

# Solid solutions

A solid solution is a single phase which exists over a range of chemical compositions. Some minerals are able to tolerate a wide and varied chemistry, whereas others permit only limited chemical deviation from their ideal chemical formulae. In many cases, the extent of solid solution is a strong function of temperature, with solid solution being favoured at high temperatures and unmixing and/or ordering favoured at low temperatures.

Types of solid solution:

1. *Substitutional solid solution*: chemical variation is achieved simply by substituting one type of atom in the structure by another.
2. *Coupled substitution*: this is similar to the substitutional solid solution, but in a compound cations of different valence are interchanged. To maintain charge balance, two coupled cation substitutions must take place.
3. *Omission solid solution*: chemical variation is achieved by omitting cations from cation sites that are normally occupied.
4. *Interstitial solid solution*: chemical variation is achieved by adding atoms or ions to sites in the structure that are not normally occupied.

Factors affecting the extent of solid solution:

1. *Atomic/ionic size*: If the atoms or ions in a solid solution have similar ionic radii, then the solid solution is often very extensive or complete. Generally, if the size difference is less than about 15%, then extensive solid solution is possible. For example,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  have a size mismatch of only about 7%,

and complete solid solution between these two elements is observed in a wide range of minerals. However, there is a 32% size difference between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and we expect very little substitution of Mg for Ca to occur in minerals.

2. *Temperature*: High temperatures favour the formation of solid solutions, so that endmembers which are immiscible at low temperature may form complete or more extensive solid solutions with each other at high temperature. High temperatures promote greater atomic vibration and open structures, which are easier to distort locally to accommodate differently-sized cations. Most importantly, solid solutions have a higher entropy than the endmembers, due to the increased disorder associated with the randomly distributed cations, and at high temperatures, the  $-TS$  term in the Gibb's free energy stabilises the solid solution.
  
3. *Structural flexibility*: Although cation size is a useful indicator of the extent of solid solution between two endmembers, much depends on the ability of the rest of the structure to bend bonds (rather than stretch or compress them) to accommodate local strains.
  
4. *Cation charge*: Heterovalent substitutions (i.e. those involving cations with different charges) rarely lead to complete solid solutions at low temperatures, since they undergo complex cation ordering phase transitions and/or phase separation at intermediate compositions. These processes are driven by the need to maintain local charge balance in the solid solution as well as to accommodate local strain.

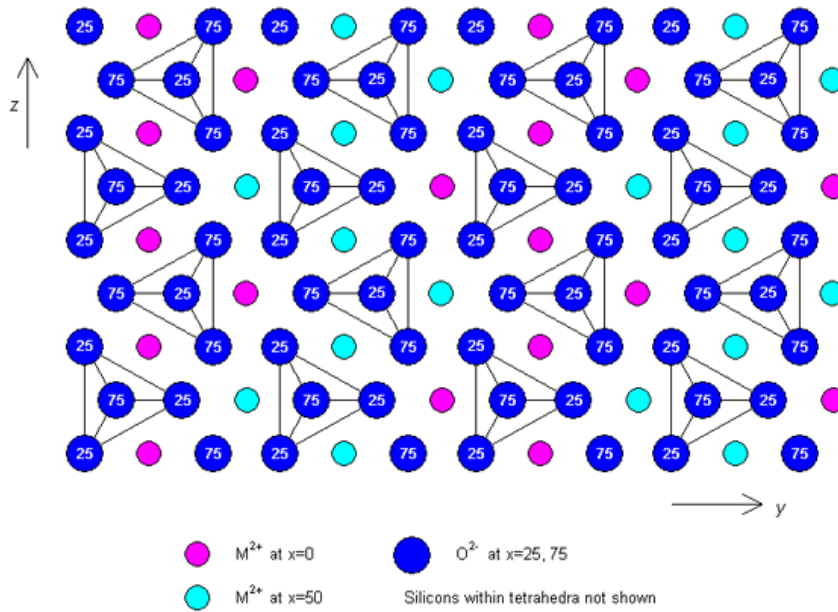
## Olivine

Olivine is a name for a series of minerals with the formula  $M_2SiO_4$ , where M is most commonly Fe or Mg. Fayalite ( $Fe_2SiO_4$ ) and forsterite ( $Mg_2SiO_4$ ) form a substitutional solid solution where the iron and magnesium atoms can be substituted for each other without significantly changing the crystal structure. As mentioned previously, there is a size mismatch of only about 7% between  $Mg^{2+}$  and  $Fe^{2+}$ , so complete solid solution between these two elements is observed in olivine.

Olivine has an orthorhombic structure. A typical set of lattice parameters for an unspecified composition are:  $a = 0.49$  nm,  $b = 1.04$  nm,  $c = 0.61$  nm. The structure consists of isolated  $SiO_4^{4-}$  tetrahedra, which are held together by M cations occupying two types of octahedral site (M1 and M2). The isolated tetrahedra point alternately up and down along rows parallel to the  $z$ -axis.

Alternatively, the structure can be described as an approximately hexagonal close-packed array of oxygen anions, with M cations occupying half of the octahedral sites, and Si cations occupying one eighth of the tetrahedral sites. If the hexagonal close packing were ideal, the M1 and M2 sites would be regular octahedra, and identical in size, but since the packing is not ideal, the M2 sites are slightly larger and more distorted than the M1.

A plan view of the structure projected along the  $x$ -axis is shown below.



Source: <http://www.doitpoms.ac.uk/tlplib/solid-solutions/solid-solutions.php>