

BUFFERING OF INCOMPATIBLE ELEMENTS IN THE LITHOSPHERIC MANTLE DURING MELT PERCOLATION: THE ROLE OF HYDROUS PHASES

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ABSTRACT

An increasing number of highly precise and accurate whole-rock trace element data is becoming available for orogenic peridotites and mantle xenoliths. Extreme LILE enrichment relative to HFSE is a common feature which is generally attributed to pervasive forms of metasomatism modelled in terms of chromatographic crystallisation effects (Navon and Stolper, 1987), possibly coupled with sink/source effects (Godard et al., 1995). Models describing propagation of melt batches through mantle rocks (Godard et al., 1995; Vernières et al., 1997) usually provide satisfactory numerical simulations for the observed LILE variations, and particularly for LREE enrichment in interstitial melts and minerals. However, they often do not account for the wide range of variations of HFSE and U, Th. Uranium anomalies may result from selective transport by fluids (Alard et al., 1999), whereas inconsistencies between measured and predicted HFSE abundances are frequently ascribed to buffering exerted by elusive Ti-oxides (Bodinier et al., 1996), particularly rutile, which is claimed to produce intra-HFSE fractionation (i.e., Zr, Hf and Ta, Nb decoupling). However, rutile is not commonly found in mantle assemblages, and experiments have shown that an unusually TiO₂-rich bulk rock composition is required to stabilize rutile (Ayers et al., 1997).

The hydrous phases phlogopite, pargasite/kaersutite and richterite could play a significant role in buffering LILE in the lithospheric mantle and must be also considered as either a complement or an alternative to Ti-oxides in buffering HFSE. Phlogopite is stable up to 1200°C at pressures higher than 20 kbar (Mengel and Green, 1989), whereas pargasite and kaersutite are stable up to 1150°C in the 25-30 kbar range under water-undersaturated conditions (Niida and Green, 1999). Phlogopite and amphibole are expected to form during migration of alkaline melts through the upper mantle domain, thus resulting in sink/source effects and buffering of incompatible elements. The buffering role of phlogopite can be easily predicted: Schmidt et al. (1999) showed that D_{Rb} is significantly higher than 1, whereas D_{Sr} is in the range 0.02-0.06, thus causing a strong decrease of Rb/Sr in the interstitial melt. Interestingly, D_{Ti} and D_{Ba} may approach or even exceed unity (D_{Ba} up to 1.6), confirming their dependence on the Ti-oxy-substitution that is expected to increase the phlogopite stability. Therefore, a more effective coupled buffering of Ba and Ti is expected at increasingly lower X_{H_2O} conditions. Among the other elements, only Nb, Li and Zr may be retained to some extent (D_s are 0.07, 0.02 and 0.015, respectively). Although very low, D_{Pb} (0.02) is at least two orders of magnitude greater than $D_{U,Th}$, which are in the order 10^{-4} - 10^{-6} , like those of the REE.

Amphibole shows more complex behaviour. From an in-

tegrated experimental, analytical and crystallographic approach we can show that trace-element partitioning behaviour differs significantly between pargasite/kaersutite and richterite. Moreover, it cannot be predicted without taking into account both the presence of dehydrogenation and the complete site distribution of the major elements.

In K-richterites, $D_s > 1$, permitting effective buffering by amphibole, are observed only for Sr, F, V, Cr; whereas D_s for the other elements are < 0.4 . $D_{REE}^{Amph/L}$ are lower by about one order of magnitude in K-richterite than in kaersutite/pargasite, in keeping with the presence of (more than) half of M4 sites occupied by monovalent cations (Na⁺). However, richterites may produce a decoupling of fractionation within the REE owing to the partitioning of LREE and part of the HREE into sites with different coordination i.e., ⁸M4 and ⁶M2. D_{HREE}^{HREE} exceed D_{LREE}^{LREE} by up to one order of magnitude (Bottazzi et al., 1999). HFSE are preferentially hosted in kaersutite/pargasite relative to K-richterite, in which the large octahedral strip does not favour the entry of small radius high-charge cations. Pargasites and kaersutites may cause significant depletion of HFSE and REE in the interstitial melt because of the high D-values for these elements (up to 1.6 for Nb and 3.6 for HREE). $D_{Amph/L}$ values increase from LREE to MREE/HREE, and are quite constant in the HREE region. Decoupling of REE from one another is not expected, because LREE and HREE are incorporated within the same cavity (M4), although they occupy different sites in the presence of significant cumingtonite component M⁴(Fe and Mg). $D_{Amph/L}$ for U and Th are sensitive to melt composition and range between 0.003 and 0.03 in kaersutite/pargasite. The incorporation of U, Th and the HREE most likely occurs in the M4' position whose dimensions control the $D_{U,Th}^{Amph/L}$ ratio (0.6-1.2). HFSE represent a special case because they are partitioned among the three independent octahedral sites depending on the end-member composition and the presence or absence of oxy-component. Zr and Hf have the same site preference (M2) as the fraction of Ti⁴⁺ which is not related to dehydrogenation, whereas Nb and Ta enter M1 and are likely to cooperate with Ti in balancing of dehydrogenation. In Ti-depleted systems, this mechanism may result in an abrupt increase of $D_{Nb,Ta}$ with D_{Nb} even > 1 and a decoupling of HFSE is observed. The $D_{Nb,Ta}^{Amph/Liq}$ is highly variable (0.7-1.7), and is ruled by the dimensions of the M1 site, which in turn depends on its Fe, Mg and Ti content. Surprisingly, pargasite/kaersutite has higher partition coefficients and consequently a stronger buffering capacity for Rb, Ba and Cs than K-richterite. This is not the case for Sr, which has a higher compatibility in K-richterite, which provides larger and less constrained M4 sites.

New partitioning data reveal that the buffering of incompatible elements by hydrous phases can be modelled with confidence only if appropriate assumptions about phase stability (and hence the geodynamic environment) and composition are made. The prediction of the behaviour of HFSE requires a reasonable estimate of the water and titanium activity in the melt. Ds of elements which are involved in charge compensation of the oxy-component (Ba and Ti in phlogopite and Ti, Nb and Ta in amphiboles) cannot be assumed to be constant during the precipitation of hydrous phases from the interstitial melt. Phlogopite with no oxy- or F- components has about 4 wt% H₂O, whereas a similar pargasite/richterite has about 2.0 wt% H₂O. Former crystallisation of hydrous phases implies sink/source effects for both H and Ti, which in turn either affect D in hydrous phases crystallised later or prevent the formation of new hydrous phase beyond the reaction zone.

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