

Announcements

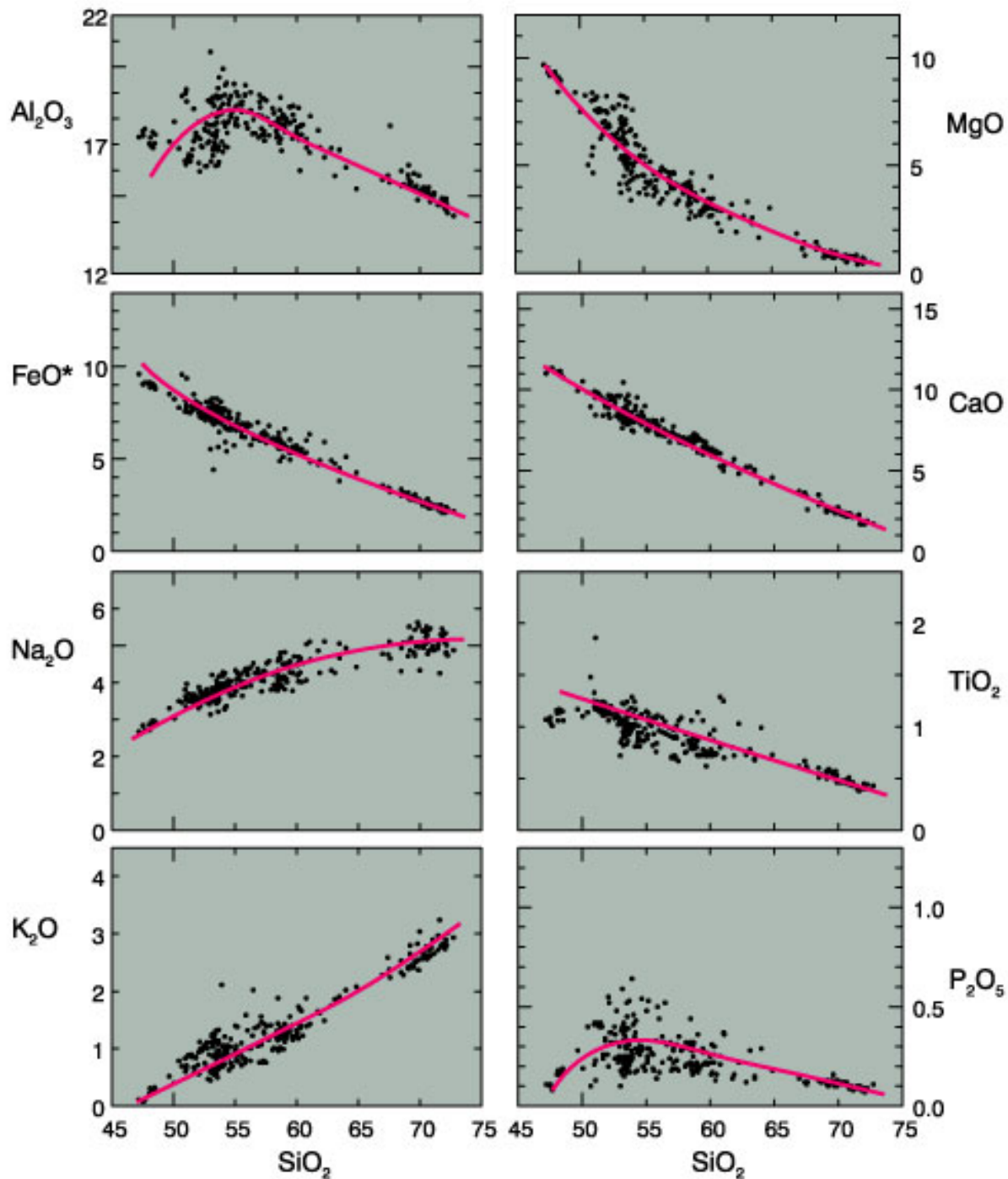
- **Reading: p.155-160**
- **Important not to fall behind in reading or assignments!**
- **Turn in field trip notes at the end of next week**
- **Gimme your pictures**
- **Homework 3 due May 8**

Harker diagram for Crater Lake

Closure
problem!

