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GEOLOGY 284: MINERALOGY

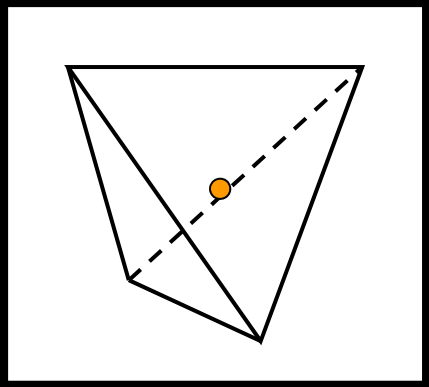
Ionic Radius and Cation Substitution in Minerals

see Chapter 13, Perkins

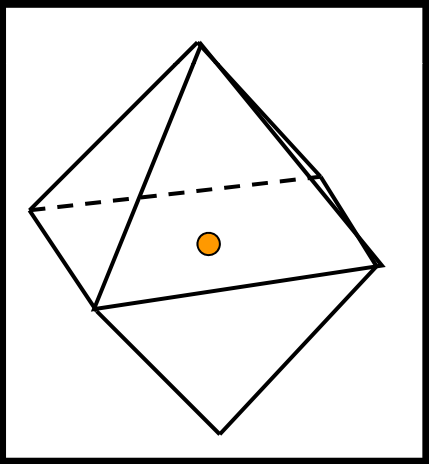
Effective Ionic Radius

- Measured 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

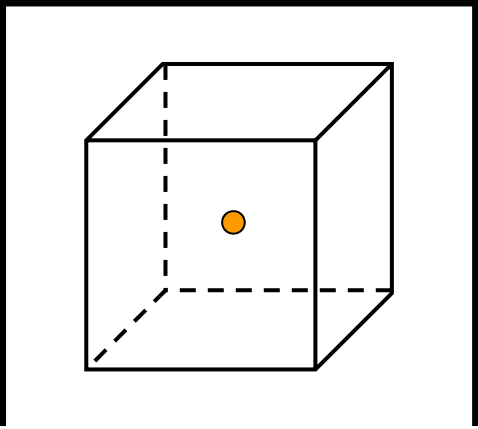
Coordination Number with Oxygen



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

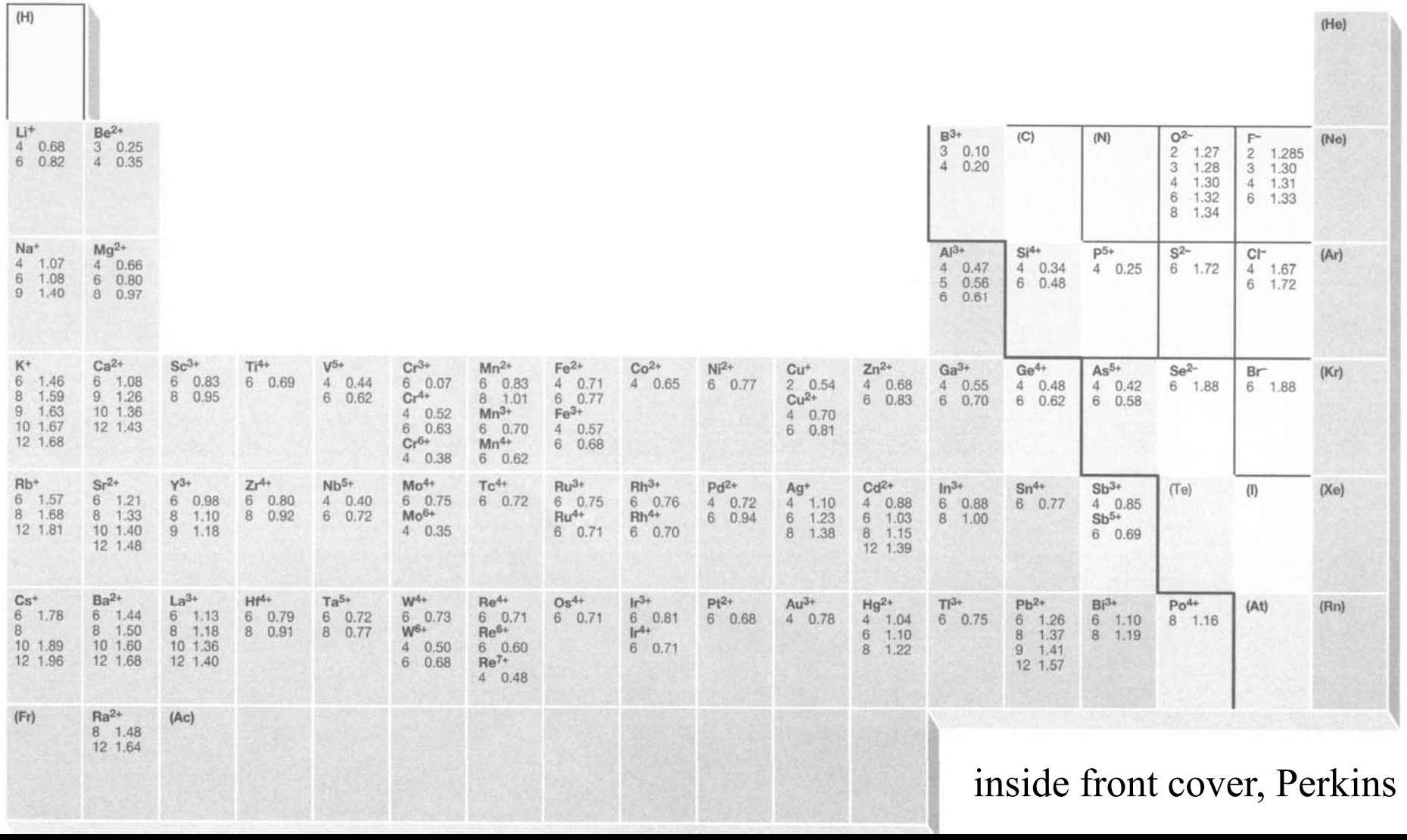


- Octahedral Coordination
- C.N. = 6
- Medium sized cations (Mg^{2+}, Fe^{2+}, Ca^{2+}, Na^{2+}) fit



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

Periodic Table with Effective Ionic Radii



(H)																(He)
Li^{+} 4 0.68 6 0.82	Be^{2+} 3 0.25 4 0.35											B^{3+} 3 0.10 4 0.20	(C)	(N)	O^{2-} 2 1.27 3 1.28 4 1.30 6 1.32 8 1.34	F^{-} 2 1.285 3 1.30 4 1.31 6 1.33	(Ne)
Na^{+} 4 1.07 6 1.08 9 1.40	Mg^{2+} 4 0.66 6 0.80 8 0.97											Al^{3+} 4 0.47 5 0.56 6 0.61	Si^{4+} 4 0.34 6 0.48	P^{5+} 4 0.25	S^{2-} 6 1.72	Cl^{-} 4 1.67 6 1.72	(Ar)
