Crystal Chemistry, Mineral Structures and Element Substitution — part II

In the first part of the lab we explored different kinds of anion packing, and the symmetry of these packing arrangements. We also investigated the nature of the interstices or holes between the anions and the sizes and symmetry associated with these interstices, and calculated the critical radius ratios of cations that allow them to coordinate ideally with anions in 6- and 8-fold configurations found in minerals. Now, we will make some mineral structures and learn a few of the subtleties of crystal chemistry.

The principle that *cations occupy interstices between anions on the basis of their size or radius ratio to the anion* is called **Pauling's first rule**. The principle is very powerful and can be used to predict which cations may substitute for each other in a mineral structure. We will discover a few other of Pauling's rules in the course of today's lab, but none is more important than the first.

We will start the lab by looking at the crystal structure of olivine $(Mg^{+2}, Fe^{+2})_2SiO_4$. To an excellent approximation, olivine can be viewed as an hcp lattice of oxygen anions with Mg^{+2}, Fe^{+2} and Si^{+4} occupying interstices in the lattice. If time permits, we will try to build the forsterite structure from styrofoam balls, but to begin with, study the wire-frame model and structure diagrams.

Structure of olivine
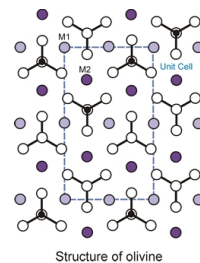
Using the ionic radii of Mg^{+2} and Si^{+4} and radius ratios for different co-ordination numbers which kinds of sites will most likely be occupied by these ions?

- There will be far more sites of both kinds available than there are Mg^{+2} and Si^{+4} in olivine

How do you decide on which are occupied? Do you try to maintain the highest symmetry in the structure? Do you try to keep the cations as far apart as possible? Do you give preference to arranging one kind of cation over another?

Think about alternative arrangements using these principles. Write down brief descriptions of what you get.

- Pauling analyzed hundreds of crystal structures and asked similar questions to the ones posed above. He came up with the following rules:

(Pauling's second rule): A *structure will be stable to the extent that the sum of the strength of the electrostatic bonds that reach an anion equals the charge on that anion* [the strength is defined as the charge divided by the coordination number of the cation].

(Pauling's third rule): *Sharing of edges and particularly faces by two anion polyhedra decreases the stability of an ionic crystal structure.*

(Pauling's fourth rule): *In a crystal structure containing different cations, those of high valency* and *small coordination number tend not to share polyhedral elements with each other.*

> Examine the olivine structure and see if it follows Pauling's rules two through four. Make some brief notes about the arrangement of the cations and their polyhedral sites in the structure.

Remember that there is an implicit rule about crystal structures that we often forget. They must be periodic; that is, the placement of atoms must be duplicated by some regular translation of the structural units in all three dimensions.

> Does your olivine structure have hexagonal symmetry like the hcp anion lattice? Explain.

Now, let's think about substituting Fe^{+2} cations for some of the Mg^{+2}. We will use the red Styrofoam balls to represent Fe^{+2}. In this lab, these are the same size as our Mg^{+2} atoms. In reality, octahedral Fe^{+2} has an ionic radius of 0.78 nm, larger than that of Mg^{+2} (0.72 nm).

> Given the size difference, how well would Fe substitute for Mg in the structure you have created?

> The size mismatch that results from trying to substitute a cation of a different size for another in a mineral structure is associated with an energy change for the structure. Do you think that energy is positive (destabilizing the structure) or negative (stabilizing the structure) and why?

The green 1.5-inch diameter Styrofoam balls are about the size of Ca^{+2} cations.

> Do you think it is possible to make Ca^{+2} substitute for Mg^{+2} in the olivine structure? How about Al^{+3}?

As a class exercise, we may try to construct a forsterite model from the styrofoam balls. Use the large 2 inch diameter Styrofoam balls to construct two layers of an hcp lattice. Now place the small blue- and red-painted balls to represent Mg^{+2} and Si^{+4}, respectively, thinking about Pauling's rules as you build the structure. The wire-frame model will be an essential guide for getting the cations into the right sites (because, like all silicates based on closed-packed oxygen layers, the structure has more vacancies than filled sites).