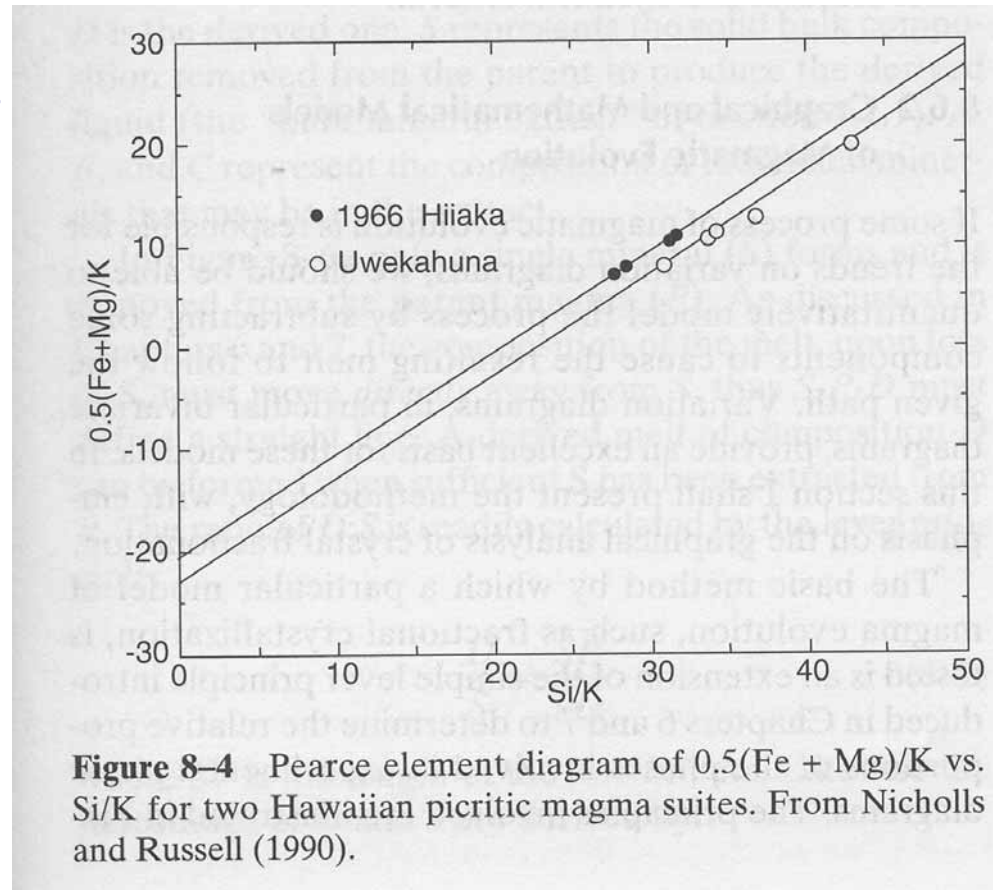
What does this
mean?

Figure 8-2. Harker variation diagram for 310 analyzed volcanic rocks from Crater Lake (Mt. Mazama), Oregon Cascades. Data compiled by Rick Conrey (personal communication).



Pearce Diagrams

- Molar units (elements or oxides)
- Ratio to a “perfectly” incompatible element (stays in melt)
- Way to test a hypothesis, or negate one
- Not a way to prove fractional crystallization



