

Geochemistry

Notes III:

I. Pure crystalline solids

II. Substitution

III. Solid Solution

Pure crystalline solids have a highly organized internal structure and have a composition that can be described with integral values for the proportions of every element in the solid.

Most naturally occurring crystalline solids (minerals) are not pure. We refer to these substances as solid solutions.

They are not pure because of substitution of ions of one or more element for ions of one or more other elements at a site or sites in a crystal.

Simple substitution refers to the substitution of ions of one element for ions of another element. In this case, the ions must have the same valence so that the crystal remains electrically neutral.

Coupled substitution refers to substitution of ions of 2 or more elements for ions of 2 or more other elements. The valences of the substituting ions differ from those of the ions that are being replaced. However, the total charge of the substituting ions must equal the total charge of the ions that are being replaced so that electrical neutrality is maintained.

In the case of a particular substitution (simple or coupled), one can envision a continuous range of compositions between two pure substances. The two pure substances are called end members. Solids that have compositions of either of the end members or compositions in between those of the end members are part of a solid solution series. For some solid solution series under the proper conditions, the compositions of both end members and all intermediate value are possible. However, in most cases not all intermediate compositions are possible, at least under some conditions. In the former case, we have complete solid solution; in the latter, limited solid solution. In general, solid solution is more extensive at high temperature.

One can characterize the composition of members of a solid solution series by the mole fraction of the end members.

Goldschmidt's Rules identify possible substitutions based on the chemical characteristics of pairs of elements. Those that are most important for our purposes are:

1. Ions of one element can replace those of another if their ionic radii are within 15% of each other.
2. Ions with charges different by one unit can substitute readily for one another (if coupled substitution is possible). If charge differences are greater than one unit, substitution is limited.

Goldschmidt also developed a geochemical classification of the elements based on observations of melts seen in ores during smelting. In this classification, elements are either lithophile (high concentrations in rocks), siderophile (high concentrations in Fe metal), chalcophile (high concentrations in sulfides), or atmophile (high concentrations in the atmosphere). See figure 8.3.