

MIT OpenCourseWare
<http://ocw.mit.edu>

12.479 Trace-Element Geochemistry
Spring 2009

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

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 $K_D^{Fe/Mg} = \frac{(Fe/Mg)_{\text{olivine}}}{(Fe/Mg)_{\text{melt}}}$; 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:

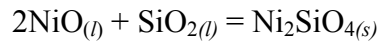
$$K_{\text{eq}} = a_{\text{Ni}}^{\text{s}} / a_{\text{Ni}}^{\text{l}} = \frac{k_{\text{Ni}}^{\text{s}} \gamma_{\text{Ni}}^{\text{s}}}{k_{\text{Ni}}^{\text{l}} \gamma_{\text{Ni}}^{\text{l}}}$$

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

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).



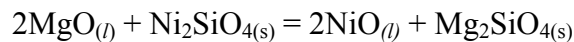
$$K_{\text{eq}} = \frac{a_{\text{Ni}_2\text{SiO}_{4(s)}}^{\text{ol}}}{(a_{\text{NiO}}^{\text{l}})^2 (a_{\text{SiO}_2}^{\text{l}})} = \frac{(\gamma_{\text{Ni}_2\text{SiO}_4}^{\text{ol}})(x_{\text{Ni}_2\text{SiO}_4}^{\text{ol}})}{(\gamma_{\text{NiO}}^{\text{l}} x_{\text{NiO}}^{\text{l}})^2 a_{\text{SiO}_2}^{\text{l}}}$$

Since $D = X_{\text{Ni}_2\text{SiO}_4}^{\text{ol}} / X_{\text{NiO}}^{\text{l}}$ it is clear that D is sensitive to $a_{\text{SiO}_2}^{\text{l}}$.

(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



$$K_{\text{eq}} = \frac{(a_{\text{NiO}}^{\text{l}})^2 (a_{\text{Mg}_2\text{SiO}_4}^{\text{s}})}{(a_{\text{MgO}}^{\text{l}})^2 (a_{\text{Ni}_2\text{SiO}_4}^{\text{s}})}$$

and

$$K_{eq} = \frac{(\gamma_{NiO}^l / \gamma_{MgO}^l)^2}{(\gamma_{Ni_2SiO_4}^l / \gamma_{Mg_2SiO_4}^l)} \frac{(x_{NiO}^l / x_{MgO}^l)^2}{(x_{Ni_2SiO_4}^s / x_{Mg_2SiO_4}^s)}$$

This is a compound partition coefficient involving the ratio of two partition coefficients (Ni and Mg), i.e. $K_D = (X_{Mg_2SiO_4} / X_{Ni_2SiO_4})^s / (X_{MgO} / X_{NiO})^l$ 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 $a_{SiO_2}^l$ 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

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

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

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

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

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

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