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., $M^2_{Ti}^{4+}$ and $M^1_{Ti}^{4+}$ 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 $[IV]$ Al (by $R^{3,4+}$ at $M2$) and of dehydrogenation (by $R^{3,4+}$ 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 HFSE$^{4+}$ 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 $D_{Ti}$ 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.

INTRODUCTION

Mineral/melt partition coefficients ($D$ values) play a crucial role in determining the composition of hydrous and anhydrous mantle- and crust-derived magmas; a knowledge of the correct values of $D$ is thus fundamental for deciphering magma evolution. Similarly, two-mineral partition coefficients measured for major and trace elements in coexisting mineral phases are potentially very powerful for the petrogenetic study of metamorphic and igneous rocks. The partitioning behavior of many elements is thus fundamental for describing petrological processes in general, but is crucial when studying mantle processes. Unfortunately, a detailed knowledge of how $D$ values vary as a function not only of $P$, $T$, and $f_{O_2}$, but also of the chemical composition ($X$) of the system must be achieved to interpret the available data more accurately.

The number of studies of partitioning behavior of major and trace elements under different $P$-$T$-$X$ conditions in both natural and synthetic assemblages has increased rapidly in recent years due to the availability of very sensitive analytical equipment [such