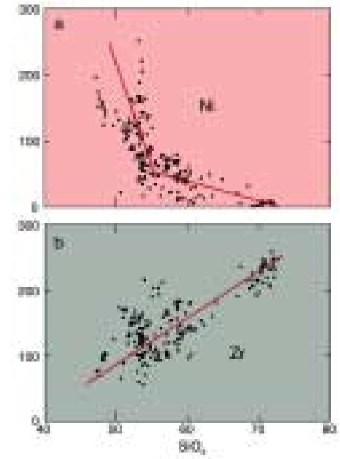
Trace Element Variation

Reading:

Winter Chapter , pp. 155-166

Note magnitude of trace element changes

Harker Diagram for Crater Lake from Winter (2001)



Goldschmidt's First Rule

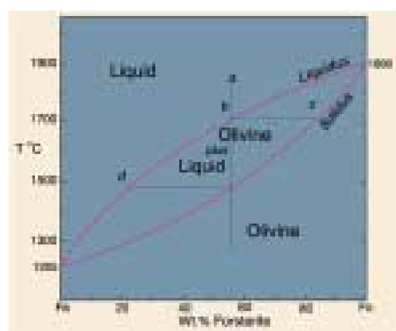
Ions with the same valence and radius should exchange easily and enter a solid solution in amounts equal to their overall proportions

What major element does Rb follow?

What major element does Ni follow?

Goldschmidt's Second Rule

If 2 ions have a similar radius and the same valence: the smaller ion is preferentially incorporated into the solid over the liquid



Isobaric T-X phase diagram at atmospheric pressure After Bowen and Shairer (1932), Amer. J. Sci. 5th Ser., **24**, 177-213.

Goldschmidt's Third Rule

If 2 ions have a similar radius, but different valence:

the ion with the higher charge is preferentially incorporated into the solid over the liquid

Chemical Fractionation

Uneven distribution of an ion between two competing (equilibrium) phases

Produces different concentrations and ratios of elements in the final product

Exchange equilibrium of a component *i* between two phases (solid and liquid)

$$i_{\text{(liquid)}} = i_{\text{(solid)}}$$

$$K = \frac{a_i^{\text{solid}}}{a_i^{\text{liquid}}} = \frac{\gamma_i X_i^{\text{solid}}}{\gamma_i X_i^{\text{liquid}}}$$

K = equilibrium constant

- Trace element concentrations are in the Henry's Law region of concentration, so their activity varies in direct relation to their concentration in the system
- Thus if X_{Ni} in the system doubles the X_{Ni} in all phases will double
  - This does not mean that X_{Ni} in all phases is the same, since trace elements do fractionate.
  - Rather the X_{Ni} within each phase will vary in proportion to the system concentration.

Incompatible elements are concentrated in the melt

(K_D or D) « 1

Compatible elements are concentrated in the solid

K_D or D » 1

For dilute solutions we can substitute D for K_D:

$$D = \frac{C_S}{C_L}$$

Where C_S = the concentration of some element in the solid phase

Incompatible Element Subgroups

- Smaller, highly charged high field strength (HFS) elements (REE, Th, U, Ce, Pb^{4+}, Zr, Hf, Ti, Nb, Ta)
- Low field strength large ion lithophile (LIL) elements (K, Rb, Cs, Ba, Pb^{2+}, Sr, Eu^{2+}) are more mobile, particularly if a fluid phase is involved

Compatibility depends on minerals and melts involved

Which are incompatible? Why?

Table 9-1. Partition Coefficients (C_S/C_L) for Some Commonly Used Trace Elements in Basaltic and Andesitic Rocks

