

Partitioning of Nb and Zr between pargasite/kaersutite and melts in Ti-depleted systems

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Investigations of trace-element residence in clinopyroxene and amphibole from mantle xenoliths and peridotite massifs (Vannucci *et al.*, 1995; Ionov *et al.*, 1997, and references therein) indicate that amphibole/clinopyroxene partition coefficients are quite constant for elements which are supposed to enter corresponding sites in the two mineral structures. This is the case for Sr ($^{Amph/Cpx}D$ from 0.8 to 2.5) and REE ($^{Amph/Cpx}D$ from 1 to 2), which both enter the [8]-coordinated $M2_{Cpx}$ and $M4_{Amph}$ sites, respectively, but not for HFSE that are assumed to enter the [6]-coordinated $M1_{Cpx}$ (Vannucci *et al.*, 1995) and $M2_{Amph}$ (LaTourrette *et al.*, 1995) sites. Among the HFSE, $^{Amph/Cpx}D$ for Nb and Ti strongly vary (from 2.7 to 8.9 and from 1.7 to 6.8, respectively) relative to $^{Amph/Cpx}D_{Zr}$ (from 0.9 to 2.1). These values result in large variations of Amph/melt partition coefficients estimated from natural mineral/mineral pairs relative to the experimentally determined ones.

This study provides insights into the D_{HFSE} behaviour obtained by means of high-pressure partitioning experiments carried out to understand the crystal-chemical control of trace-element partitioning in a variety of amphibole structures (see also Brumm *et al.*, 1998; Tiepolo *et al.*, 1998). SIMS analyses have been combined with single-crystal X-ray structure refinements (SREF) to obtain reliable estimates of major element site partitioning and of the size of the various structural sites.

The results relevant to the behaviour of HFSE are reported in Fig. 1, in which $^{Amph/Liq}D_{Nb}$ and $^{Amph/Liq}D_{Zr}$ are plotted against $^{Amph/Liq}D_{Ti}$. It can be noted that $^{Amph/Liq}D_{Nb}$ increases by a factor of 16 and shows a good correlation with $^{Amph/Liq}D_{Ti}$, whereas $^{Amph/Liq}D_{Zr}$ increases by a factor of 9 and has a much more scattered relationship with $^{Amph/Liq}D_{Ti}$.

Moreover, $^{Amph/Liq}D_{Zr}$ does not significantly increase for $^{Amph/Liq}D_{Ti} > 4$. It is noticeable that $^{Amph/Liq}D_{Nb}$ significantly exceeds unity, thus providing evidence for compatible behaviour of Nb under the experimental conditions, whereas $^{Amph/Liq}D_{Zr}$ only approaches unity.

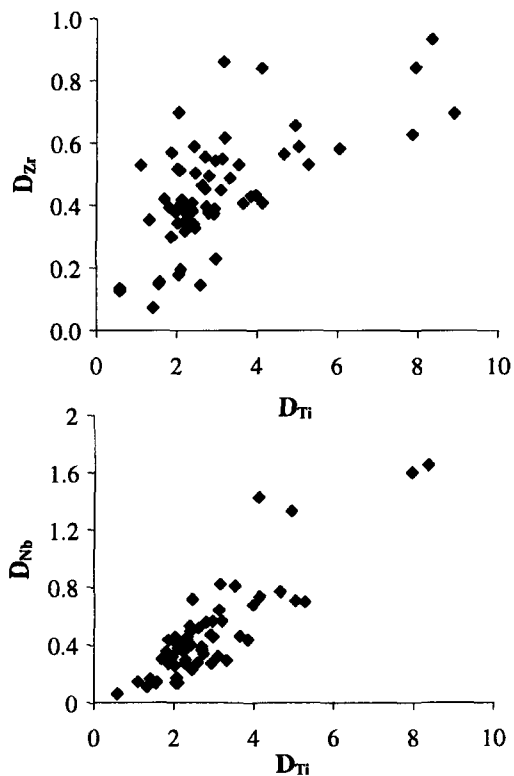


FIG. 1. D_{Zr} and D_{Nb} vs D_{Ti} .

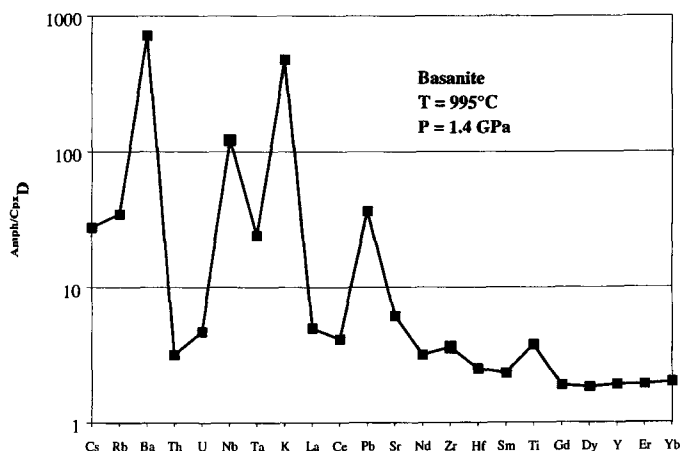


FIG. 2. Experimentally determined Amph/Cpx partition coefficients.

The results of SREF investigations indicate that pargasite and kaersutite from this study have a significant oxy-component and that most Ti (>65%) is ordered at the M1 site (along with some Fe^{3+} in the most dehydrogenated samples) to balance for dehydrogenation (Oberti *et al.*, 1998). The increase of $^{Amph/Liq}D_{Ti}$ thus should be interpreted as the need for incorporating nearly the same quantity of Ti (even if the melt is increasingly depleted in Ti) in order to balance the nearly constant dehydrogenation occurring at these P, T conditions. When Ti is no longer available, decoupling of HFSE occurs: those elements which are more similar in size to Ti (i.e. Nb and Ta) enter the M1 site, whereas Zr (and Hf) are hosted at M2. As a result, a significant increase of $^{Amph/Liq}D_{Nb}$ relative to $^{Amph/Liq}D_{Zr}$ is observed.

Further evidence for the presence of Nb (and Ta) but not of Zr (and Hf) at the M1 site to balance dehydrogenation, is provided in Fig. 2, in which representative Amph/Cpx partition coefficients from our experiments show that $^{Amph/Cpx}D_{Nb}$ and $^{Amph/Cpx}D_{Zr}$ differ by more than one order of magnitude, thus suggesting different substitution mechanisms. The major conclusion is that Zr (and Hf) is incorporated in pargasite/kaersutite and clinopyroxene with the same mechanism, whereas Nb (and Ta) cooperates with Ti (and Fe^{3+}) in the balance of the dehydrogenation. It is noticeable that this does not hold for richterite, in which the relevant structural

sites have very different (relative) dimensions; in richterite, Zr and Hf are order at M1 (Oberti *et al.*, 1998).

The results of this study are important for the interpretation of volcanic arc magmas, because they demonstrate that decoupling of Nb and Ta from Zr and Hf may operate during melting or fractional crystallization not only by rutile, but also by pargasite/kaersutite. On the other hand, in mantle sectors where richterite is stable the decoupling of HFSE cannot be ascribed to the presence of amphibole.

References

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