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12.479 Trace-Element Geochemistry
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Lecture 7

A Determination of Partition Coefficients: Discussion of Experimental Approach

1. Simple or Natural Composition?

Experimental Studies of trace element partitioning are desirable because the effects of pressure and temperature, plus mineral and melt composition, on partition coefficients can be determined. In planning an experimental study one must choose what elements and minerals to study. As with all experimental studies a first step is deciding whether to study natural systems whose composition is complex but realistic or compositionally simple systems where it is easier to distinguish and determine the effects of variable temperature and composition of mineral and melt phases.

2. Analytical Approach – there are several possibilities, e.g.,

(a) Physical separation of phases prior to analysis. The small grain sizes typical of experimental charges generally preclude this approach, but some studies have separated phases by treating the experimental products with acids that preferably dissolve one of the phases, such as quenched melt.

(b) Autoradiography, i.e., adding a radioactive isotope of the trace element being studied and detecting the spatial distribution of the radioactive element in the run products. The approach was popular (e.g., Mysen and Seitz, 1974) but has some experimental difficulties and is not now commonly used.

(c) Addition of trace element to the experimented system in quantities that enable precise determination of TE content in all phases by in situ analysis techniques. Initially the analytical technique of choice was the electron microprobe whose sensitivity for TE is limited; hence the TE was added to the system in amounts

such as 0.1% or more. Such TE contents are commonly well above those found in natural systems, and there is the possibility of non-Henry's Law behavior if the concentrations exceed the dilute solution limit (see Lecture 2, Figure 3 and Watson, 1985).

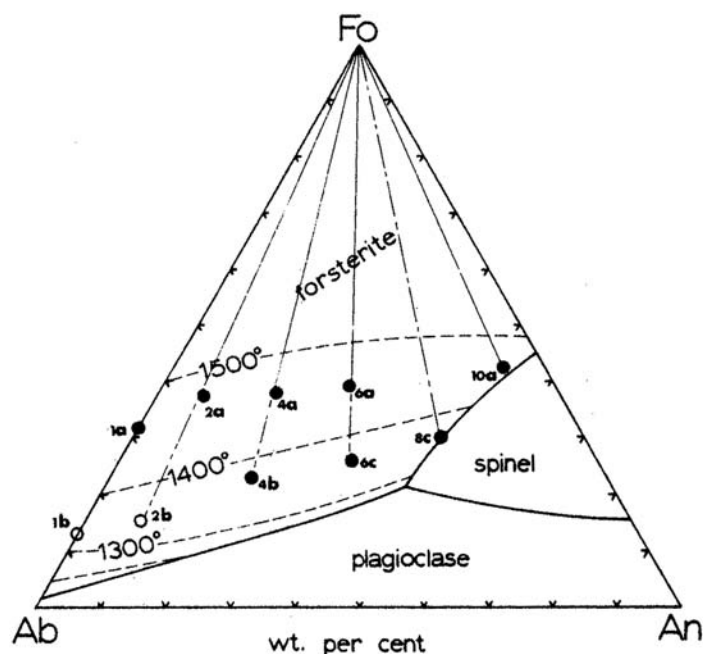
Most recently, in situ analytical techniques with greater sensitivity for detection of TE are used for analysis of experimental products, e.g., secondary ion mass spectrometry (SIMS) commonly known as an "ion-microprobe", and laser ablation inductively coupled mass spectrometry (LA-ICP-MS).

Today there is a very large literature on Experimental Studies of TE Partition Coefficients. I cannot provide a comprehensive listing of references but Appendix 1 is a listing of relevant references.

B. Partitioning of manganese behavior forsterite and silicate melt, Watson, E.B., *Geochimica Cosmochimica et Acta*, 1363-1374, 1977.

1. My approach is to discuss early experimental papers that illustrate the usefulness of experimental determination of TE partition coefficients. This paper involves a study of the simple system Fo-Ab-An at 1 atm over a temperature range of 1250-1450 C. There are two reasons for choosing this system to study:

(a) The mineral forsterite (Fo) is in equilibrium with a wide range of melt compositions at a constant temperature and pressure (Figure 20); consequently the effects of melt composition on $D_{Mn}^{Fo/melt}$ can be determined and (b) Mn typically is at the 0.1% abundance level in basalt with a $D_{Mn}^{Fo/melt} \sim 1$; consequently Mn abundance in Fo and quenched melt can be precisely determined by electron microprobe.



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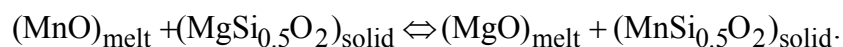
Figure 20. Liquidus diagram for the system forsterite (Fo) – albite (Ab) – anorthite (An). Circles indicate melt composition in equilibrium with Fo at 1350 C and 1450 C; experimental run numbers are indicated. Figure is from Watson, 1977.

2. Results:

(a) $D_{\text{Mn}}^{\text{Fo/melt}}$ was found to be independent of Mn concentration in the range of 0.03 to 0.6% MnO in Fo (see Figure 3 of Watson, 1977).

(b) $\ln D_{\text{Mn}}^{\text{Fo/melt}}$ increases with decreasing temperature but the experimental data do not define the expected linear trend in a $\ln D$ vs. $1/T$ plot (see Figure 4 of Watson, 1977 and Lecture 3).

