are three polyhedra with different coordination numbers (CN): a large distorted polyhedron with CN = 8 (translucent in the figure), an octahedron with CN = 6 (light gray) and a tetrahedron, CN = 4 (dark gray). Given the three cations Ca^{2+} , Fe^{3+} , and Si^{4+} , where would you predict they would fit in the garnet? You’d put the

biggest cation, Ca^{2+} , in the biggest site and the smallest cation, Si^{4+} , in the smallest site. This leaves the intermediate site (CN = 6) for the intermediate-sized cations (Fe^{3+}); thus the site assignments would be Ca^{2+} in the CN = 8 site, Fe^{3+} in the CN = 6 site, and Si^{4+} in the CN = 4 site.

Let's try another orthosilicate group, the olivines, and use the same three elements. Olivine group minerals have the general formula $(\text{Ca}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+})_2\text{SiO}_4$, so we'll consider two different olivines: fayalite, Fe_2SiO_4 (Figure 10.7a), and monticellite, CaFeSiO_4 (Figure 10.7b). The olivine structure has three different polyhedra: two octahedral sites, which are called M1 and M2 (this "M" nomenclature is used to denote a "metal" or cation site in a mineral without regard to what cation actually occupies the site) and the isolated tetrahedral sites. So it's a safe bet to assign Si^{4+} to the tetrahedral site, but what about the M sites? Recall that the olivine structure is based on two edge-sharing octahedral chains that run parallel to the c axis (Figure 10.7); the M1 octahedron is the darker shaded one, while the M2 site is translucent. In fayalite (Figure 10.7a), both of these octahedra appear to be about the same size; in monticellite (Figure 10.7b), one of them is larger, and somewhat distorted from a perfect octahedron. What's your guess on where Ca would go in monticellite? Hopefully you'd put Ca in the larger, distorted site. Thus in fayalite, M1 and M2 are

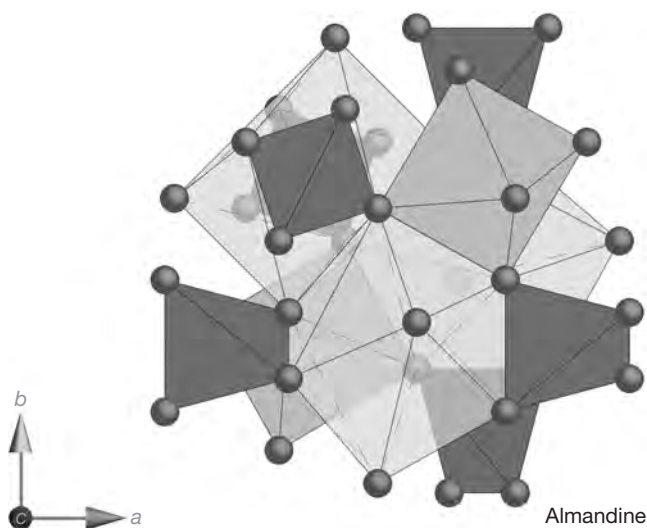


Figure 10.6. A portion of the crystal structure of a garnet, showing its three coordination polyhedra. From largest to smallest these are: a distorted CN = 8 site (translucent gray), an octahedron CN = 6 (light gray), and a tetrahedron CN = 4 (dark gray). Large cations like Ca^{2+} would enter the CN = 8 site, intermediate cations like Fe^{2+} would enter the CN = 6 site, while small cations like Si^{4+} would reside in the CN = 4 site. The oxygen anions defining the corners of each polyhedron are shown as small spheres.

about the same size (Figure 22.41), but in monticellite, $\text{M2} > \text{M1}$ because M2 stretched to house the larger cation. (Recall the house analogy from the start of the chapter, as a family would grow in size, they'd need to enlarge the house!)

The situation for site assignments gets more complicated when you think about including Mg^{2+} and Mn^{2+} in the M1 and M2 sites. Fe^{2+} , Mg^{2+} , and Mn^{2+} are all about the same size, so their respective site occupancies (i.e., M1 vs. M2) cannot be predicted simply on the basis of charge or ionic radius. To solve the puzzle of where these cations lie in any olivine, it is necessary to get additional information, usually from X-ray diffraction or spectroscopic studies.