K^{+} 6 1.46 8 1.59 9 1.63 10 1.67 12 1.68	Ca^{2+} 6 1.08 9 1.26 10 1.36 12 1.43	Sc^{3+} 6 0.83 8 0.95	Ti^{4+} 6 0.69	V^{5+} 4 0.44 6 0.62	Cr^{3+} 6 0.07 Cr^{4+} 4 0.52 6 0.63 Cr^{6+} 4 0.38	Mn^{2+} 6 0.83 8 1.01 Mn^{3+} 6 0.70 Mn^{4+} 6 0.62	Fe^{2+} 4 0.71 6 0.77 Fe^{3+} 4 0.57 6 0.68	Co^{2+} 4 0.65	Ni^{2+} 6 0.77	Cu^{+} 2 0.54 Cu^{2+} 4 0.70 6 0.81	Zn^{2+} 4 0.68 6 0.83	Ga^{3+} 4 0.55 6 0.70	Ge^{4+} 4 0.48 6 0.62	As^{5+} 4 0.42 6 0.58	Se^{2-} 6 1.88	Br^{-} 6 1.88	(Kr)
Rb^{+} 6 1.57 8 1.68 12 1.81	Sr^{2+} 6 1.21 8 1.33 10 1.40 12 1.48	Y^{3+} 6 0.98 8 1.10 9 1.18	Zr^{4+} 6 0.80 8 0.92	Nb^{5+} 4 0.40 6 0.72	Mo^{4+} 6 0.75 Mo^{6+} 4 0.35	Tc^{4+} 6 0.72	Ru^{3+} 6 0.75 Ru^{4+} 6 0.71	Rh^{3+} 6 0.76 Rh^{4+} 6 0.70	Pd^{2+} 4 0.72 6 0.94	Ag^{+} 4 1.10 6 1.23 8 1.38	Cd^{2+} 4 0.88 6 1.03 8 1.15 12 1.39	In^{3+} 6 0.88 8 1.00	Sn^{4+} 6 0.77	Sb^{3+} 4 0.85 Sb^{5+} 6 0.69	(Te)	(I)	(Xe)
Cs^{+} 6 1.78 8 10 1.89 12 1.96	Ba^{2+} 6 1.44 8 1.50 10 1.60 12 1.68	La^{3+} 6 1.13 8 1.18 10 1.36 12 1.40	Hf^{4+} 6 0.79 8 0.91	Ta^{5+} 6 0.72 8 0.77	W^{4+} 6 0.73 W^{6+} 4 0.50 6 0.68	Re^{4+} 6 0.71 Re^{6+} 6 0.60 Re^{7+} 4 0.48	Os^{4+} 6 0.71	Ir^{3+} 6 0.81 Ir^{4+} 6 0.71	Pt^{2+} 6 0.68	Au^{3+} 4 0.78	Hg^{2+} 4 1.04 6 1.10 8 1.22	Tl^{3+} 6 0.75	Pb^{2+} 6 1.26 8 1.37 9 1.41 12 1.57	Bi^{3+} 6 1.10 8 1.19	Po^{4+} 8 1.16	(At)	(Rn)
(Fr)	Ra^{2+} 8 1.48 12 1.64	(Ac)															

