Today’s Goal: Finish crystals, brief discussion of silicate liquids, brief intro to spectroscopy.

Plan:
1. Ions in crystals (and more on solutions):
   a. Ionic crystals simple: NaCl example
   b. Mg-O bonds: ~23% covalent
   c. Si-O bonds: ~50% covalent
   d. C-O bonds: ~80% covalent (note C right above Si in periodic table)
   e. Silicate minerals:
      i. SiO$_4^{4+}$ units
      ii. One SiO$_4^{4+}$ unit can share O’s with others
      iii. Example: Quartz… awkward 3-D network
      iv. Feldspars: 3-D network with Al and cations
   f. Micas:
      i. Sheets of silicate tetrahedra (Si$_2$O$_5$: - charge overall)
      ii. Sandwiched by sheets of cations (+ charge)
         a. Mg in octahedral coordination
         b. Fe can substitute for Mg
         c. Al$_2$O$_3$ sheets
   g. Leftover charge balanced by loose ions in between layers
   h. Clays: similar to micas, but with H’s in the structure
   i. Pyroxenes- silicate tet’s forms chains glued together by , Mg$^{2+}$, Ca$^{2+}$ and Fe$^{2+}$.
   j. Olivine- isolated tet’s, glued together by Mg$^{2+}$ and Fe$^{2+}$
2. Substitution rules (SEE FAURE FOR LIST OF GOLDSCHMIDT’S RULES)
   a. Dominant elements determine a crystal’s “sites”
   b. Why and when do other elements substitute for the major ions?
   c. Think of a crystal growing from an aqueous solution or silicate liquid…
      i. Atoms added at steps, for example…like building a brick wall.
      ii. The bricks must fit (both charge and size) if not, there’s a good chance they will pop out and get replaced by something better before they get covered by another layer
      iii. Tendency for higher ionic potential ions to be preferred…get bonded in more tightly- e.g., olivine prefers Mg over Fe (“capture”)- important exceptions to this
      iv. Reverse is true for lower ionic potential ions (“admission”)
      v. Bond type differences (covalent vs. ionic)
   d. But what if size is the same but charge is different?
i. e.g., Ca\(^{2+}\) for Na\(^+\)
ii. Coupled substitution: e.g., substitute Al\(^{3+}\) for Si\(^{4+}\) in neighboring site to compensate for extra + on Ca

3. Partition Coefficients/Distribution Coefficients for minor/trace elements
   a. Concentration ratio, D- T and/or P dependent
   b. Sometimes useful as a T or P indicator
      i. liquid/crystal ratios useful if liquid is preserved (rare)
      ii. crystal/crystal ratios if you know 2 crystals formed from the same liquid

4. Ions in silicate liquids
   a. Short-range order is similar to crystals-
      i. Silicate tetrahedral may be isolated or connected (polymerized)
      ii. E.g., Chains, sheets, depending on the amount of silica in the melt
         1. amount of polymerization determines viscosity
         2. Low silica melts- low polymerization, low viscosity
         3. High silica- more polymerization, high viscosity
      iii. Cation coordination similar to crystals, some differences
   b. Long-range disorder, loss of rigidity

5. Jargon used for grouping elements:
   a. Siderophile- in the core, Fe-loving
   b. Chalcophile- in sulfides, sulfur-loving
   c. Lithophile- in silicates, stone-loving
   d. Atmophile- in atmosphere

6. Spectroscopy: Photon-matter interactions
   a. Important: Specific energies of photons- emission and absorption
      i. Atoms and ions CANNOT absorb energy at all wavelengths
      ii. Specific energies/wavelengths only
   b. Energies depend on:
      i. Type of atom
         1. heavier elements have greater charge on nucleus, and thus greater binding energies for each electron type
         2. DIFFERENCES between levels, and thus the energies of the photons emitted or absorbed, also increase with atomic number
         3. for example, see x-ray energies at:
            http://www.edax.com/support/EDS_Periodic_Table.html
      ii. Electronic config.
      iii. Bonding
   c. Inner electrons- generally x-rays
      i. X-ray fluorescence (XRF): Use to get chemical data on rock powders. Hit sample with intense x-ray beam, measure x-rays given off at other wavelengths
ii. X-ray absorbance spectroscopy (XAS): usually synchrotron x-rays are used, so they can be very intense and very fine details in the spectra can be measured; x-ray absorption energies are somewhat sensitive to bonding

d. Outer electrons - UV-Visible

i. Visible colors- ions without d electrons are usually not colored

ii. ICP- OES (Inductively coupled plasma optical emission spectroscopy): Inject aqueous sample into a plasma. Temperature is so high that outer electrons are elevated to higher energy levels, then decay back down again to lower energies. Emitted photons are in the visible and UV range.

iii. AA (atomic absorption): Inject aqueous sample into a flame. Each element has certain wavelengths at which it will absorb photons. Outer electron transitions.

iv. Atomic Emission: Inject aqueous sample into a flame. Not as hot as a plasma, but a few elements (e.g., Na, K) have outer electrons that can be elevated to higher levels anyway.

v. Colorimetry- Measure the absorbance of certain visible or UV wavelengths. For example, Cr(VI) bearing solutions are strongly yellow when concentrated. Usually, an organic reagent is added to bind with the ion of interest and greatly increase its absorbance of certain wavelengths. Good for only a few elements (e.g., Fe, Cr, Mn)

e. Bonds (e.g., C-O stretch in carbonate)- infrared

i. Infrared spectroscopy can be used to detect certain bonds, such as O-H or C-O bonds in crystals, glasses, maybe liquids?

f. Unstable nuclei decay- gamma rays