Pyroxenes. Next, let's take a look at the issue of site occupancy in the pyroxenes and finally learn why we write MgSiO_3 as $\text{Mg}_2\text{Si}_2\text{O}_6$. The pyroxenes are based on single chains of Si tetrahedra, and the unbonded apical oxygens in these chains form octahedra between them, while another octahedral site lies beneath the bases of the chains. Portions of the structures of enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$ (Figure 10.8a), and diopside, $\text{CaMgSi}_2\text{O}_6$ (Figure 10.8b), show these octahedral sites and the tetrahedral chains. There are again two octahedral sites: the M1 site formed by the apical oxygens between the chains (shaded gray), and the M2 sites below the bases of the chains and next to M1. M2 is larger than M1 (Figure 22.28). (In fact, you may be seeing a trend here in that, in general, as the number of the M-site increases, so does its size). In enstatite, both the M1 and M2 sites contain Mg^{2+} , while in diopside, M2 contains the larger Ca^{2+} cation and Mg^{2+} is in M1. Thus, when site assignments are made for the pyroxenes, large cations like Ca^{2+} and Na^{1+} can only enter M2 because M1 is too small. Notice that M2 has some room to expand laterally into the cavity created below the base of the tetrahedral chains. Now we can see why the pyroxene formula is written as $\text{Mg}_2\text{Si}_2\text{O}_6$: because there are two octahedral sites, and the Ca^{2+} content (as shown in Figure 10.4) cannot exceed one apfu because Ca^{2+} can only go in M2.

Amphiboles. Now we are ready to undertake the site assignments in amphiboles, which some folks call "garbage can" minerals. They have earned this lovely name because they can contain lots of different elements; the many substitutions are possible because amphiboles have several sites of different sizes! So if your professor insists on using this name, you need to think of garbage cans ranging in size from the small wastebasket in your dorm room (for the small cations like Si^{4+} and Al^{3+}) to the large dumpster outside (for the large cations like K^{1+} and Na^{1+}) as well as inter-

