Solid Solution

The two most fundamental properties that characterize a mineral and distinguish it from other minerals are its chemical composition and crystal structure. Thus, a given mineral has a specific composition that in part defines it. For example, the mineral quartz contains oxygen and silicon in a fixed ratio of 2O:1Si. In nature, however, no minerals are truly pure; they always contain some elements other than those that define them. Most minerals can allow extensive substitutions between certain elements among specific sites in their crystal structures and can thus exhibit extensive variation in chemical composition; this is called a solid solution.

In nature, however, no minerals are truly pure; they always contain some elements other than those that define them. For example, quartz usually contains some M and Ge as well as Si and O. Although both of these impurities substitute for Si in the crystal structure of quartz, their concentrations rarely exceed parts-per-million (1 ppm = 0.0001 wt. %) levels. Thus, minerals such as quartz are typically "close" to being pure in composition.

Unlike quartz, most minerals can allow extensive substitutions between certain elements among specific sites in their crystal structures and can thus exhibit extensive variation in chemical composition; this is called a solid solution. Let's consider a simple example: olivine. In the olivine crystal structure, the identical ionic charges and similar sizes of Fe$^{2+}$ and Mg$^{2+}$...
allow these ions to substitute freely for each other within any given octahedral site--i.e., they form a solid solution. As a result, olivine's chemical formula can be written as $X_2SiO_4$, where $X$ can be either Fe$^{2+}$ or Mg$^{2+}$ or any combination of the two. The conventional way to express this relationship is to place the elements that make up the solid solution in parentheses--i.e., $(Fe,Mg)_2SiO_4$. This formula tells us that there can be any proportion of Fe and Mg from $Fe_2SiO_4$ (pure fayalite) to $Fe_1Mg_1SiO_4$ to $Mg_2SiO_4$ (pure forsterite). This is shown schematically in figure 1.

In cases where solid solutions occur, it is convenient to think of a mineral structure as a collection of crystallographic sites (e.g., tetrahedral and octahedral sites) with specific linkages and arrangements in which variable but specific elemental constituents can reside. Indeed, Klein and Hurlbut (1999) state that "a solid solution is a mineral structure in which specific atomic site(s) are occupied in variable proportions by two or more different chemical elements (or groups)." Extreme cases are found in mineral groups such as apatite, amphibole, pyroxene, feldspar, and tourmaline. The formula for fluorapatite is $Ca_5(PO_4)_3F$, but numerous solid solutions occur among most of the crystallographic sites in its structure (fig. 2). To express this we can write the formula as $A_5(BO_4)_3C$ where the $A$-site can be occupied to varying degrees with Ca, Sr, Na, Mn, Fe, Y, Pb, Ba, La, Ce, U, Th, and so forth; the $B$-site with P, As, Si, V, S, and so forth; and the $C$-site with F, Cl, OH, and so forth (Pan and Fleet 2002). Because the structure of apatite allows for so many substitutions, many of which form complete or extensive solid solutions, there are more than twenty-eight different minerals with this structure, all of which are said to be apatite-group minerals.

There are actually three types of solid solution in minerals, namely, substitutional, interstitial, and omission solid solutions. Substitutional solid solution, the most common type, is where one ion substitutes for another in a regularly occupied crystallographic site. This is exemplified by olivine and apatite (described above). The relative sizes and charges of the ions that are substituting for one another as well as the temperature at which the substitutions take place determine the extent to which a given substitutional solid solution will occur. If all degrees of substitution are possible, it is said that it is a complete solid solution.

In the case where a solid solution occurs between two ions with different charges (e.g., Ca$^{2+}$ and La[sub3+] in fluorapatite), other substitutions must occur in order to maintain charge neutrality (a necessity for a stable mineral). This is known as a coupled substitution. In apatite, there are several known substitutions that can couple with the Ca[sub2+] $\leftrightarrow$ La[sub3+] substitution to maintain charge balance. These include Na$^{+1}$, Ca$^{2+}$, Si$^{4+}$, P$^{5+}$, O$^{2-}$, F$^-$, and a vacancy (an unoccupied Ca$^{2+}$) site represented as $\leftrightarrow$. These coupled substitutions can be expressed as follows:

\[ (1) \text{La}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Ca}^{2+} + \text{P}^{5+} \]
\[ (2) \text{La}^{3+} + \text{Na}^{1+} \leftrightarrow 2\text{Ca}^{2+} \]
\[ (3) \text{La}^{3+} + \text{O}^{2-} \leftrightarrow \text{Ca}^{2+} + \text{F}^{-} \]
\[ 4 \text{La}^{3+} \leftrightarrow 3\text{Ca}^{2+} \]

Note that if you add up all of the charges on the left and right side of each coupled substitution, they are equivalent. The $2\text{La}[\text{sub3+}] \leftrightarrow 3\text{Ca}^{2+}$ is an example of an omission solid solution, where the presence of a vacant site is part of the substitution.
In an interstitial solid solution, substituent atoms or ions are added to void spaces (interstitial sites) between normal atomic sites. The structure of fluorite, CaF$_2$, exemplifies this nicely (fig. 3). In fluorite, Ca$^{2+}$ is surrounded (coordinated) by 8 F$^-$ in a cubic geometry. These Ca-F$_8$ cubes alternate with cubically coordinated void spaces along the axial directions of the structure. A common group of substituents that form partial solid solutions with Ca in fluorite are the lanthanides (e.g., La). Lanthanide ions most commonly have a 3+ charge. Thus, if they are to substitute for Ca$^{2+}$, another substitution must be coupled with it to maintain charge neutrality. The most common substitution coupled with Ca$^{2+}$ ⇔ La$^{3+}$ is IS ⇔ F, where IS is an interstitial site. In everyday usage, the term solution is most commonly applied to a liquid. For instance, seawater is a solution in which solids such as NaCl and gases such as CO$_2$ and many other solids and gases are dissolved. Solutions can exist in any state of matter, however, including a gas solution (e.g., air), and as just discussed, a solid solution. In this issue of Rocks & Minerals, Simmons et al. describe recent tourmaline discoveries from Mount Mica, Maine. One of the pockets recently exposed at this deposit contained the tourmaline species schorl, elbaite, rossmanite, and foitite, which represent four different solid solutions in tourmaline. The substitutions in the tourmaline structure are so varied and extensive that mineralogists often refer to it as a "garbage can" mineral.

As one can imagine, with so many possible compositional variations due to solid solutions, the naming of minerals can get quite complicated. Nomenclature recommendations for solid solutions, as set forth by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association, can be found in Nickel (1992). This and other nomenclature recommendations of the CNMMN can be downloaded from the CNMMN Web site, http://www.geo.vu.nl/users/ima-cnmmn/.

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![Figure 1](http://www.novapdf.com)
Figure 2. Ball-stick representations of the apatite structure: (001) projection, and the A, B, and C atomic sites. There are two distinct A-sites, labeled A1 and A2, which are normally occupied by Ca. The complete coordination spheres of the A2 and B sites are not visible in this orientation.

Figure 3. Ball-stick (left) and polyhedral (right) representations of the fluorite structure. The
red sphere represents La\(^{3+}\) that has substituted for Ca\(^{2+}\) on a regularly occupied site with cubic coordination. An extra F\(^{-}\) is added to an interstitial site to charge balance the La\(^{3+}\) ⇔ Ca\(^{2+}\) substitution.

**REFERENCES**


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