

On the correct determination of D_{Ti} in amph/liq and amph/cpx partitioning: the key role of the crystal-chemical mechanisms

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Recent work on spinel-facies mantle assemblages has shown that $D_{Ti}^{Amph/Cpx}$ (a) are always higher than 1; (b) may vary in the range 2.7–8.9, and (c) are significantly higher than those of REEs and Zr (Vannucci *et al.*, 1995). Therefore, in amphibole-bearing systems Ti can strongly fractionate relative to REEs and Zr, with important implications for the modelling of geochemical processes.

The behaviour of Ti^{4+} in amphibole is rather complex, and has recently been the subject of a number of systematic studies based on complete (EMP+SIMS) chemical characterization and X-ray single-crystal structure-refinement (SREF) of calcic, sodic-calcic and sodic amphiboles (Oberti *et al.*, 1992, Hawthorne *et al.*, 1993, 1998). These studies have shown that Ti^{4+} can enter the amphibole structure according to three different crystal-chemical mechanisms: (a) Ti^{4+} Ti^{4+} Ti^{4+} ; (b) Ti^{4+} Ti^{4+} Ti^{4+} ; (c) Ti^{4+} Ti^{4+} Ti^{4+} . According to these results, a straightforward procedure has been designed which now allows the determination of Ti partitioning on the basis of the structure refinement, i.e. of bond distances and refined site-scatterings at the involved sites.

It is pertinent to the present work to note that mechanisms (a) and (b) are peculiar to the amphibole structure [in particular, (a) is peculiar to only richteritic compositions], whereas mechanism (c) is available for both amphibole and clinopyroxene. Therefore, the higher Ti preference observed in amphibole has to be related to the larger number of crystal-chemical mechanisms (and also of structural sites) available. However, it is also evident that the correct calculation of both $D_{Ti}^{S/L}$ and $D_{Ti}^{S/L}$ from chemical analyses is not straightforward. Firstly, when comparing different mineral phases (for instance amphibole and clinopyroxene), only the Ti

fractions involved in the same crystal-chemical mechanism should be taken into account in the calculation of $D_{Ti}^{S/L}$. Secondly, when fitting D_{4+} to calculate r_0 , D_0 and E according to the Blundy and Wood (B&W, 1994) model, we must be sure to take into account only the fraction of Ti which enters the involved structural site.

These conclusions have been verified on natural and synthetic samples available at the CNR-CSCC. A number of representative crystals were selected, and underwent SREF analysis followed by additional EMP and SIMS analyses in order to avoid the problems due to intercrystalline compositional variations. In particular, the requirements for the use of the B&W model were checked on selected synthetic richterite, pargasite and kaersutite crystals with significant oxy-components crystallised under controlled P, T and X conditions as described in Tiepolo *et al.* (1998).

In pargasite and kaersutite, Ti^{4+} can only enter the octahedral strip, which is built up of three independent M1, M2 and M3 sites. Fig. 1 shows the relationship observed between the $\langle M2-O \rangle$ distance obtained from SREF and the r_0 for the M2 site calculated according to the B&W model on the basis of the following assumptions: (a) $M2Ti = Ti_{tot}$; (b) $M2Ti = Ti_{tot} - \frac{1}{2} O^{2-}$; (c) $M2Ti = Ti_{tot} - \frac{1}{2} O^{2-} - M3Ti$. With the increasing crystal-chemical soundness of Ti partitioning, the calculated r_0 's definitely increase and move towards values compatible with the ideal dependence (a line with slope 1 and intercept equal to the O^{2-} ionic radius); moreover, their scattering decreases. Concerning the other parameters of the B&W model, D_0 's (i.e. the strain-compensated partition coefficients) calculated with the correct Ti partitioning are about half of those calculated with the total Ti contents, whereas E's (which are an inverse measure of the compliance of

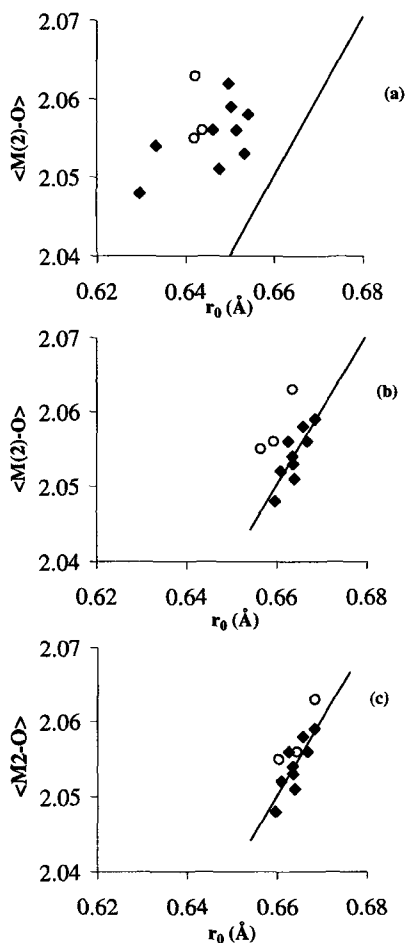


FIG. 1. Changes in r_0 with different assumptions on Ti contents at M2 in pargasite.

the site) increase by a nearly constant value of 600 GPa.

In richterite, Ti^{4+} can be present in both tetrahedral and octahedral coordination, and orders at the T2 and M1, M2 sites, respectively. Moreover, the refined values of the r_0 and distances may be consistent with the presence of tetravalent trace-elements at the M1 site. Fig. 2 shows the variations in the calculated r_0 for the two hypotheses (R^{4+} at M1 and R^{4+} at M2) by assuming that (a) $M1, M2 Ti = Ti_{tot}$; (b) $M1, M2 Ti = Ti_{tot} - T2Ti$; (c) $M1, M2 Ti$ from site populations. It is evident from Fig. 2 that no correlation can be obtained by using the total amount of Ti, whereas a linear correlation with absolutely reasonable values for the slope (1.04) and the intercept (1.38 Å) can be obtained for M1 when the correct site populations are

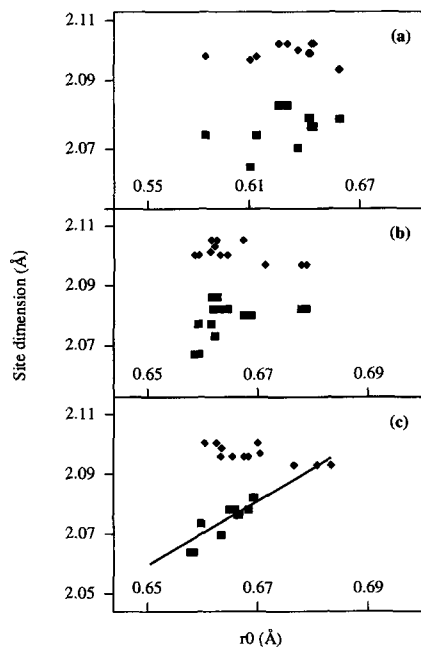


FIG. 2. Changes in r_0 with different assumptions on Ti contents at M1 (■) and M2 (◆) in richterite.

taken into account. Therefore, tetravalent trace-elements order at the M1 site in richterite, whereas Fig. 1 shows that they order at the M2 site in pargasite and kaersutite. This work thus indicates that the structure exerts a very stringent control on the site preference of trace elements, as the latter can even reverse as a function of the relative dimensions of the available sites in different amphibole end-members.

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