# Towards a predictive model for garnet-melt trace element partitioning: experimental and computational results

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Garnet-melt trace element partition coefficients (D's) are a key component of all models involving melting of the garnet-bearing part of the Earth's mantle. However, until recently, a lack of systematic partitioning studies prevented prediction of changes in garnet-melt D's with pressure, temperature and composition (*P*, *T* and *X*). In a previous study (Van Westrenen *et al.*, 1998) we quantified the large influence of garnet major element composition (*X*) on *REE* partitioning by performing experiments at 3.0GPa along the pyrope-grossular join in CMAS. Our findings, presented in the form of Onuma diagrams (ionic radius *r* versus *logD*), are summarised in Fig. 1. Viewed in the light of the simple lattice strain model of Blundy and Wood (1994), the following key observations were made: 1) For both divalent and trivalent cations entering the garnet X-site, the value of the 'ideal' ionic radius $r_0$ increases significantly from pyrope-rich to grossular-rich garnets. This is in accordance with the known variation of the X-site size with composition. 2) Simultaneously, the tightness of the partitioning parabolas, determined by the Young's modulus E of the X-site, decreases towards grossular, again in accordance with known variations of the Young's modulus of pyrope and grossular.

Here we report a two-fold extension to our previous study: firstly, new data are presented for garnet-melt partitioning in FCMAS at 3.0 GPa and ~1545°C, the same conditions as for our earlier experiments in CMAS. Concentrations of trace elements (including Li, LILE, HFSE, *REE*, In, Sc and Cd) were measured with SIMS at Edinburgh University. Results allow us to extend our earlier observations on the influence of garnet major element composition (Fig. 1) to iron-bearing garnets. This is an important step on the way to a predictive model applicable to natural systems, in which Py+Gr+Alm typically comprise over 90% of the garnet.

Secondly, we performed atomistic computer simulations of isovalent ion substitution on the X-site of end-member garnets pyrope, grossular and almandine, using the GULP package. Integral charges were assigned to the ions involved, and

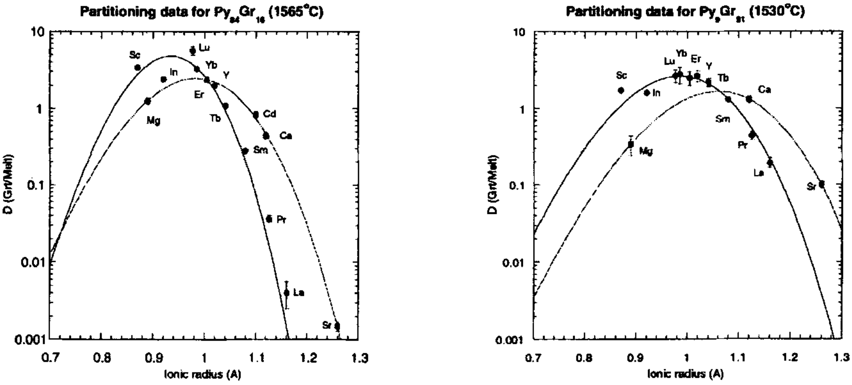

FIG. 1. Partition coefficients for divalent and trivalent ions between pyrope-rich (left) and grossular-rich (right) garnets and anhydrous silicate melt in CMAS.

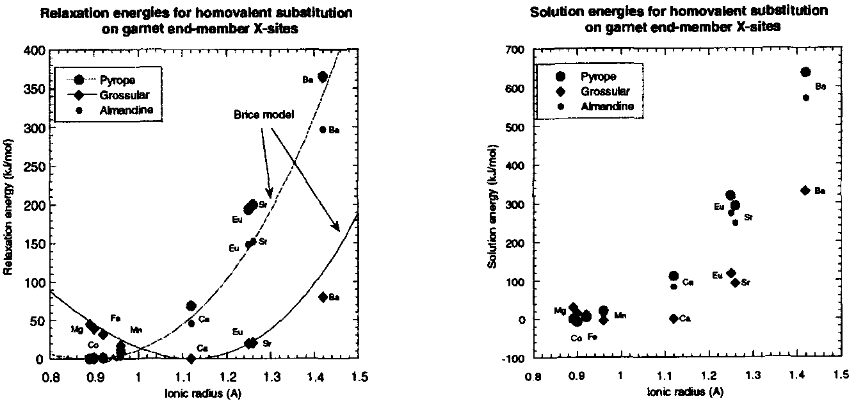

FIG. 2. Computed relaxation (left) and solution (right) energies for homovalent substitution on garnet X-sites.

some account was taken of oxygen polarisation using the shell model of Dick and Overhauser (1958). An inner region immediately surrounding the X-site, consisting of around 250 atoms, was assumed to accommodate most of the perturbations caused by insertion of the substituent cation, while the outer region was taken to remain largely unperturbed (two-region approach). The consistent set of interatomic potentials and shell parameters from Purton *et al.* (1996) was used to calculate unrelaxed and relaxed defect energies, the difference between the two giving the relaxation energy. Finally, solution energies were calculated from the defect energies and the difference in lattice energies between the binary oxides of the host and dopant cations. Computed relaxation and solution energies for eight divalent cations substituting on the X-sites of three end-member garnets are given in Fig. 2.

Although quantitative comparison between D's from experiments and computer simulations at 0 K requires incorporation of finite concentration effects and melt structure, qualitative comparisons can be made. Both relaxation and solution energies show a parabolic dependence on ionic radius. The variations in curvature of the parabolas (shown in Fig. 2 for grossular and pyrope) mirror the known variation in the compressibility of the different X-sites, in a similar way to curvatures in the experimental results for divalent cations shown in Fig. 1. Solution energies show a minimum at a radius corresponding to that of the host cation, a trend mirrored in the shift of $r_0$ to higher values for Ca-rich garnets (Fig. 1). Both experimental (Fig. 1) and computational Fig. 2) results therefore show that crystal chemistry has a large influence on garnet-melt partitioning

## References

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