

ELECTRONIC APPENDIX 5: PLAGIOCLASE-MELT PARTITION COEFFICIENTS

Partition coefficients for many elements in plagioclase vary systematically with anorthite content of the crystal and temperature (e.g. Blundy & Wood, 1991; Bindeman *et al.*, 1998). Pressure may play an additional role in controlling partitioning (Bédard, 2006) while variable fO_2 is known to affect the partitioning of elements with multiple vacancies (e.g. Eu; Aigner-Torres *et al.*, 2007).

Attempts to parameterise partitioning of elements as a function of anorthite content and temperature were carried out by Blundy & Wood (1991) (for Sr and Ba) and Bindeman *et al.* (1998) (for 29 elements including some REEs). The Lattice Strain Model (LSM) for crystal-melt partitioning (Blundy & Wood, 1994), which was employed for clinopyroxene partitioning by Wood & Blundy (1997), has also been applied to plagioclase by Blundy & Wood (1994) and Blundy & Wood (2003a). In the latter work, some of the parameters required for calculating melt trace element compositions from crystal trace element compositions alone (*i.e.* needing no *a priori* knowledge of any partition coefficients) were provided. Based on new experimental data and reviews of multiple datasets respectively, Aigner-Torres *et al.* (2007) and Bédard (2006) have also calculated full sets of parameters for use in the lattice strain model.

The key equation for the LSM, based on that of Brice (1975) is:

$$D_i = D_0 \exp \left(\frac{-4\pi EN_A \left(\frac{r_0}{2} (r_i - r_0)^2 + \frac{1}{3} (r_i - r_0)^3 \right)}{RT} \right) \quad (\text{A. 1})$$

where D_i is the partition coefficient of an element i which has ionic radius r_i , and N_A is the Avogadro constant. The pre-exponential factor D_0 is the ‘strain-compensated’ partition

coefficient for a (fictive) ion with radius r_0 . In terms of the positions on the parabola defined by the LSM on an Onuma diagram (Onuma *et al.*, 1968), D_0 and r_0 refer to the y- and x-coordinates, respectively, of the apex of the curve. The LSM for plagioclase best describes partitioning onto the large cation site (M-site) in plagioclase (Blundy & Wood, 2003b), where E is the Young's Modulus of the site. Ionic radii for cations in VIII-fold co-ordination are taken from Shannon (1976). For 3+ ions that partition into plagioclase, including REEs and Y, r_0 is larger than the radius of the largest 3+ ion, La^{3+} . This means that one limb of the Onuma parabola for 3+ cations is unconstrained, and thus values of the lattice strain parameters for 3+ cations, r^{3+}_0 , D^{3+}_0 and E^{3+}_M have been difficult to derive in past studies. Nevertheless, from fitting the data of Bindeman *et al.* (1998) and Bindeman & Davis (2000) to the LSM, Blundy & Wood (2003a) derived values for r^{3+}_0 and E^{3+}_0 . From new experiments Aigner-Torres *et al.* (2007) independently derived values for these two parameters which were almost identical to those of Blundy & Wood (2003a), and also calculated a value for D^{3+}_0 . Bédard (2006) compiled the data from many partitioning studies and also presented equations for the lattice strain parameters r^{3+}_0 , D^{3+}_0 and E^{3+}_M for plagioclase, which differ from those of Aigner-Torres *et al.* (2007) and Blundy & Wood (2003a), perhaps because of the inclusion of data from natural samples as well as experiments. Because the studies of Aigner-Torres *et al.* (2007) and Blundy & Wood (2003a) depend exclusively on partitioning experiments where conditions are generally well-constrained, it is considered better to use the mean D^{3+}_0 value provided by the former, and the r^{3+}_0 equation (given as a function of anorthite content) and E^{3+}_M value from the latter. In using the D^{3+}_0 value provided by Aigner-Torres *et al.* (2007), it is worth noting that the experiments in this work were conducted at 1180–1220°C with a starting composition of East Pacific Rise MORB (Sinton *et al.*, 1999). This starting composition is likely to be close in composition to the Icelandic melts from which the plagioclase in the current work crystallised. The plagioclase formed in the Aigner-

Torres *et al.* experiments had an average composition of $An_{76.4\pm 1.4}$, fairly close to the range of anorthite contents in the Borgarhraun plagioclase ($\sim An_{80-90}$). The mean D^{3+}_0 value from this work (mean and $1\sigma = 0.055\pm 0.025$) can therefore be reasonably applied to the conditions of plagioclase crystallisation in Borgarhraun basalts.

