Geology 284 - Mineralogy, Fall 2009
Dr. Helen Lang, West Virginia University

Ionic Radius and Cation Substitution in Minerals

see Chapter 13, Perkins

Effective Ionic Radius

- Measure bond lengths of oxides
- Assume average ionic radius for O^{2-} of 1.32Å
- It is possible to tabulate ionic radii of common cations
- Ionic radii depend on Coordination Number, C.N. = number of nearest-neighbor anions of a cation

Coordination Number with Oxygen

- Tetrahedral Coordination
- C.N. = 4
- Smaller cations (Si^{4+}, Al^{3+}) fit

- Octahedral Coordination

- C.N. = 6
- Medium sized cations (Mg^{2+}, Fe^{2+}, Ca^{2+}, Na^{2+}) fit

- Cubic Coordination or higher
- C.N. = 8
- Large cations (K^{+}) fit

Periodic Table with Effective Ionic Radii (see handout)

Effective Ionic Radii of Common Cations and Anions (see handout)

Two Cations substitute readily for each other if:

- their ionic radii differ by less than about 15%

- they have the same charge, or if their charges differ, the charge difference must be compensated by another substitution elsewhere in the mineral
- they form bonds of similar character – related to electronegativity

Substitution is easier and more common at high temperature than at low temperature

Ions that readily substitute for each other

- $Mg^{2+} \leftrightarrow Fe^{2+} \leftrightarrow Mn^{2+}$

  very common substitutions in mafic silicates
- $Mg^{2+} \leftrightarrow Fe^{2+} \leftrightarrow Mn^{2+} \leftrightarrow Ca^{2+}$

  Ca^{2+} substitutes for Mg^{2+}, Fe^{2+} in some silicates
- $Ca^{2+} \leftrightarrow Na^{1+}$ in plagioclase

  must be coupled to $Al^{3+} \leftrightarrow Si^{4+}$

  written [$Ca^{2+}Al^{3+} \leftrightarrow Na^{1+}Si^{4+}$]
- $Al^{3+} \leftrightarrow Si^{4+}$ in some of the tetrahedra (C.N.=4) in sheet silicates, requires presence of K^{+} or Na^{+} between t-o-t sandwiches to balance the charge

Ions that readily substitute for each other

(continued)

- Na^{1+} (1.08Å) ↔ K^{1+} (1.46Å) in alkali feldspar violates the <15% size difference rule (~30% difference)

  That's the driving force for exsolution – perthites!
- Fe^{3+} and Al^{3+} can substitute for Mg^{2+}, Fe^{2+} in octahedral positions, but they're a little small, and the charge difference must be compensated

Anions also substitute for each other

- F^- and Cl^- commonly substitute for $(OH)^-$
- Br^- for Cl^- in halides
- Se^{-2} for S^{-2} in sulfides