

# The compositional dependence of HFSE partitioning: a comparison between pyroxene- and magnetite-melt systematics

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## Introduction

The dependence of trace element partition coefficients on the composition of the phases has been known qualitatively for over 20 years. It has also been long known that this is a consequence of how we describe partitioning behavior, and of non-ideal mixing in both mineral and melt. One of the many techniques have been applied to describe the compositional dependencies of the important trace elements is the correlation of the behavior of a trace element with the partitioning behavior of a major element. This has been successful to some degree in different systems (Ni-Mg in olivine; Hart and Davis, 1978, Sr-Ca in plagioclase; Blundy and Wood, 1990), but is dependent on the degree to which the correlated elements are controlled by the same system parameters.

## Technique

Over the past 6 years, we have conducted over 700 doped experiments using natural starting materials. These investigations had as their goal, the creation of a set of expressions that would better describe magnetite- and pyroxene-melt trace element partitioning for the rare earth elements (REE) and the high field strength elements (HFSE). The use of doped experiments, analyzed by electron microprobe, allowed us to perform the large number of experiments necessary to cover the full range of mafic to intermediate composition magmas.

## Magnetite

Mineral-melt partition coefficients ( $D$ ) do not necessarily show a simple correlation with any single variable. Examination of our data for the HFSE shows that there is no coherent relationship between  $D_{Zr}$  and temperature. In fact, the values for most HFSE have a range of two orders of

magnitude at any individual temperature ( $D_{Zr}$  - 0.02-1.78;  $D_{Nb}$  - 0.01-1.80;  $D_{Ta}$  - 0.01-2.53) regardless of the composition of the starting material. This range is consistent with the published values for phenocryst-matrix determinations (Nielsen, 1992). This demonstrates that for magnetite, and probably the entire spinel group, concentrations are poor approximations of activities. Therefore, partition coefficients are a particularly poor representation of equilibrium constants, as one would expect based the strong non-ideality in the mixing properties of the spinel end members (Sack and Ghiorso, 1991).

Due to a similarity in charge, Ti is often correlated with the behavior of the HFSE (Zr, Nb, Hf and Ta). This overall correlation is apparent in our experimental data, but in detail,  $D_{Zr}$  at any fixed value of  $D_{Ti}$  has a range of a factor of 10, outside the analytical error in the determination of  $D_{Zr}$ . Therefore, even though the behavior of Zr is similar to Ti, there are statistically significant variations. We found that at any  $D_{Ti}$  the concentration of Al in the magnetite proved to have a strong inverse correlation with  $D_{Zr}$ . The negative correlation of  $D_{Zr}$  with Al is present for the entire data set the correlation is not absolute. For example,  $D_{Zr}$  ranges over an order of magnitude for experiments with magnetites containing between 4 and 7 mole % Al, again significantly exceeding the analytical error. In addition, at any Al mole fraction in the magnetite, we find that there is a correlation between  $D_{Zr}$  and the Fe/Mg ratio of the magnetite.

To quantify the dependencies described above, data from this study were regressed against  $D_{Ti}$ , mole % Al, and Fe/Mg ratio in the magnetite. The resulting equations are of the form

$$D_{HFSE} = C_0 + C_1(D_{Ti}) + C_2(\text{Fe/Mg in magnetite}) + C_3(\text{Al in magnetite})$$

where  $C_0$ ,  $C_1$ ,  $C_2$ , and  $C_3$  are regression constants

and the compositional parameters are calculated in cation normalized mole %. We used these regressions from to calculate D's for each experimental composition and compared them to the experimental values. The results for the Zr, Nb, Hf and Ta are predicted to within 20% ( $1\sigma$ ) over a total range in D of 1000%.

Two of our most important observations from our investigation were that the D's for Zr, Nb, Hf and Ta are all similar to one another, and are more sensitive to the composition of the spinel than is DTi. We interpret this observation as evidence that the miscibility gap between HFSE-ulvospinel and Mg-Al-Cr rich spinels is wider than for Ti-ulvospinel and Mg-Al-Cr-rich spinels (i.e. more strongly non-ideal).

### Pyroxene

The systematics of pyroxene-melt partitioning are equally complex. The strongest correlations in our data were with Ca content in pyroxene, alkali/Al in the melt and  $D_{Ti}$ . As with magnetite, pyroxene-melt  $D_{Ti}$  and  $D_{HFSE}$  have same dependencies, but to different degrees, with Ti being less sensitive to Ca content. We attribute this again to the higher degree of non-ideality of HFSE mixing compared to Ti, possibly linked to their occupancy of different M sites. The primary substitution mechanism for HFSE in pyroxene is as a HFSE tshermak component. This explains the importance of Al activity of the melt. It may also explain the strong correlation with the behavior of Ti, whose primary substitution mechanism is also as a Ti-Al component.

To quantify these dependencies, data from our

study were regressed against  $D_{Ti}$ , mole fraction Ca, in the pyroxene. The resulting equations are of the form:

$$D_{HFSE} = C_0 + C_1(D_{Ti}) + C_2$$

(Ca mole fraction in pyroxene)

where  $C_0$ ,  $C_1$ , and  $C_2$ , are regression constants. We used these regressions to calculate D's for each experimental composition and compared them to the experimental values. The experimental results for Zr, Nb, Hf and Ta are predicted to within 15–25% ( $1\sigma$ ) over a variation in D of almost 200%.

### Conclusions

This empirical approach is successful for these systems because Ti and the HFSE have similar substitution mechanisms in each mineral group. However, even though Al is an important link in magnetite and pyroxene-melt partitioning, that linkage is for different reasons in the two mineral groups. Correlation of partitioning behavior can only be made over a limited range of composition, and can not be extrapolated significantly outside the range of the experimental data set used to calibrate the expressions.

### References

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