It should be noted that, since the pre-exponential factor D^{3+}_0 cancels out during calculation of $D_{REE^{3+}}/D_{REE^{3+}}$ values (the coefficient needed for calculation of equilibrium melt La/Y ratios), uncertainties in its value have no effect on calculated melt REE/Y values. Some effect from uncertainty in the appropriate value of D^{3+}_0 for Borgarhraun plagioclase crystals are expected in calculated $D_{Y^{3+}}/D_{Sr^{2+}}$ ratios; inaccuracy in this ratio would essentially shift the calculated Sr/Y values of the dataset by the same proportion.

For calculation of $D_{Sr^{2+}}$, equation 19a of Bédard (2006) was used. This equation was derived from regression of $RT(\ln D_{Sr})$ against anorthite content for a variety of natural and experimental data, including those of Bindeman *et al.* (1998). The r^2 value of this regression is 0.57. The values of $D_{Sr^{2+}}$ calculated using this equation are within $\sim 20\%$ of those calculated using the similar regressions of Blundy & Wood (1991) and Bindeman *et al.* (1998).

Additionally, the LSM was tested using r^{2+}_0 and E^{2+}_M values from Blundy & Wood (2003a) and the D^{2+}_0 value of Aigner-Torres *et al.* (2007). However, the difference between $D_{Sr^{2+}}$ thus calculated and $D_{Sr^{2+}}$ calculated by the Bédard (2006) equation is negligible (typically $<5\%$ relative).

Due to a paucity of experimental data concerning the partitioning of trace elements into plagioclase at pressures >1 atm, the effect of pressure on calculated D values is more uncertain. Based on the available data, Bédard (2006) suggested that D_{Sr} decreases by a factor of ~ 1.4 for every increase of 1 GPa. The effects of pressure on 3+ cation partitioning in plagioclase are unknown, and thus a constant E^{3+}_M was provided by Blundy & Wood

(2003a), rather than a P-dependent value as presented for clinopyroxene by Wood & Blundy (1997). Because the full effects of pressure variation are not known, they are not included in the calculation of trace element concentrations and ratios of equilibrium melts. While there may therefore be an offset between calculated and true melt concentrations and ratios, it should be noted that the effect of pressure on individual partition coefficients across the Borgarhraun plagioclase dataset is likely to be of lesser importance than the dependencies on temperature and anorthite content of plagioclase (dependencies which are better constrained) given that the range of pressures calculated for Borgarhraun melt crystallisation is fairly well constrained (2σ range of ± 2.2 kbar). As noted for clinopyroxene partition coefficient calculations by Winpenny & MacLennan (2011), the effect of pressure on $D_{REE^{3+}}/D_{REE^{3+}}$ values is likely to be minimal; however, because of the differing effects of pressure on 2+ and 3+ element partitioning (see Wood & Blundy, 2001), pressure may have slightly more influence on $D_{Y^{3+}}/D_{Sr^{2+}}$ ratios, and thus on calculated melt Sr/Y ratios. It is extremely unlikely, however, that varying pressure over the range of crystallisation depths of Borgarhraun plagioclase would significantly affect the observed four-fold spread (5.04–22.71) in calculated melt Sr/Y ratios. Taking all accuracy considerations (particularly D_0 and pressure) into account, the accuracy of the calculated melt Sr/Y dataset as a whole may be around 40% relative; for La/Y and similar ratios of 3+ cations in plagioclase, accuracy may be around 20% relative. The wide variability in melt trace element concentrations and ratios within each dataset is nonetheless considered to be robust because of the limited range of crystallisation conditions for Borgarhraun melts cannot explain this variability, and the fact that the anorthite content of each plagioclase zone is employed in the calculation of partition coefficients for each zone.

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