Energetics of element partitioning between minerals and melts

J.D. Blundy
B.J. Wood

CETSEI, Department of Geology, Bristol University,
Bristol BS8 1RJ, UK.

Introduction

The partitioning of elements between minerals and melts depends on the mechanical and electrostatic energies associated with substitution of mismatched cations into crystal lattices. Using new experimental data on the partitioning of 15 elements between plagioclase, clinopyroxene and silicate melt, we demonstrate that a simple model of elastic strain in an isotropic ionic crystal successfully describes the partitioning behaviour of any isovalent cation series. In this model partitioning is dominated by the elasticity of a lattice site, as measured by its Young's Modulus (E_a), which is shown to be a linear function of the formal charge on the substituent cation (z_c). The relationship between E_a and z_c is similar to that previously reported for cation-oxygen polyhedra in silicate minerals (Hazen and Finger, 1979). Thus, if the polyhedral characteristics of a mineral site are known, its element partitioning behaviour can be predicted.

Theory

The energetics of element partitioning can be divided into two parts: an ideal part (ΔG_{ideal}) and an excess part (ΔG_{excess}), such that:

$$D_i = \exp\left(\frac{\Delta G_{ideal} + \Delta G_{excess}}{RT}\right) \quad (1)$$

where D_i is the Nernst partition coefficient, R is the gas constant and T is the temperature in °K. To a first approximation ΔG_{ideal} is equal in magnitude but opposite in sign to the free energy of fusion (ΔG_{fusion}) for the host mineral. Conversely ΔG_{excess} is related to the work required to remove from the melt and insert into the crystal lattice a cation differing in size and/or charge from the host cation. As crystals are usually less compressible than melts of equivalent composition, ΔG_{excess} is likely dominated by the mechanical strain energy around misfit cations in the crystal lattice (e.g. Nagasawa, 1966; Tsang *et al.*, 1978; Brice, 1975; Colson *et al.*, 1988; Blundy and Wood, 1991) with melt structure playing a subordinate role.

Brice (1975) presents an expression which relates the mechanical strain energy around a misfit homovalent cation (ΔG_{strain}), to the Young's Modulus (E_a) of the host crystal:

$$\Delta G_{strain} = -4\pi E_a N_A\left[\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3\right] \equiv \Delta G_{excess} \quad (2)$$

where r^0 is the optimum radius of the lattice site, r_i is the radius of the substituent cation and N_A is Avogadro's Number. By replacing ΔG_{ideal} in (1) with a term, D_0, describing the partition coefficient for the 'optimal' cation ($r_i = r_0$) at the pressure and temperature of interest, we obtain an expression relating D_i to D_0, r_0 and E_a:

$$D_i = D_0 \cdot \exp\left(\frac{-4\pi E_a N_A\left[\frac{r_0}{2}(r_i - r_0)^2 + \frac{1}{3}(r_i - r_0)^3\right]}{RT}\right) \quad (3)$$

where D_0 is related to ΔG_{fusion} for the mineral of interest.

Method

In order to test this simple theory we have performed mineral-melt partitioning experiments for clinopyroxene and plagioclase over the pressure range 1 bar to 30 kbar in the simple system $CaMgSi_2O_6$–$NaAlSi_3O_8$–$CaAl_2Si_2O_8$ doped with ppm levels of Li, K, Rb, Cs, Sr, Ba, Zn, Ga, Y, La, Sm, and Pb. Experiments were performed in air in vertical quench furnaces (1 atm), and in piston cylinder apparatus (10–30 kbar) with $BaCO_3$ pressure cells and graphite furnaces. Starting materials were glassed gel mixtures welded into Pt capsules. Quenched run products were analysed by electron microprobe (EMP; University of Bristol) and secondary ion mass spectrometry (SIMS; University of Edinburgh).

Results

By fitting equation (3) to our experimentally-determined partition coefficients for each isovalent series of cations substituting onto the M-site in

plagioclase or the M2-site in clinopyroxene we can obtain best-fit values for D_0, E_a and r_0. Where D_i's for only three elements on a site have been determined it is necessary to fix one parameter for the purposes of regression. In the case of clinopyroxene we have chosen to fix r_0 at 1.13Å, in keeping with mean M2–O bond lengths in diopside (Levien and Prewitt, 1981). For the plagioclase experiments r_0 is found to increase from anorthite to albite. There is a greater sensitivity of r_0 to cation charge in the albite structure relative to the anorthite structure which may be related to the different topological consequences of inserting charge-balancing Al cations into the two structures. In keeping with the observations from $1+$ and $2+$ cations, we have imposed a linear dependence of r_0^{3+} on plagioclase composition.

The values of E_{plag} obtained by regression depend both on plagioclase composition and, to a greater extent, on the charge of the substituent cation. Thus for univalent cations F_{plag}^{1+} decreases from 0.59 ± 0.08 Mbar at anorthite to 0.46 ± 0.04 Mbar at albite, while E_{plag}^{2+} decreases from 1.11(7) to 0.79(5) and E_{plag}^{3+} decreases from 1.56(8) to 1.38(6) Mbar over the same interval. For clinopyroxene E_{cpx} also varies similarly with charge: mean values of E_{cpx}^{1+}, E_{cpx}^{2+} and E_{cpx}^{3+}, from 7 experiments, are 0.38(8), 1.89(21) and 2.39(27) Mbar, respectively.

Two features of these results are significant. Firstly, for homovalent substitution, E_a for the site is similar in magnitude to the Young's Modulus of the bulk crystal, suggesting that the elastic properties of the crystal are strongly influenced by the elastic properties of the cation site, rather than the relative rigid Si–O(–Al) tetrahedra (cf. Levien and Prewitt, 1981). Secondly E_a is an approximately linear function of cation charge (z_c). A similar dependence of bulk modulus (K_s) on z_c has been demonstrated for cation-oxygen co-ordination polyhedra in a wide variety of silicates and oxides (Hazen and Finger, 1979). Indeed, when our values of site E_a are converted to site K_s, using the Poisson's Ratio of the bulk crystal, they are shown to follow an identical relationship between K_s and z_c as that shown by Hazen & Finger.

We conclude that a simple polyhedral approach can be used to quantitatively describe element partition coefficients. The simple model requires only a knowledge of the geometry of the site of interest, an estimate of Poisson's ratio (typically 0.25), and a value for the partition coefficient of any single element from the valence group of interest (e.g. Na^+, Ca^{2+}). This approach can be used predictively to estimate partition coefficients for a variety of putative lower mantle phases and thereby constrain geochemical models of mantle evolution and differentiation.

References

Blundy, J.D. and Wood, B.J. (1991) *Geochim. Cosmochim. Acta*, **55**, 193–209.

Brice, J.C. (1975) *J. Crystal Growth*, **28**, 249–53.

Colson, R.O., McKay, G.A. and Taylor, L.A. (1988) *Geochim. Cosmochim. Acta*, **52**, 539–53.

Hazen, R.M. and Finger, L.W. (1979) *J. Geophys. Res.*, **84**, 6723–8.

Levien, L. and Prewitt, C.T. (1981) *Amer. Mineral.*, **66**, 315–23.

Nagasawa, H. (1966) *Science*, **152**, 767–9.

Tsang, T., Philpotts, J.A. and Yin, L. (1978) *J. Phys. Chem. Solids*, **39**, 439–42.