	Olivine	Opx	Cpx	Garnet	Plag	Amph	Magnetite
Rb	0.010	0.022	0.031	0.042	0.071	0.29	
Sr	0.014	0.040	0.060	0.012	1.830	0.46	
Ba	0.010	0.013	0.026	0.023	0.23	0.42	
Ni	*14*	5	*7*	0.955	*0.01*	6.8	29
Cr	0.70	10	34	1.345	*0.01*	2.00	7.4
Rare Earth Elements: La	0.007	*0.03*	0.056	0.001	0.148	0.544	2
Ce	0.006	0.02	0.092	0.007	0.082	0.843	2
Nd	0.006	0.03	0.230	0.026	0.055	1.340	2
Sm	0.007	0.05	0.445	0.102	0.039	1.804	1
Eu	0.007	0.05	0.474	0.243	0.1/1.5*	1.557	1
Dy	0.013	0.15	0.582	1.940	0.023	2.024	1
Er	0.026	0.23	0.583	4.700	0.020	1.740	1.5
Yb	0.049	0.34	0.542	6.167	0.023	1.642	1.4
Lu	0.045	0.42	0.506	6.950	0.019	1.563	

Data from Rollinson (1993). * Eu^{3+}/Eu^{2+} *Italics* are estimated

- For a rock, determine the bulk distribution coefficient D for an element by calculating the contribution for each mineral

eq. 9-4: $\bar{D}_i = \Sigma W_A D_{i_A}$

W_A = weight % of mineral A in the rock

D_{i_A} = partition coefficient of element i in mineral A

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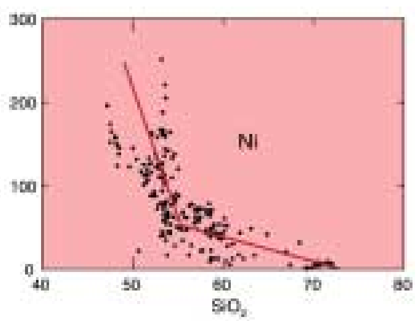
Example: hypothetical garnet lherzolite = 60% olivine, 25% orthopyroxene, 10% clinopyroxene, and 5% garnet (all by *weight*),

$\bar{D}_{Er} = (0.6 \cdot 0.026) + (0.25 \cdot 0.23) + (0.10 \cdot 0.583) + (0.05 \cdot 4.7) = 0.366$

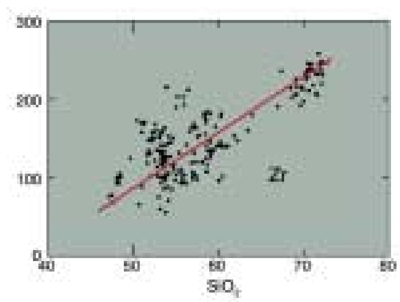
Strong Partition of Ni in Olivine



Ni Harker Diagram for Crater Lake from Winter (2001)

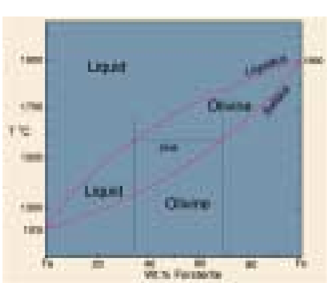
Incompatible trace elements concentrate in the liquid

They reflect the proportion of liquid at a given state of crystallization or melting



Zr Harker Diagram for Crater Lake from Winter (2001)

The concentration of a major element in a phase is usually buffered by the system, so that it varies little in a phase as the system composition changes



At a given T we could vary X^{melt} from between 20 and 60 % Mg/Fe without changing the composition of the melt or the olivine

Henry's Law Effect

Because trace element aabundances are in the Henry's Law region of concentration, their activity varies in direct relation to their concentration in the system

Thus if X_{Ni} in the system doubles the X_{Ni} in all phases will double

Therefore, *ratios* of trace elements are often more appropriate than the concentration of a single element in identifying the role of a specific mineral

Use of K/Rb Ratio

- K/Rb often used to estimate the importance of amphibole in a source rock
- K & Rb behave very similarly, so K/Rb should be ~ constant
- If amphibole is present, it contains almost all the K and Rb in the source rock

Amphibole has a D of about 1.0 for K and 0.3 for Rb

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Most common minerals except, plagioclase, exclude Sr

Ba is similarly excluded, except in alkali feldspar

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Compatible Element Example

- Ni is strongly fractionated, in olivine > pyroxene
- Cr and Sc are more in pyroxenes » olivine
- Ni/Cr or Ni/Sc can distinguish the effects of olivine and augite in a partial melt or a suite of rocks produced by fractional crystallization

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