<center>**Lecture 3**</center>

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 $K_D^{Fe/Mg} = \dfrac{(Fe/Mg)_{olivine}}{(Fe/Mg)_{melt}}$; that is, K_D or K_C are ratios of two partition coefficients.

B. Relationship between partition coefficient and equilibrium constant

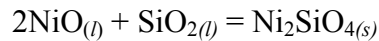Consider partitioning of Ni between forsterite solid (Mg_2SiO_4) and a melt of the same composition:

$$K_{eq} = a_{Ni}^s / a_{Ni}^\ell = \frac{x_{Ni}^s \gamma_{Ni}^s}{x_{Ni}^\ell \gamma_{Ni}^\ell}$$

Therefore $D = x_{Ni}^s / x_{Ni}^\ell = K_{eq}(\gamma_{Ni}^\ell / \gamma_{Ni}^s)$

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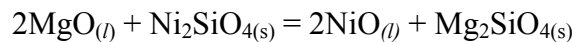
$$2NiO_{(l)} + SiO_{2(l)} = Ni_2SiO_{4(s)}$$

$$K_{eq} = \frac{a_{Ni_2SiO_{4(s)}}^{ol}}{(a_{NiO}^\ell)^2 (a_{SiO_2}^\ell)} = \frac{(\gamma_{Ni_2SiO_4}^{ol})(x_{Ni_2SiO_4}^{ol})}{(\gamma_{NiO}^\ell x_{NiO}^\ell)^2 a_{SiO_2}^\ell}$$

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

(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

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

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

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.

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

So

$$\ln K_{eq} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R}$$

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

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

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

$$\left(\frac{\delta \ln K}{\partial P}\right)T = \frac{-\Delta V°}{RT}$$

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

12.479 Trace-Element Geochemistry

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