The Basalt Tetrahedron and the Ne-Ol-Q base

Alkaline and subalkaline fields are again distinct

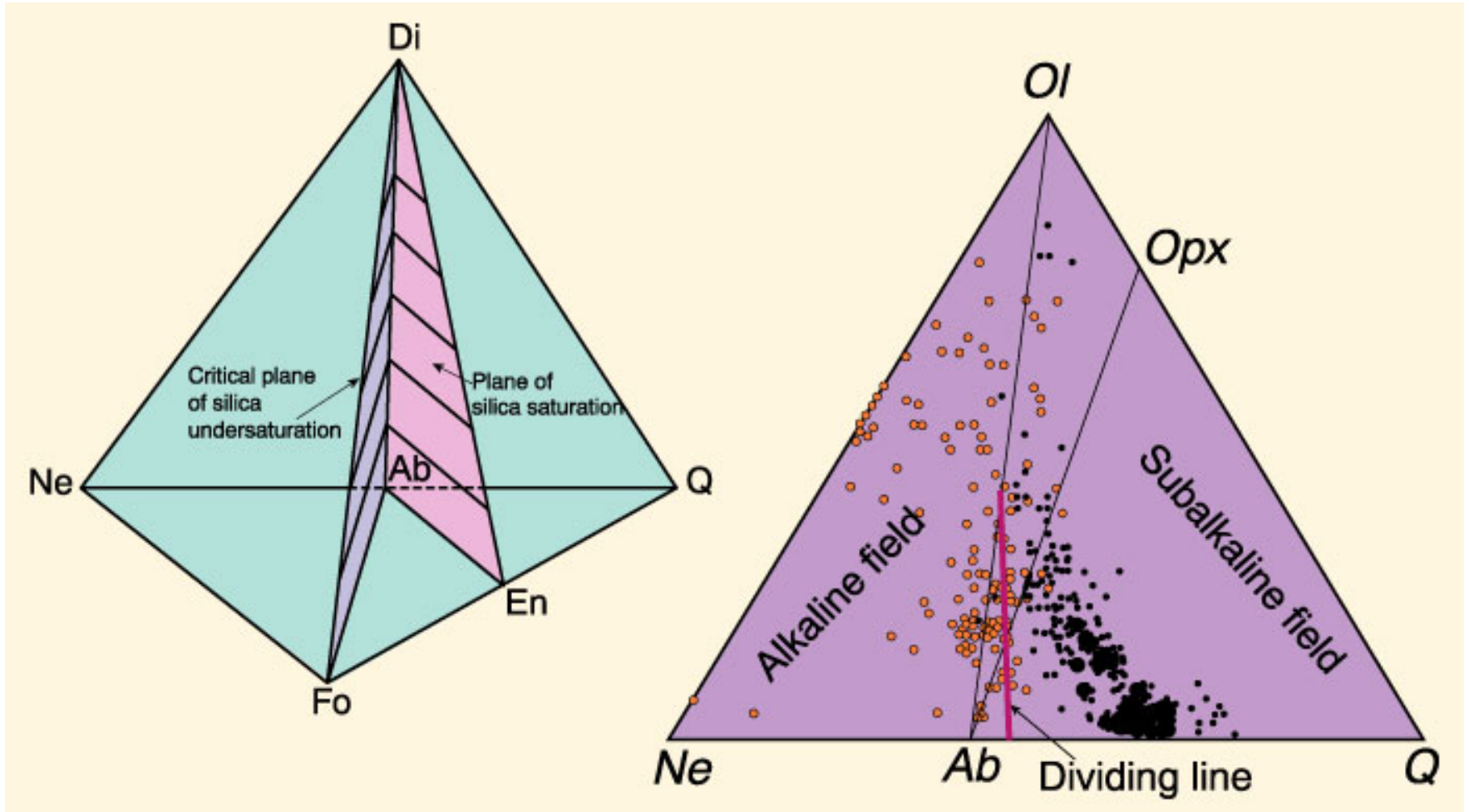
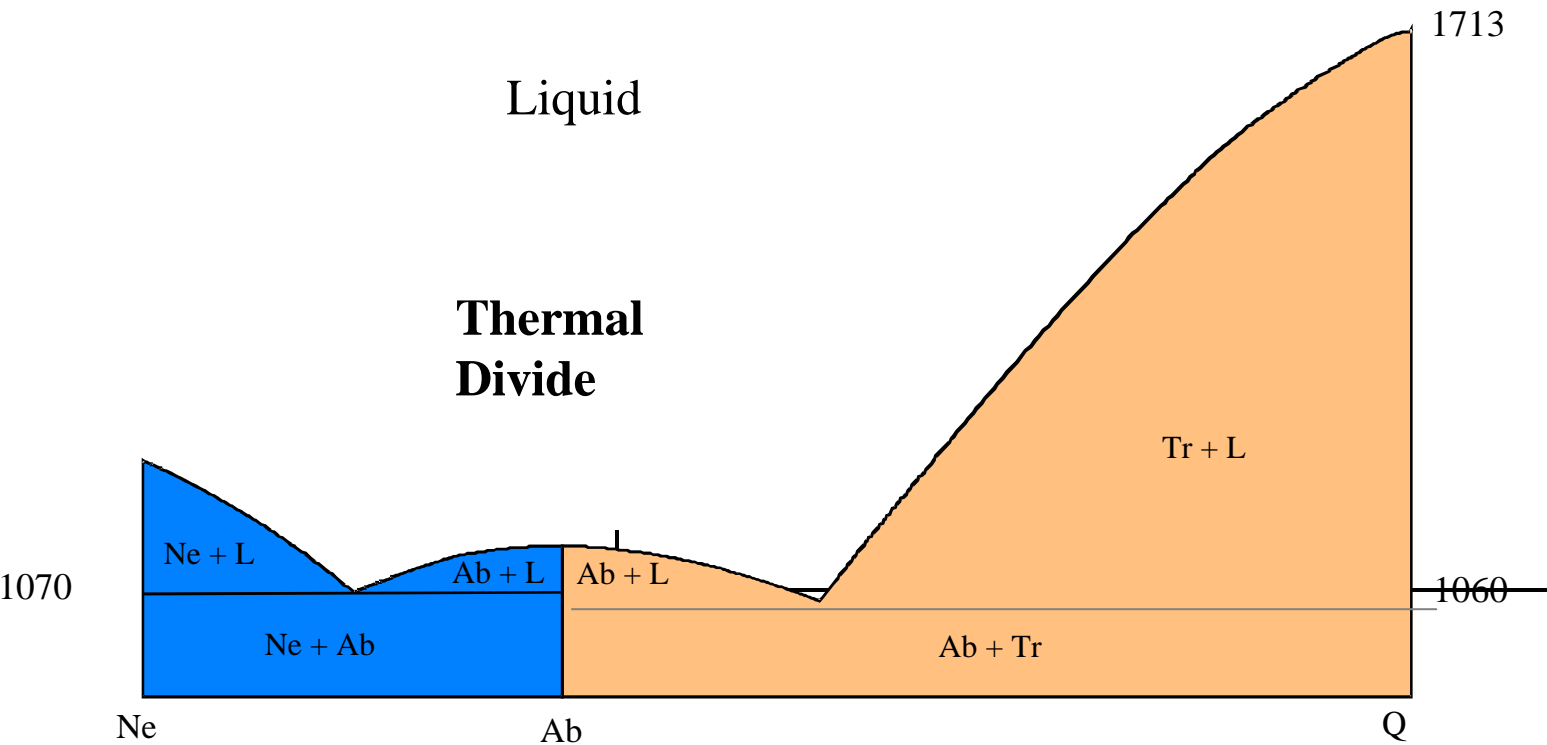
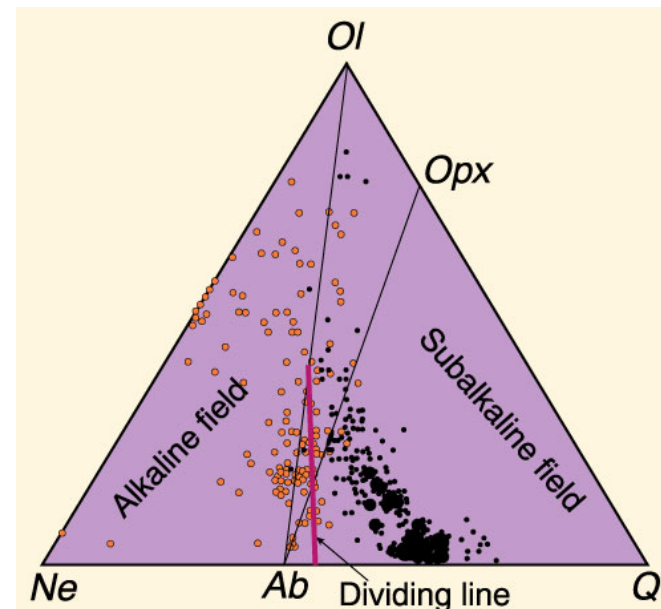