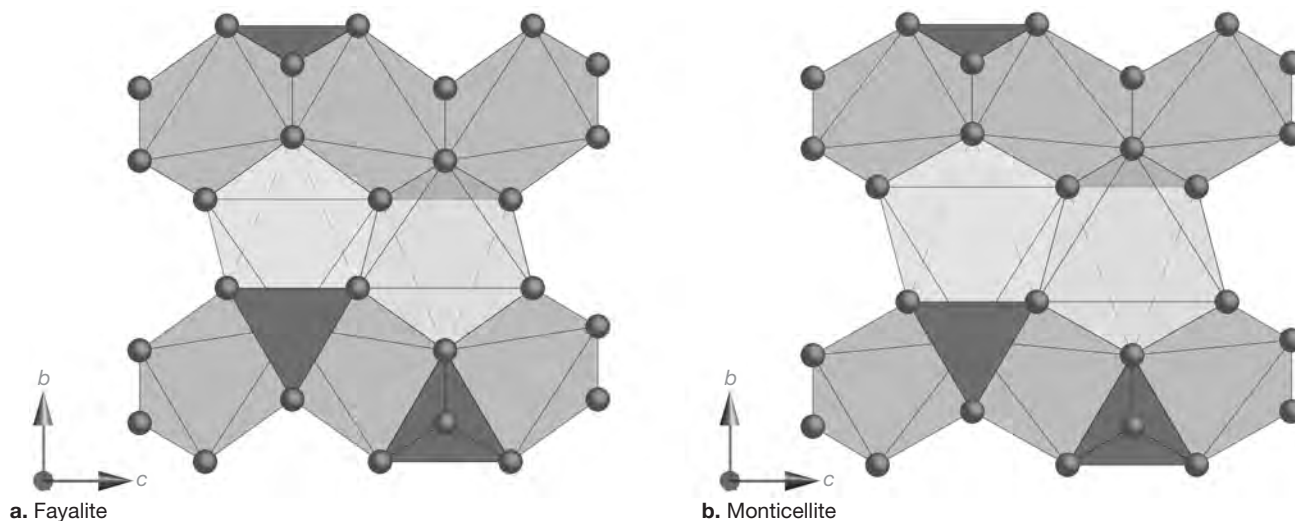


Figure 10.7. Portions of the crystal structure of two olivine minerals. The larger M2 octahedra are translucent light gray and sandwiched between the smaller M1 octahedra which are dark gray, and the Si^{4+} tetrahedra are darkest gray; small spheres represent O and define the three coordination polyhedra. **a.** The structure of the olivine group mineral fayalite, Fe_2SiO_4 ; Fe^{2+} occupies both of the octahedral coordination polyhedra. **b.** The structure of the olivine group mineral monticellite, CaFeSiO_4 ; Ca^{2+} has enlarged the M2 site while the Fe^{2+} -containing M1 site remains nearly the same size as in fayalite.

