

Partition coefficients as sums of multiple substitution mechanisms

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Many trace elements can partition into minerals by more than one substitution mechanism. One particularly significant geological example is given by water in olivine, where H^+ can be associated with Si vacancies, Mg vacancies, coupled to trivalent cations (especially Cr^{3+} and Fe^{3+}) and coupled to Ti [1]. However, the principles potentially apply to any trace element substituting in a crystal by more than one mechanism, and such situations which may be common where there is a charge mismatch between the trace element and the major element for which it substitutes.

In a series of 1-atm experiments at 1406 °C in the system $CaO-MgO-SiO_2 \pm Al_2O_3 \pm TiO_2$ saturated in both forsterite and protoenstatite, thus imposing nearly constant silica activity, we demonstrate that the rare earth elements (REE^{3+}) substitute for Mg^{2+} in both minerals by two mechanisms: (a) $2 Mg = 4/3 REE + \text{vacancy}$, and (b) $Mg + Si = REE + Al$. We show that the crystal/melt partition coefficients can be calculated as the sums of the two individual mechanisms, e.g., in the case of protoenstatite/melt, $D_{Li} = 0.015 + 0.064 \times X_{Al}$, where X_{Al} is the mole fraction of $AlO_{1.5}$ in the melt. For a typical X_{Al} for basalts of 0.15, the Al-coupled mechanism dominates by ~ 5 for all the REE and also Sc in protoenstatite, whereas in forsterite the vacancy mechanism dominates by a factor of 12 for a light REE (Pr) but by factors of less than 2 for the heaviest REE and by only 1.2 for Sc.

The implications for modelling trace element behaviour are significant. Where the different substitution mechanisms involve charge-balancing by different stoichiometric controls, partition coefficients may be much more sensitive to melt composition than if only one mechanism were involved, for example through their response to thermodynamic variables such as silica activity. Moreover, the variables of temperature and pressure may be expected to have different effects on different mechanisms. This complexity is likely to account for many of the difficulties that have arisen in deriving generalised parameterizations of trace-element partitioning.

To extend this approach to other minerals, experiments designed to control as many major-element activities as possible are needed to disentangle the substitution mechanisms and evaluate their relative magnitudes.

[1] Berry et al. (2005), *Geology* 33, 869-872.