Figure 8-12. Left: the basalt tetrahedron (after Yoder and Tilley, 1962). *J. Pet.*, 3, 342-532. Right: the base of the basalt tetrahedron using cation normative minerals, with the compositions of subalkaline rocks (black) and alkaline rocks (gray) from Figure 8-11, projected from Cpx. After Irvine and Baragar (1971). *Can. J. Earth Sci.*, 8, 523-548.

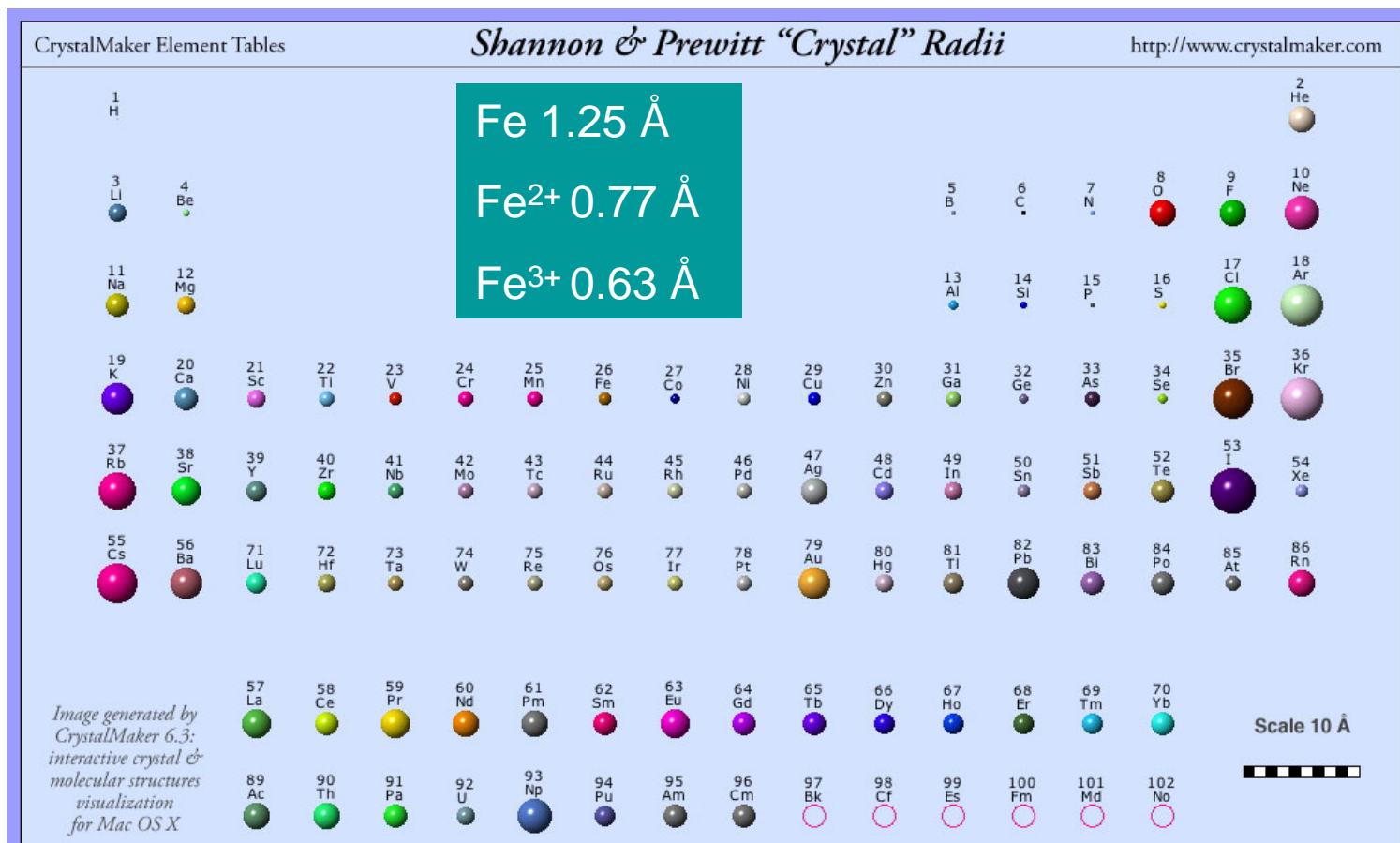


Thermal divide separates the silica-saturated (subalkaline) from the silica-undersaturated (alkaline) fields at low pressure

Cannot cross this divide by FX, so can't derive one series from the other (at least via low-P FX)