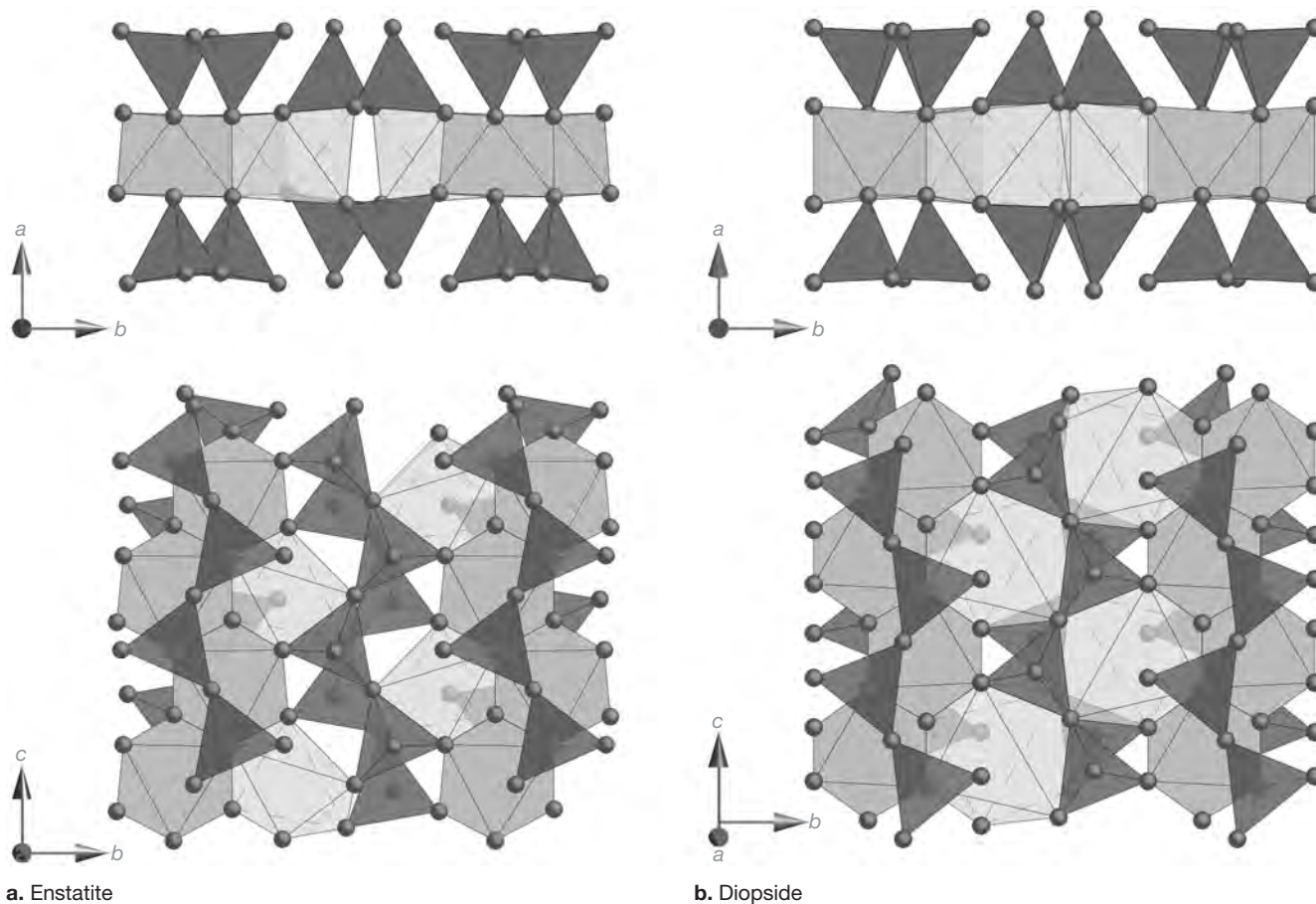


Figure 10.8. Portions of the crystal structure of two pyroxene mineral species. The larger M2 polyhedron is light translucent gray, the smaller M1 octahedron is dark gray, the Si tetrahedra are darkest gray, while small light spheres are O^{2-} anions and define the corners of the polyhedra. The upper projection is looking down the chains, while the lower projection is a top view perpendicular to the chains. **a.** The structure of enstatite, $\text{Mg}_2\text{Si}_2\text{O}_6$; both M2 and M1 contain Mg^{2+} . **b.** The structure of diopside, $\text{CaMgSi}_2\text{O}_6$; in this case, the larger cation Ca^{2+} occupies the larger M2 polyhedron while Mg^{2+} is in M1. Notice how the M2 sites have expanded into the cavity in the center of the structure.

mediate-sized cans (for cations like Mg^{2+} and Fe^{2+}) like the ones your parents have at home.

To put this in context, examine Table 10.11, which lists the general formulas for the above examples (garnets, olivines, and pyroxenes) as well as for amphiboles, micas, and feldspars, to be covered next. For each general formula, the table lists the sites and elements that can fit in them. (This is not an all-inclusive list, but gives the most commonly-encountered elements, which are also the most common elements in the Earth's crust!) For amphiboles, there are two separate formulas: the first, $A_{0-1}M_4M_3M_2M_1Si_8O_{22}(OH)_2$, lists the four M sites individually, while the second, $A_{0-1}B_2C_5T_8O_{22}(W)_2$, combines M1-3 (because these sites are of similar size) into the C site and M4 into the B site.

Figure 10.9 shows portions of three different amphibole group minerals in two different orientations. Figure 10.9a shows a portion of the structure of the amphibole group mineral anthophyllite, $Mg_7Si_8O_{22}(OH)_2$. The upper drawing shows a projection down the double chains. On its left and right sides are octahedral strips formed by the apical oxygens of the double chains pointing inward. In the center of the figure is a large cavity formed under the bases of two sets of double chains with their apical oxygens pointing outward. In the lower portion of the drawing, we are looking down on the chains and octahedral strip. Notice how there is an alternation of two and three dark-shaded octahedra. The two-wide strips are the two M1 sites. The three-wide strip has two M2's on the outside with an M3 sandwiched in the middle. (Notice how these numbers fit the ratio in the general formula.) Next, there is a polyhedron in a light transparent shade that occurs on the edges of the M1 octahedral strip protruding into the cavity; this is the M4 site.

The M4 site in amphibole should remind you of the M2 site in pyroxene, while the M1-3 sites are reminiscent of the M1 site in pyroxene. Given the similarities between the two structures, you might predict where the cations are going to fit, based on the observation that the size of $M4 > M1-3$; again, M1-M3 are lumped together because they are of similar size.

Next, consider the structure of tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, as shown in Figure 10.9b. Note how similar it is to anthophyllite when projected down the c axis. When it's rotated to look down on the octahedral layer, notice how the occupancy by Ca^{2+} has expanded the M4 site. In Figure 10.9b for tremolite, we've also shown the H atom, which bonds off an O^{2-} in an octahedron located below the center of the ring formed by the above tetrahedral chains. Finally, a less common amphi-

Table 10.11.

