

A crystal chemical re-evaluation of amphibole/melt and amphibole/clinopyroxene D_{Ti} values in petrogenetic studies

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ABSTRACT

Constraints on the calculation and use of mineral/melt and two-mineral partition coefficients for Ti (D_{Ti}) have been derived from current knowledge of the distinct crystal-chemical mechanisms for the incorporation of Ti^{4+} in the amphibole structure as follows: (1) mineral/melt partition coefficients for Ti, and other tetravalent high field-strength elements (HFSE), can be compared only when considering the fraction of Ti^{4+} that enters the same structural site; (2) accurate two-mineral partition coefficients can be obtained only when considering the fraction of Ti^{4+} that is involved in the same crystal-chemical mechanism in the two relevant phases (i.e., $^{\text{M2}}\text{Ti}^{4+}$ and $^{\text{M1}}\text{Ti}^{4+}$ for amphibole and clinopyroxene, respectively).

The complete crystal-chemical characterization of synthetic titanian pargasite and kaersutite and of synthetic richterite (all crystallized under P , T , X , f_{O_2} conditions of interest for upper-mantle studies) shows that the site preference of Zr and Hf differs between the two amphibole compositions; these elements are essentially ordered at M2 in pargasite and kaersutite, but preferentially enter M1 in richterite. In the latter case, Ti segregates into the split M1' site with distorted coordination and shorter Ti-O3 distances, whereas Zr and Hf most likely prefer the larger and more regular M1 site. The observed site preference is strongly controlled by the relative dimensions of the available sites. The crystal-chemical mechanisms that govern the incorporation of octahedral high-charge cations are the local charge balance of $^{\text{IV}}\text{Al}$ (by $\text{R}^{3,4+}$ at M2) and of dehydrogenation (by $\text{R}^{3,4+}$ at M1); thus the incorporation of Zr and Hf depends on distinct intensive parameters in the two amphibole compositions.

Calculation of partition coefficients and of elastic-site parameters under the assumption that all Ti and other HFSE⁴⁺ order at the M2 site in amphibole, as is currently done in geochemical studies, is strongly biased. In the presence of significant dehydrogenation, amphibole/melt D_0 values obtained from modeling based on the elastic-strain theory starting from the more-accurate site populations for Ti may be only 1/4 of those obtained by using the total Ti content, and the derived site parameters E and r_0 are more consistent with octahedral coordination. This result has important consequences for the prediction of D values under P - T conditions different from those of the experimental work.

Applying the above concepts to data from natural assemblages, we obtained a significantly narrower (0.3–2.4 vs. 1.5–8.9) and more reasonable range of variation for amphibole/clinopyroxene D_{Ti} . A relationship between these values for D_{Ti} and pressure is also now apparent.