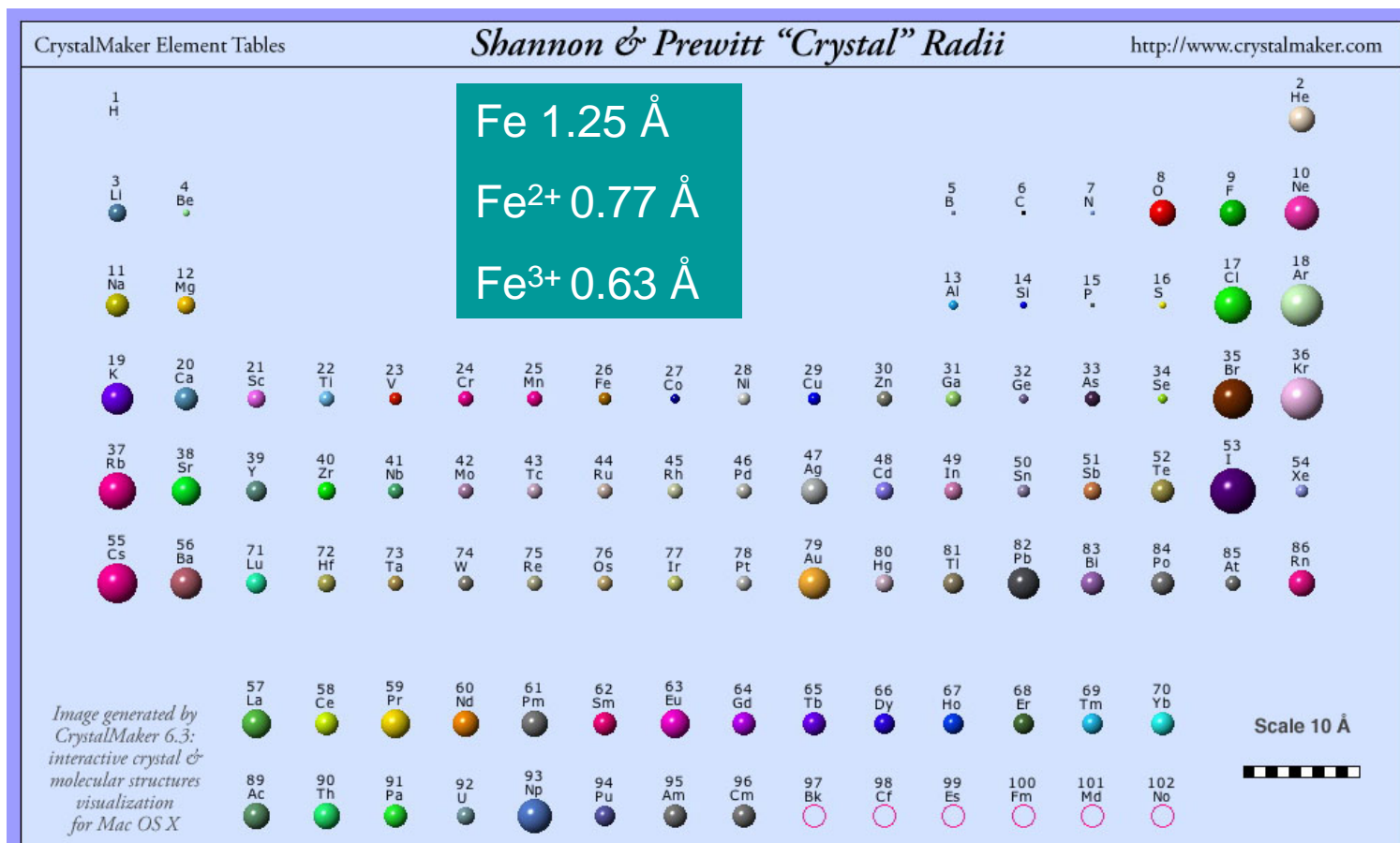


Ionic radii



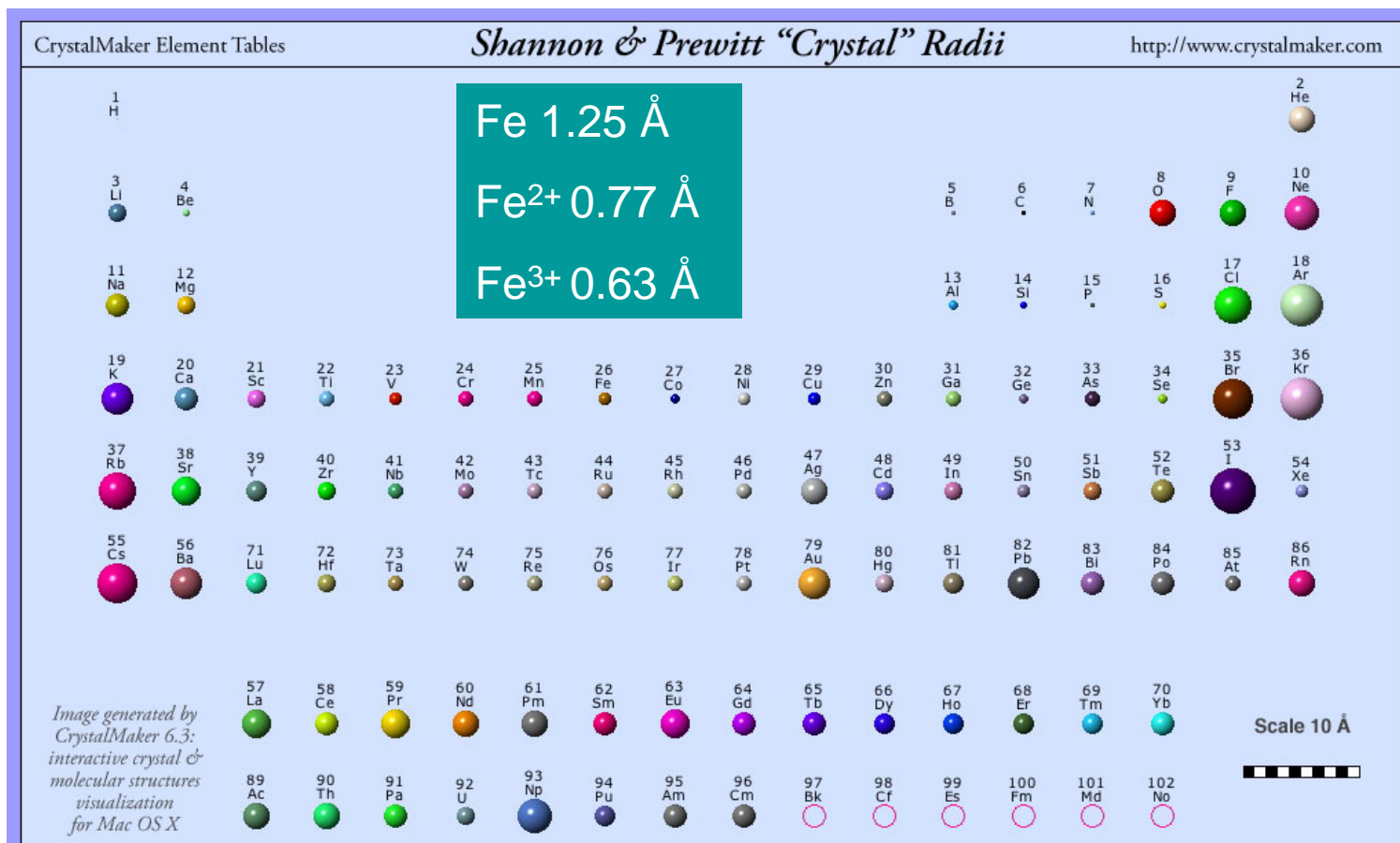
- Cations are smaller than neutral atoms, anions are larger. For a given element, size decreases with increasing charge.

