What determines the values of mineral/melt partition coefficients?

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The concentrations of trace elements in coexisting minerals and melts can be defined in terms of a mineral/melt partition coefficient. Thus an accurate knowledge of the values of mineral/melt partition coefficients for a wide range of trace elements is essential if petrogenetic information is to be extracted from trace element concentrations measured in lavas. In principle one would like to be able to predict the values of these partition coefficients as functions of the concentration, ionic radius and charge of the trace element of interest, the pressure and temperature, the composition of each phase and known physical and thermochemical properties of the mineral and melt phases. In this paper I will show how the dependence of partitioning on these parameters can be modelled. I will use olivine/melt partitioning to illustrate these calculations.

Experimental and analytical methods

Many of the early data of mineral/melt partitioning were obtained by analysis of phenocryst-matrix pairs. However the bulk analysis of separated phases appears to have been unable to measure partition coefficients smaller than 10^{-3}. Most recent partitioning studies have involved the analysis of mineral/melt pairs produced in experiments. The partition coefficients measured are dependent on the cooling and crystal growth rates during an experiment. Anomalously large partition coefficients can be observed at high cooling or crystal growth rates. For example partition coefficients for some elements can be increased by more than 200% if a sample is cooled from above its liquidus, owing to the rapid growth of crystals from supersaturated solutions. In particular, partition coefficients measured from skeletal crystals should be treated with some caution, as the high crystal growth rate associated with this texture may have prevented chemical equilibrium occurring at the crystal/melt interface.

Many different analytical techniques have been used to measure mineral/melt partition coefficients; of these only secondary ion mass spectrometry (SIMS), synchrotron x-ray fluorescence spectrophotometry (SXRFS) and perhaps laser-ablated inductively coupled plasma mass spectrometry (LICPMS) have been demonstrated to be able to measure the partition coefficients for very incompatible elements.

Henry's Law

Most studies of trace element partitioning are conducted with concentrations of the elements of interest much larger than those found in the earth. If Henry's Law is satisfied, partition coefficients will be independent of the concentration of the trace element. Although deviations from Henry's Law at low concentrations were found in some studies using beta-track autoradiography, these results have been shown to be artefacts of the counting technique (Beattie, 1993a). There is therefore no evidence that trace elements fail to satisfy Henry's Law at crystalline concentrations between those found in the earth and 1%.

Pressure, Temperature and Composition

Partition coefficients can be calculated as a function of composition, pressure and temperature if activity-composition relationships can be determined. Regular solution models of the melt phase do not yield accurate estimates for partition coefficients, presumably because the entropy of mixing of oxide components is not configurational. Using an empirical solution model for the melt phase, in which the network forming quasi-lattice is allowed to be non-ideal, olivine and orthopyroxene melt partition coefficients can be accurately calculated for Mg, Fe, Mn, Co and Ni if the pressure, temperature and melt composition are known (Beattie 1993b).

Although partition coefficients change with pressure and temperature, this effect is probably due to their effect on melt composition. A series of experiments has been conducted in the system CMAS such that forsterite coexists with a melt phase of almost identical composition at 1773K at 1 bar, 1848K at 1.5GPa and 1848K at 2GPa. Olivine/melt partition coefficients for the divalent cations are equal in all these experiments, suggesting that the dependence on pressure and temperature is small for these elements. By contrast, the Al partition coefficient increases greatly with *P* and *T*. Thus the values of partition coefficients for elements whose substitution into crystalline phases is charge balanced by a coupled AlSi-1 substitution may also be dependent on pressure and temperature.

The partition coefficients for the divalent cations are correlated with those of Mg. As the effect of pressure and temperature on the partition coefficients of these elements is small, it is possible to combine correlations of the partition coefficients of these elements with the constraint of mineral stoichiometry to calculate Mg partition coefficients from the composition of the melt phase alone. The average absolute difference between the calculated and measured Mg partition coefficients is only 3% for olivine/melt pairs and 5% for orthopyroxene/melt pairs.

Ionic radius and charge

Mineral/melt partition coefficients should decrease with increasing ionic radius owing to the energy required to strain the crystalline lattice to accommodate the substituent ion. Thus partition coefficients for large cations can be calculated from those of Mg or Ca if this strain energy can be calculated. Nagasawa (1966) demonstrated that the energy required to expand a continuous isotropic medium to incorporate an ion of given size can be calculated from the site size at minimum energy, the medium's bulk modulus and Poisson's ratio, and the cation's ionic radius.

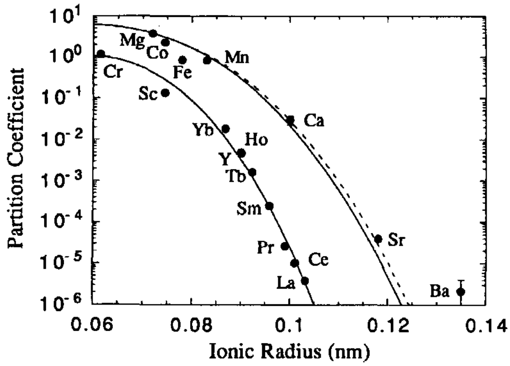

FIG. 1. Olivine/melt partition coefficients for divalent and trivalent cations are smooth functions of ionic radius. These partition coefficients were measured using SIMS on an experiment conducted at 1463K and 1 bar, the standard errors of the partition coefficients are shown except where smaller than the symbol size. The solid curves give the partition coefficients calculated from the Mg partition coefficient and lattice strain energy. The dashed line shows the fit to the divalent partition coefficients if an empirical ocatahedral bulk modulus of 90 GPa is used.

Assuming the site size is 0.057nm (that for a close packed mineral) and olivine bulk moduli and Poisson's ratios of 95.3 GPa and 0.25 respectively (Isaak *et al.*, 1989) it is possible to calculate olivine/melt partition coefficients for the divalent cations. The figure shows that the partition coefficients for most of these elements can be calculated with a precision comparable to that of the experiments in which they were measured. The poor fit for the Co and Fe partition coefficients may reflect crystal field effects.

The substitution of trivalent cations is not charge balanced by defects of vacancies, as the deviations from Henry's Law that this mechanism would require are not observed. Charge balance is therefore maintained by a coupled Al for Si exchange. The partition coefficients of the trivalent cations can be modelled using the same equation for the strain energy of the crystalline lattice. The fit to the trivalent partition coefficients shown in the figure requires that the Al–Si exchange heat capacity is 55 J K^{-1} mol^{-1} and that the bulk modulus of the octahedral site is 180 GPa: i.e. twice that measured for forsterite. This local increase of the bulk modulus is consistent with stiffening of the crystalline lattice adjacent to sites where Si has been replaced by the larger Al tetrahedron.

This approach can also be used to model partitioning for other minerals. For example, the partition coefficients for the alkaline earths can be accurately predicted from the Ca partition coefficients for garnet, clinopyroxene, orthopyroxene and plagioclase using values of the bulk modulus and Poisson's ratio taken from the literature if minimum energy size of the largest site is determined empirically. A similar approach may also be used to model the partition coefficients of the trivalent cations for these minerals.

References

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