General formulas and site assignments for garnets, olivines, pyroxenes, amphiboles, micas, and feldspars. (Many more cations can enter these minerals, but we are listing the major elements in the Earth's crust plus Cr, Mn, Ti and the anions Cl and F. More details for each mineral group will be given in Chapter 21.)

Garnets: $A_3B_2Si_4O_{12}$

where,

$A > B$, and

$A = Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$

$B = Al^{3+}, Fe^{3+}, Cr^{3+}$

Olivines: $M_2M_1SiO_4$

where,

$M_2 > M_1$, and

$M_2 = Ca^{2+}, Mg^{2+}, Fe^{2+/3+}, Mn^{2+}$

$M_1 = Mg^{2+}, Fe^{2+/3+}, Mn^{2+}$

Pyroxenes: $M_2M_1Si_2O_6$

where,

$M_2 > M_1$, and

$M_2 = Ca^{2+}, Na^{1+}, Mg^{2+}, Fe^{2+}$

$M_1 = Mg^{2+}, Fe^{2+/3+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Ti^{4+}$

Amphiboles: $A_{0-1}M_4M_3M_2M_1Si_8O_{22}(OH)_2$ or

$A_{0-1}B_2C_5T_8O_{22}(OH)_2$

where,

$A > M_4 > M_3 \rightarrow M_2 = M_1$, or $A > B > C > T$, and

$A = K^{1+}, Na^{1+}$

$B = Na^{1+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$

$C = Mg^{2+}, Fe^{2+/3+}, Mn^{2+}, Al^{3+}, Cr^{3+}$

$T = Si^{4+}, Al^{3+}, Ti^{4+}$

$OH = (OH)^{-1}, F^{-1}, Cl^{-1}, O^{2-}$

Micas: $IM_{2-3}VaC_{0-1}T_4O_{10}(OH)_2$

where,

$I > M > T$, and

$I = K^{1+}, Na^{1+}, Ca^{2+}$

$M = Al^{3+}, Mg^{2+}, Fe^{2+/3+}, Ti^{4+}$

$T = Si^{4+}, Al^{3+}, Fe^{3+}$

$OH = (OH)^{-1}, F^{-1}, Cl^{-1}, O^{2-}$

Feldspars: $M_{1-2}T_4O_8$

where,

$M > T$, and

$M = K^{1+}, Na^{1+}, Ca^{2+}$

$T = Si^{4+}, Al^{3+}, Fe^{3+}$

bole called richterite, $Na(CaNa)Mg_5Si_8O_{22}(OH)_2$, is shown in Figure 10.9c. The main thing to notice here is the addition of Na^{1+} in the A site, which is located in center of the cavity formed by basal oxygens in the double chains. Here the M4 site contains one Ca^{2+} and one Na^{1+} , so Na^{1+} occupies two sites in this amphibole.

These three examples should lend insights into site assignments and the general formulas for amphibole group minerals. Basically there are five types of sites in this mineral: the A site (CN = 12), the B site or M4 (CN = 6–8), the C site or M1-3 (CN = 6), the T site (CN = 4), and the OH site, which can either be a H^+ bonded to an O^{2-} , or Cl^- or F^- replacing the O^{2-} in the octahedral layer. Once you have calculated the number of cations for each formula unit in an amphibole, you need to assign them to these five sites. The process is based on what we've

learned in the pyroxenes and some good old mineralogical common sense. First, the A site is the only place in the structure that could house atoms as large as K^+ . Na^+ could fit in either A or M4. M4 would be the only one of the M sites big enough to house Ca^{2+} (the A site is too big, and M1-3 are too small); this is why no more than two Ca^{2+} atoms can enter the structure. Smaller cations like Mg^{2+} , Fe^{2+} , and Al^{3+} would fit just fine in M1-4, while the smallest cations, like Si^{4+} and Al^{3+} would fit in the T sites. This would leave $(OH)^-$, Cl^- , and F^- in the last site.