Ionic radii



- Ionic radius increases down a chemical group. Many exceptions: REE's, many d-block transition elements

Ionic radii



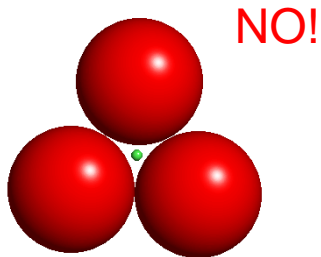
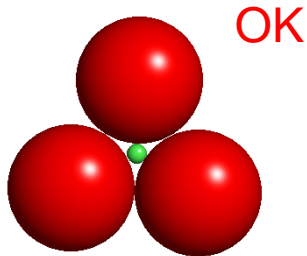
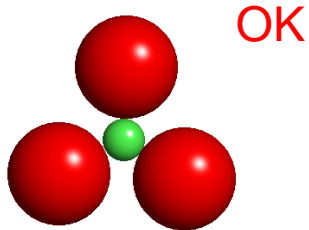
- For ions with same electronic structure within a period (i.e., Na⁺, Mg²⁺) size decreases with increasing charge (increasing attractive charge of nucleus)

Pauling's Rules



- Basic mineral structures can be understood by looking at the relative sizes and the charges of different elements in their common oxidation states!
- Nobel Prize in Chemistry 1954:
 - “for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances”
- Nobel Peace Prize 1962

Pauling's Rules

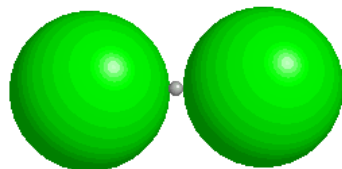


1. The Coordination Principle

- Cation-anion distance is determined by the sum of the cation and anion radii
- Number of anions coordinating with cation is determined by relative size of cation and anions.
 - Cations want to fit snugly in anions- equal bonding environments for all.
 - Assumptions!

