

Fine-scale structural control of REE site-preference: the case of amphibole

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The models currently adopted to predict isovalent element partitioning assume that the composition and structure of the solid phase, rather than melt composition or temperature, exerts the greater control on trace-element mineral-liquid partition coefficients. Blundy and Wood (1994) proposed a model that relates crystal-lattice site parameters to element partitioning and allows the optimum ionic radius, r_0 , the site Young's modulus E of the site and the strain-compensated partition coefficient D_0 to be calculated. This type of analysis has been proven to be applicable to plagioclase-melt and clinopyroxene-melt (Blundy and Wood, 1994) and has been also used to discuss experimental amphibole and phlogopite partitioning results (LaTourrette *et al.*, 1995; Brennan *et al.*, 1995). However, owing to the complexity of both the amphibole structure and of its consequent cation-ordering patterns, which depends not only on P , T and X , but also on f_{H_2} , amphibole-melt partitioning experiments are not yet comprehensive.

A study of structural control by means of single-crystal X-ray structure refinement (SREF) performed on the same crystal on which S/LD have been measured, is presented here for the first time. In this work we investigate the role of the structural and crystal-chemical control on trace-element partitioning in amphiboles with a significant oxy component crystallised under conditions relevant to mantle processes (T and P range, f_{O_2} close to the NNO buffer) from natural and synthetic basanitic and lamproitic melts doped with 33 trace elements. The concentration of each element has been designed to optimize counting statistics in SIMS and LAM-ICP-MS analysis. The Na/(Na+K), Mg/(Mg+Fe) and Ti/(Ti+Si) ratios of the starting material obtained from oxide mixture has been varied in order to verify their influence on trace element $^{Amph/Liq}D_{REE}$.

In the hypothesis of ordering of Na^+ , K^+ and Rb^+ at the A site, REE^{3+} at the M4 site, and of Ti^{4+} , Zr^{4+} , Hf^{4+} at the M2 site, least-squares fitting procedures have been applied to cation partitioning between amphibole (specifically pargasite, kaersutite, richterite) and silicate melt. The values of r_0 derived by fitting for the M2, M4 and A sites have been compared with the results of SREF results (Fig. 1). In this figure, a good agreement between measured site dimensions and calculated r_0 values is observed, thus suggesting that the predictive approach can be extended to amphiboles. However, from Fig. 1 it is also apparent that the r_0 values calculated by fitting REE^{3+} at the M4 site deviate from the 1:1 reference line with intercept at 1.38 Å (the ionic radius of O^{2-}).

Fig. 2 shows representative behaviours of $^{Amph/Liq}D_{REE}$ in the hypothesis of ordering at the M4 site for (a) kaersutite with significant (Mg,Fe) occupancy

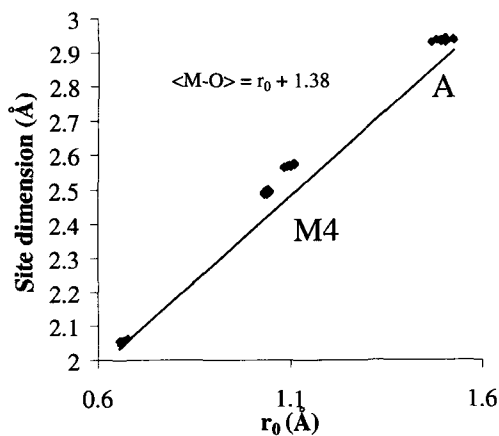


FIG. 1. Site dimension (SREF) vs the r_0 parameter.

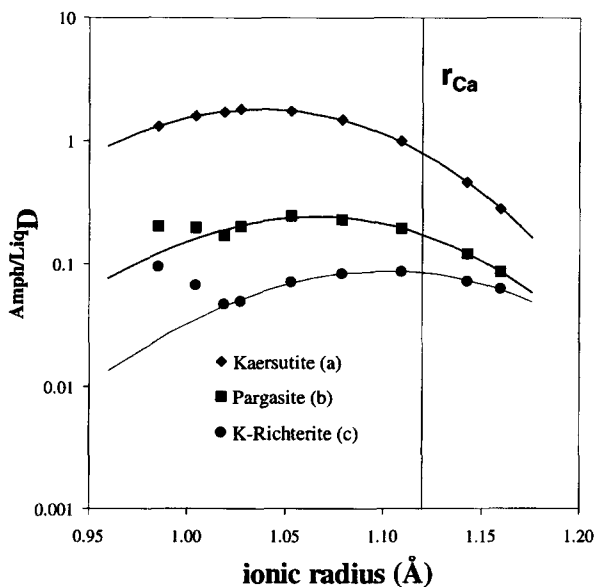


FIG. 2. Representative $^{Amph/Liq}D_{REE}$ at the M4 site.

at M4, (b) pargasite with no (Fe,Mg) occupancy at M4 and (c) richterite. In this figure discrepancies between the calculated r_0 and the observed $\langle M4-O \rangle$ distance are apparent. In the case of richterite (c), the parabola is centered close to the ionic radius of Ca, whereas the measured $\langle M4-O \rangle$ distance takes into account the presence of predominant Na occupancy at M4. Cases (a) and (b) are even more surprising, as there is a clear difference between r_0 and $\langle M4-O \rangle$ and the top of the parabola is not centered to Ca, even if Ca is the major cation at the M4 site of both pargasite and kaersutite.

In spite of the observed discrepancies, the experimental data can be interpreted in the frame of the Blundy and Wood model but making different assumptions for *REE* distribution. In the case of kaersutite with significant (Fe, Mg) occupancy in the M4 cavity, *HREE* distribute between the two split $^{[8]}M4$ and $^{[6+2]}M42$ positions, with significant preference for the latter (which implies their preference for a site geometry similar to that of Mg and Fe), whereas *LREE* order at the M4 position (implying a preference for site geometry similar to that of Ca). In the case of pargasite with no (Fe,Mg) occupancy at M4 and of richterite, *HREE* are allowed to enter the M2 site (their preference being a function of increasing $\langle M2-O \rangle$ distances), whereas *LREE* order at M4. Further support for this interpretation is provided by EXAFS data on the structural environments of *HREE* which have been proven to be 6-fold

coordinated in silicate glasses (Ponader and Brown, 1989).

By using this more complex model, we obtain excellent agreement between calculated and measured *D* and between r_0 and observed bond distances. The two different kinds of deviation from a predictive approach based on single unsplit site which is observed for cases (b) and (a, c) indicate that using first-order approximation models of the crystal structure and of cation site-distribution may fail to explain *REE* fractionation and point out the need of incorporating a more accurate model based on fine-scale cation partitioning into the frame of the Blundy and Wood's theory.

References

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