12.479 Trace-Element Geochemistry
Spring 2009

Lecture 3

A. Partition Coefficient (read "Terminology for trace-element partitioning", Beattie et al., Geochim. Cosmochim. Acta, 57, 1603-1606, 1993)). The partition coefficient is the concentration ratio of an element (i) between two phases (α and β) is

$$D_i^{\alpha/\beta} = C_i^{\alpha}/C_i^{\beta}$$

Within the region of Henry's Law behavior, the partition coefficient is independent of the concentration of "i" but it is dependent on temperature, pressure and phase composition.

Nomenclature: for applications to igneous rocks where partitioning of elements between solid phases (s) and melt (ℓ) are important, most papers follow the convention of

$$D_i^{s/\ell} = C_i^{s}/C_i^{\ell}$$

($D_i^{s/\ell}$) the partition coefficient is also known as the distribution coefficient).

Note that D is commonly used for partition coefficient but if kinetic considerations are combined with studies of trace element partitioning, D has precedence for designating Diffusion Coefficient. Also K designates equilibrium constant, and K_D or K_C are used to designate compound partition coefficients. A common example is $K_D^{Fe/Mg} = \frac{(Fe/Mg)_{olivine}}{(Fe/Mg)_{melt}}$; that is, K_D or K_C are ratios of two partition coefficients.

B. Relationship between partition coefficient and equilibrium constant

Consider partitioning of Ni between forsterite solid (Mg_2SiO_4) and a melt of the same composition:

$$K_{eq} = a^{s}_{Ni} / a^{\ell}_{Ni} = \frac{k^{s}_{Ni}\gamma^{s}_{Ni}}{k^{\ell}_{Ni}\gamma^{\ell}_{Ni}}$$

Therefore D = $x^{s}_{Ni} / x^{\ell}_{Ni} = K_{eq}(\gamma^{\ell}_{Ni} / \gamma^{s}_{Ni})$

i.e., the partition coefficient is related to the equilibrium constant by a ratio of activity coefficients (γ).

C. Formation Reaction

The partitioning of Ni between Mg_2SiO_4 solid and melt can also be described by a formation reaction (see Wood and Fraser, Chapter 6).

$$2NiO_{(l)} + SiO_{2(l)} = Ni_2SiO_{4(s)}$$

$$K_{eq} = \frac{a^{ol}_{Ni_2SiO_{4(s)}}}{(a^{\ell}_{NiO})^2 (a^{\ell}_{SiO_2})} = \frac{(\gamma^{ol}_{Ni_2SiO_4})(x^{ol}_{Ni_2SiO_4})}{(\gamma^{\ell}_{NiO} x^{\ell}_{NiO})^2 a^{\ell}_{SiO_2}}$$

Since D = $X^{ol}_{Ni_2SiO_4} / X^{\ell}_{NiO}$ it is clear that D is sensitive to $a^{\ell}_{SiO_2}$.

(We will see later that mineral/melt D's vary with the SiO_2 content of melts).

D. Exchange Reaction

The same partitioning process can be described by

$$2MgO_{(l)} + Ni_2SiO_{4(s)} = 2NiO_{(l)} + Mg_2SiO_{4(s)}$$

$$K_{eq} = \frac{(a^{\ell}_{NiO})^2 (a^{s}_{Mg_2SiO_4})}{(a^{\ell}_{MgO})^2 (a^{s}_{Ni_2SiO_4})}$$

and

$$K_{eq} = \frac{(\gamma^{\ell}_{NiO}/\gamma^{\ell}_{MgO})^2}{(\gamma^{\ell}_{Ni_2SiO_4}/\gamma^{\ell}_{Mg_2SiO_4})}\frac{(x^{\ell}_{NiO}/x^{\ell}_{MgO})^2}{(x^{s}_{Ni_2SiO_4}/x^{s}_{Mg_2SiO_4})}$$

This is a compound partition coefficient involving the ratio of two partition coefficients (Ni and Mg), i.e. $K_D = (X_{Mg_2}SiO_4/X_{Ni_2}SiO_4)^s/(X_{MgO}/X_{NiO})^l$ so that $K_{eq} = K_D$ times a ratio of activity coefficients. If Ni and Mg are non-ideal to similar extents, it might be expected that the ratio of activity coefficients for NiO/MgO is near unity. As a result K_D may be more nearly constant than D. Also note that the $a^{\ell}_{SiO_2}$ term has cancelled out.

E. Geothermometer/Geobarometer

Since equilibrium constants vary with pressure and temperature, partition coefficients are also a function of pressure and temperature; hence there is the potential of using variations in TE partition coefficients to infer P and T.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \Delta U^\circ + P\Delta V^\circ - T\Delta S^\circ = -RT\ln K_{eq}$$

So

$$\text{Ln } K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial T}\right)_P = \frac{\Delta H}{RT^2} \quad \text{or}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial\ 1/T}\right)_P = \frac{-\Delta H^\circ}{R} \quad \text{so}$$

a plot of ln K_{eq} (lnD) versus 1/T yields a straight line. Similarly a geobarometer for pressure is

$$\left(\frac{\delta \ln K}{\partial P}\right)_T = \frac{-\Delta V^o}{RT}$$

(relatively little is known about D variations versus pressure).