Crystal chemical constraints on the partitioning of U-series elements during mantle melting

B. J. Wood
J. D. Blundy
J. A. C. Robinson

CETSEI, Department of Earth Sciences, University of Bristol,
Bristol BS8 1RJ, U.K

We develop recent models of crystal-liquid partitioning of trace elements (Blundy and Wood, 1994; Wood and Blundy, 1997) to predict the effects of charge and ionic radius on the partitioning of 2+, 3+ and 4+ ions between clinopyroxene, garnet and silicate melt. These are found to exert important controls on partitioning of U-series elements and on the generation of ^{230}Th excesses.

Blundy and Wood (1994) and Wood and Blundy (1997) showed that partitioning of 1+, 2+ and 3+ cations between plagioclase and silicate melt and clinopyroxene and silicate melt closely follows the lattice strain energy model of Brice (1975). The latter predicts an approximately parabolic dependence of Nernst partition coefficient D_i ($= \frac{[i]_{crystal}}{[i]_{melt}}$) on the radius of the ion r_i:

$$D_i = D_o \exp \left[\frac{-4\pi E N_A \left(\frac{r_o}{2} (r_o - r_i)^2 - \frac{1}{3} (r_o - r_i)^3 \right)}{RT} \right] \quad (1)$$

In equation (1), D_o is the partition coefficient of an ion of radius r_o which has the same charge as i and which enters the cation site without straining the lattice, N_A is Avogadro's Number and R the gas constant. In general, r_o depends on the major element composition of the crystal and may vary substantially. Wood and Blundy (1997), for example, investigated the partitioning of rare earth elements (REE) between clinopyroxene and anhydrous silicate melt at high temperatures. By fitting the Brice model to 82 independent experiments in which D values were measured for 3 or more REE they found that the apparent value of r_o for the clinopyroxene M2 site is a function of clinopyroxene composition:

$$r_o = 0.974 + 0.067 X_{Ca}^{M2} - 0.051 X_{Al}^{M1} \text{ Å} \quad (2)$$

where X_{Ca}^{M2} and X_{Al}^{M1} refer, respectively, to the atomic fractions of Ca and Al on the clinopyroxene M2 and M1 sites. The pressure-temperature dependence of pyroxene composition along the mantle solidus should, therefore affect the size of the site, r_o and

hence the partitioning behaviour between clinopyroxene and silicate melt.

With increasing pressure along the mantle solidus, we find that clinopyroxene becomes richer in Na_2O and Al_2O_3 and that these components (from eq. 2) reduce the size of the large M2 site. Since U^{4+} has an ionic radius about 0.05 Å smaller than Th^{4+}, the reduction in the M2 site size should decrease the preference for Th relative to U. We find, in fact, that the compositional effects are sufficiently great that D_U/D_{Th} should change from <1.0 at pressures of about 1.0 GPa to >1.0 above 1.5 GPa. Thus, melting in the stability field of clinopyroxene should produce excess ^{238}U relative to ^{230}Th at low pressure and excess ^{230}Th above 1.5 GPa. Observed excesses of ^{230}Th in MORB should not, therefore, require the presence of garnet in the source region.

We performed experiments at 1.5–1.9 GPa on compositions doped with U and Th to test the predictions. Crystals and quenched melts were analysed by ion microprobe. On the mantle solidus at 1.5 GPa, D_U/D_{Th} for clinopyroxene was found to be 1.07 ± 0.08, while a value of 1.19 ± 0.04 was obtained at 1.9 GPa. This confirms our model prediction that residual garnet is not required to generate excess ^{230}Th in mantle melts.

Solid-liquid partition coefficients for other members of the U decay series, Ra, Ac and Pa may be calculated from the model. For clinopyroxene we obtain D_{Ra} of 3×10^{-8}, D_{Ac} of 5×10^{-4} and D_{Pa} of approximately 10^{-5}. Orthopyroxene is found to be elastically similar to clinopyroxene, which enables us to calculate for this phase, D_{Ra} of 4×10^{-10} and D_{Ac} of 1×10^{-5}.

References

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