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Effective Ionic Radii of Common Cations and Anions

Ion	C.N.* w/ Ox.	Ionic Radius Å
O^{2-}		1.32
F^{-}		1.33
Cl^{-}		1.72
K^{+}	8	1.59
K^{+}	6	1.46
Na^{+}	6	1.08
Ca^{2+}	6	1.08
Mg^{2+}	6	0.80
Mn^{2+}	6	0.83
Fe^{2+}	6	0.77
Fe^{3+}	6	0.68
Al^{3+}	6	0.61
Al^{3+}	4	0.47
Si^{4+}	4	0.34

*C.N. = Coordination Number = number of nearest anion neighbors

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 – i.e., they have similar electronegativity

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

Ions that readily substitute for each other

Ion	C.N.* w/ Ox.	Ionic Radius Å
O^{2-}		1.32
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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, charges different,
  must be coupled to $Al^{3+} \leftrightarrow Si^{4+}$ to balance charge
  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

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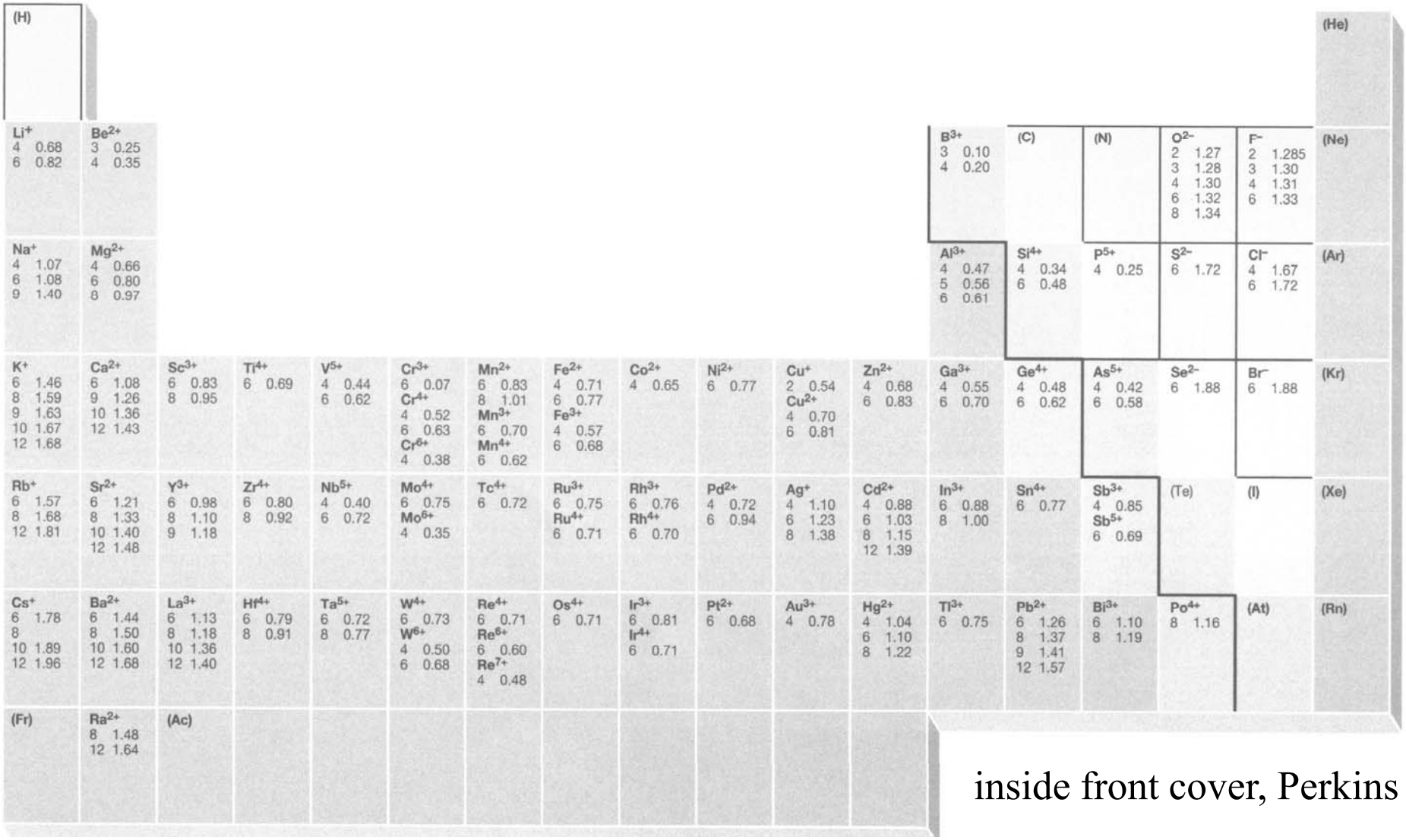

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