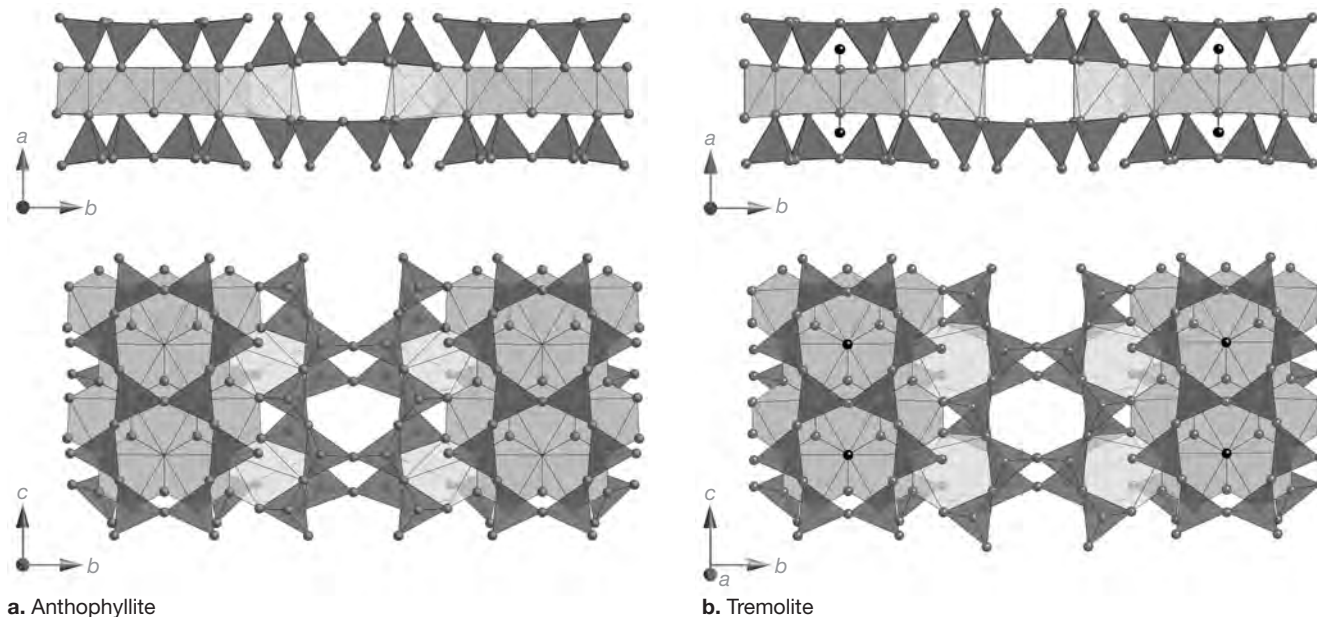


Figure 10.9. Portions of the crystal structures of three amphibole group minerals. The double chains of silicate tetrahedra (dark gray) point inward to form the octahedral strips that contain the M1-3 sites (light gray). The larger M4 site (translucent gray) is at the edge of these strips, and intrudes into the cavity created between the bases of another set of chains whose apical oxygens point upward, while small light spheres are O atoms and define the corners of the polyhedra. Two projections are shown, the top one looking down the chains and the lower one looking perpendicular to the chains. **a.** The structure of anthophyllite, $Mg_7Si_8O_{22}(OH)_2$; Mg^{2+} occupies all four of the M sites. **b.** The structure of tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$. In this structure, Ca^{2+} replaces the Mg^{2+} from A in the M4 sites. Notice how M4 is bigger (seen best in the bottom projection perpendicular to the chains) now that Ca^{2+} occupies it. H^+ atom positions (small black sphere) have been added to show how H^+ bonds to an oxygen in the octahedral layer that is below the six-membered rings in the tetrahedral layer. That O^{2-} also is the only O^{2-} in the octahedral layer that is not bonded to the tetrahedral layer. **c.** The structure of richterite, $Na(CaNa)Mg_5Si_8O_{22}(OH)_2$. In this structure, Na^+ occupies the A site in the cavity created by the basal oxygens of the silicate chains. This site is 12-coordinated to six oxygens above and six below, both sets being in the six-membered rings formed by the double chains (best seen in the bottom projection).