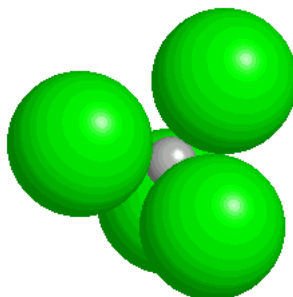
Pauling's Rules

$$RR = R_c/R_a$$



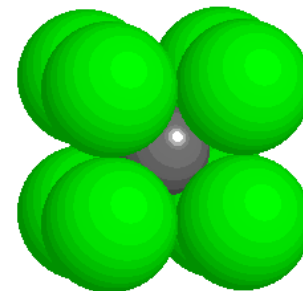
$$CN = 2$$

$$RR < 0.155$$



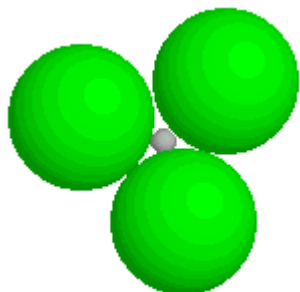
$$CN = 4$$

$$RR = 0.225-0.414$$



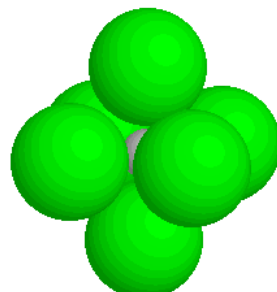
$$CN = 8$$

$$RR = 0.732-1$$



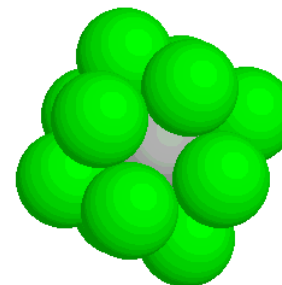
$$CN = 3$$

$$RR = 0.155-0.225$$



$$CN = 6$$

$$RR = 0.414-0.732$$



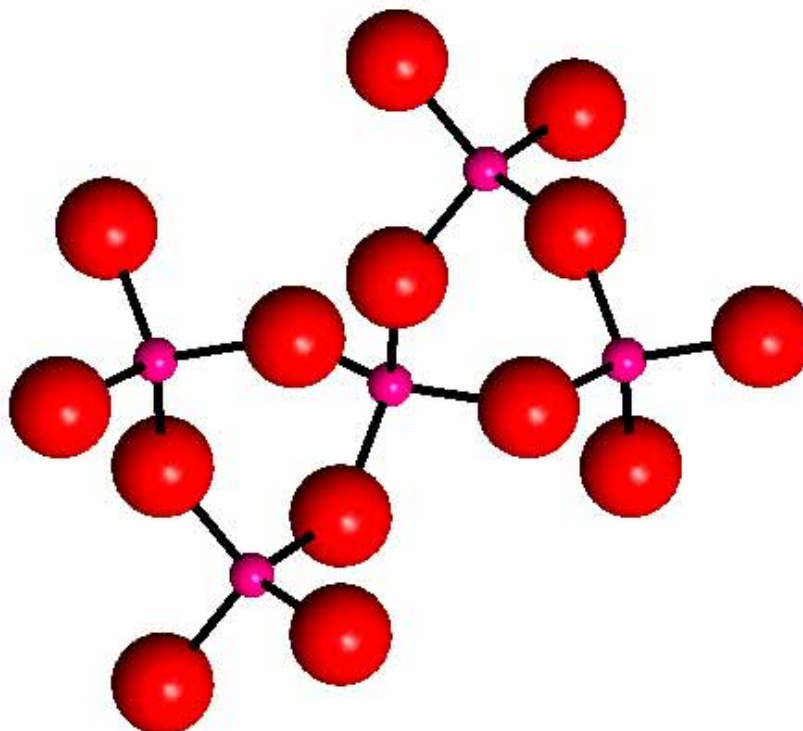
$$CN = 12$$

$$RR \sim 1$$

Pauling's Rules

2. The Electrostatic Valency Principle

Total strength of valency bonds that reach an anion from all neighboring cations = charge of anion.



Pauling's Rules

3. Sharing of Polyhedral Elements I

The stability of ionic structures is decreased when coordination polyhedra share edges and faces.

Melting temperature of

Forsterite = 1890 °C

Enstatite = 1550 °C

4. Sharing of Polyhedral Elements II

In a crystal containing different cations, large valence, small CN cations tend not to share polyhedral elements with each other.

More than half of ionic charge is occupied with small, highly-charged cation: CO_3^{2-} , PO_4^{3-}

Pauling's Rules

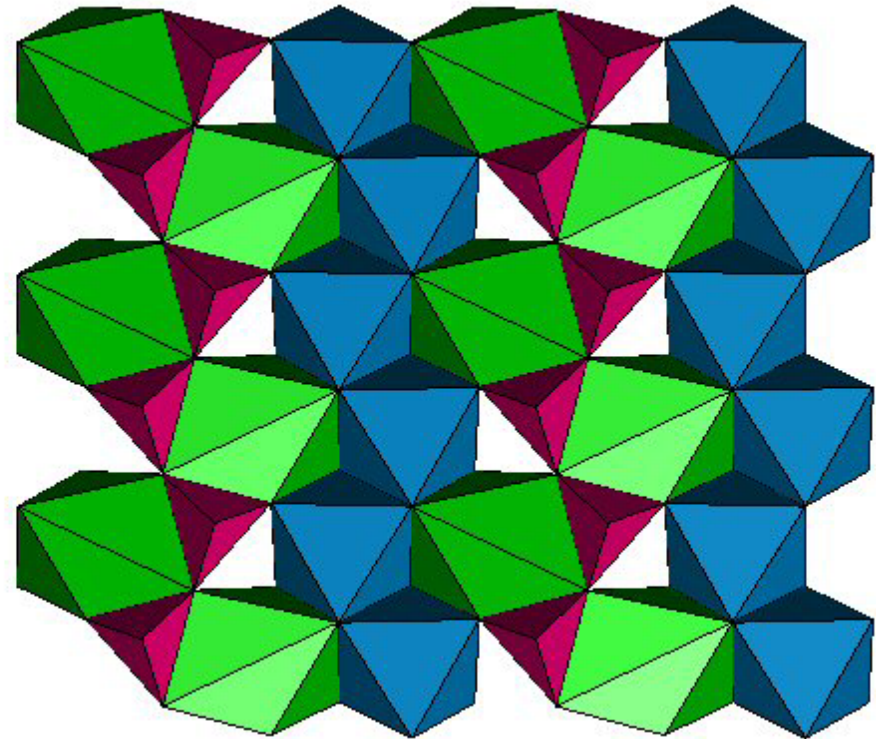
5. Principle of Parsimony

Nature tends towards simplicity!

Mineral structures tend to be simple, with only one or a few different cation sites – but each may accommodate many different cations.

M1 = Mg, Fe²⁺, Fe³⁺, Al

M2 = Mg, Fe²⁺, Ca, Na, Li



Goldschmidt's Rules: general guidelines

Cation A^{X+} :

Radius = R_A
Charge = X



Cation B^{Y+} :

Radius = R_B
Charge = Y



$$R_A \sim R_B$$

$$K^A \sim K^B$$

+2

+2

- Partition coefficient:

K_D or D (mineral-melt)

$$K_D^A = [A]_{\text{mineral}}/[A]_{\text{melt}}$$

$$K_D^B = [B]_{\text{mineral}}/[B]_{\text{melt}}$$

If radii are the same but charges are different ($X > Y$)

$$R_A \sim R_B$$

$$K^A > K^B$$

+3

+2

If charges are the same ($X = Y$) but radii are different

$$R_A > R_B$$

$$K^A < K^B$$

+2

+2

Example: olivine

- Na : 0.02
- Mg : 6.1
- Ni : 14

- Expect to see a Na olivine? Ni?

- Partition coefficient:
 K_D or $D_{(\text{mineral-melt})}$

$$K_D^A = [A]_{\text{mineral}}/[A]_{\text{melt}}$$

$$K_D^B = [B]_{\text{mineral}}/[B]_{\text{melt}}$$