(c) In order to understand the effects of melt composition on Mn partitioning, consider the exchange reaction:



For this reaction the equilibrium constant is:

$$K_{eq} = \frac{(a_{MgO})_{melt} (a_{MnSi_{0.5}O_2})_{solid}}{(a_{MnO})_{melt} (a_{MgSi_{0.5}O_2})_{solid}}$$

where “a” represents activity and $a_{MgSi_{0.5}O_2}$ is assumed to be one because Mn is a trace element and the Fo is nearly pure. Therefore:

$$K_{eq} = \frac{(a_{MgO})_{melt} (x_{MnSi_{0.5}O_2})_{solid} (\gamma_{MnSi_{0.5}O_2})_{solid}}{(x_{MnO})_{melt} (\gamma_{MnO})_{melt}}$$

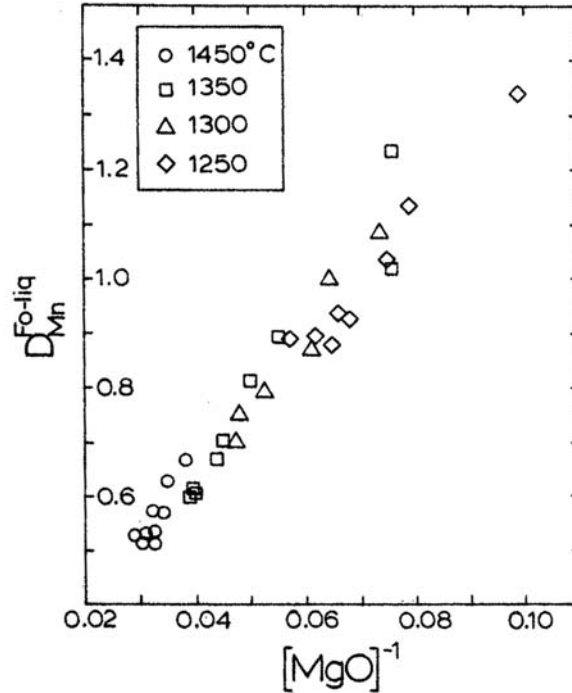
and by definition

$$D_{Mn}^{Fo/melt} = \frac{(x_{MnSi_{0.5}O_2})_{solid}}{x_{(MnO)}_{melt}}$$

so that

$$D_{Mn}^{Fo/melt} = \frac{K_{eq}}{(a_{MgO})_{melt}} \frac{(\gamma_{MnO})_{melt}}{(\gamma_{MnSi_{0.5}O_2})_{solid}}$$

If we assume that $(a_{MgO})_{melt}$ is proportional to $(x_{MgO})_{melt}$, we predict that $D_{Mn}^{Fo/melt}$ should vary inversely with the MgO content of the melt. Indeed Watson’s experimental data show this inverse relation thereby demonstrating a marked increase in $D_{Mn}^{Fo/melt}$ as the MgO content of the melt decreases from 24 to 6 wt. % (Figure 21).

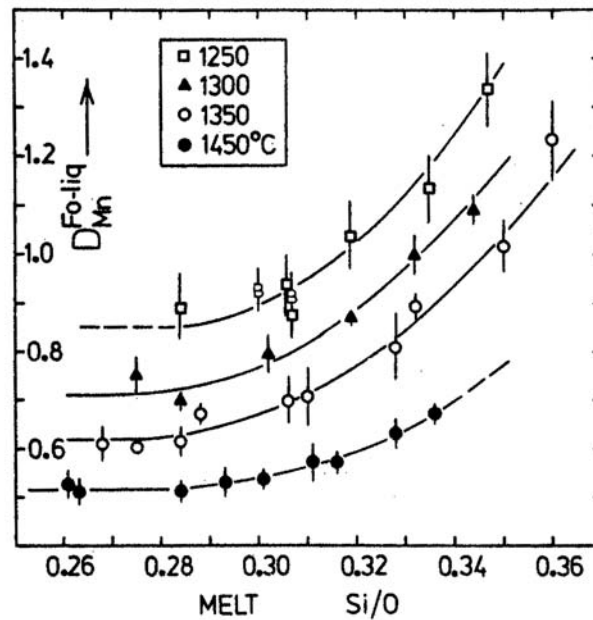


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Figure 21. $D_{\text{Mn}}^{\text{Fo/melt}}$ versus reciprocal molar MgO in the melt showing that D increases markedly as MgO content of melt decreases. Figure is from Watson, 1977.

(d) Note that no temperature dependence is apparent in Figure 21. However, Watson (1977) found that if the Si/O atomic ratio of the melt is plotted vs. $\ln D_{\text{Mn}}^{\text{Fo/melt}}$, the partition coefficient increases as Si/O increases but each temperature defines a distinct trend (Figure 22); therefore the effects on $D_{\text{Mn}}^{\text{Fo/melt}}$ of temperature and melt composition are distinguished. Si/O was proposed to reflect the extent of melt polymerization since the completely polymerized melt of SiO_2 has $\text{Si/O} = 0.5$ and a depolymerized melt consisting only of SiO_4^{-4} units has $\text{Si/O} = 0.25$. An implication resulting from Figure 22 is that over the Si/O range from 0.25 to 0.30 (typical of basaltic melts), $D_{\text{Mn}}^{\text{Fo/melt}}$ is not sensitive to Si/O

ratio but as Si/O increases beyond 0.3 (andesitic to rhyolitic melts) $D_{Mn}^{Fo/melt}$ significantly increases implying that as melt polymerization increases the melt is a less hospitable host for Mn^{+2} . This result is consistent with the higher partition coefficient for REE in dacitic melts found for amphibole phenocryst/melt (Figure 19).



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Figure 22. $D_{Mn}^{Fo/melt}$ vs. Si/O atomic ratio of melt using different symbols for different temperatures. Note that for a completely polymerized melt such as SiO_2 , Si/O = 0.5 whereas for a completely depolymerized melt of SiO_4^{-4} anions has Si/O = 0.25.