

EXPERIMENTAL DIVALENT ELEMENT PARTITIONING BETWEEN ANORTHITE AND CAI MELT.

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Introduction: A quantitative description of crystal-liquid trace element partitioning is critical to understanding the igneous differentiation history of the terrestrial planets. Anorthitic plagioclase is the type mineral of terrestrial planet crusts, and for the Moon, specifically, quantitative understanding of trace element partitioning in anorthite is key to testing models of the lunar magma ocean.

Although the partition coefficient, D , is expected to be independent of trace element concentration (Henry's Law), it will vary with pressure (P), temperature (T), and the major element composition or structure of both mineral and melt. The relative contributions of melt and mineral structures to element partitioning between the phases have been debated at length. Over the past decade Blundy and Wood [1,2] have developed and utilized a compelling element partitioning model based entirely on considerations of energetics in the mineral phase, drawing on insights of numerous workers [e.g., 3].

This study focuses on the Blundy-Wood quantitative thermodynamic model of partitioning, which interprets D values in terms of crystal lattice strain theory [4]. D is parameterized as a function of mineral composition, pressure, and temperature:

$$D_i(X, P, T) \equiv D_o \cdot e^{-4\pi \cdot E \cdot N_A \cdot \frac{r_o \cdot (r_i - r_o)^2 + \frac{1}{3}(r_i - r_o)^3}{R \cdot T}}$$

where D_o is related to the enthalpy of fusion of the mineral, E is the Young's modulus for volume strain of the crystallographic site, N_A = Avogadro's number, r_o = the ideal site radius, r_i = the substituting cation radius, and R = the gas constant. Although the authors have since acknowledged that melt plays a subordinate role [e.g., 2], its exact nature has been obscured by the complexity of systems investigated thus far.

Anorthite partitioning provides a good test of the role of liquid composition in that this phase can be crystallized as the liquidus phase from a wide range of melt compositions, allowing the melt structure and crystal chemical effects to be isolated. Six different CMAS bulk compositions with anorthite as the liquidus phase on an isothermal surface have been calculated using the MELTS formalism [5]. The MELTS thermodynamic model of the liquid will enable us to test whether composition (as such), component activities, or structural parameters provide the best prediction of liquid dependence. Our chosen compositions range from 40 to 65 wt. % SiO_2 . For comparison, a more "natural" CAI composition (224 [6]) has been studied. Rigorous quantification of melt contributions

to partitioning behavior via Onuma theory requires systems simpler than our CAI composition. Deviations in divalent anorthite-CAI partitioning from the Blundy-Wood model shed light on liquid phase involvement in element partitioning.

Experimental Approach: All starting materials have been synthesized and have been demonstrated to crystallize anorthite with little evidence of nucleation problems. Oxide reagent SiO_2 , Al_2O_3 , TiO_2 , MgO , and CaCO_3 were dried overnight at 800°C and vacuum cooled. Weighed quantities were ground under ethanol in an agate mortar for five hours. After drying, the mixture was heated to 1000°C in $200^\circ/\text{hour}$ steps where it was held for 24 hours. The powder was then fused in a Pt crucible at 1450°C and reground for 3 hours. A 1 g separate was spiked with a Sr and Ba trace element solution and dried. Initial experiments have focused on the 224 composition. Percent levels of Ba were added to guarantee electron microprobe measurements of Ba partitioning. The high Ba anorthite will also serve as a standard for future ion probe measurements for samples spiked at lower Ba levels. The spiked 224 and CMAS separates were then fused at 1390 and 1450°C , respectively, and ground under ethanol for another 3 hours.

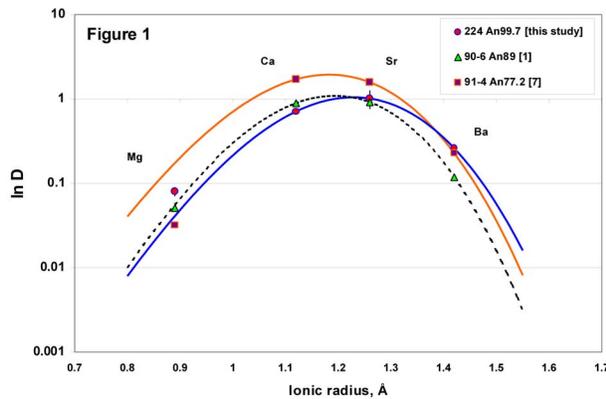
All experiments were conducted in Deltech vertical muffle furnaces in air, with temperatures monitored and maintained by Pt-Pt_{0.9}Rh_{0.1} thermocouples. The liquidus of the 224 composition was estimated as $1340 \pm 5^\circ\text{C}$ and that of the CMAS compositions range from 1395 to $1415 \pm 5^\circ\text{C}$. All experiments used ~ 40 mg of starting material adhered to Pt wire loops with polyvinyl alcohol. After allowing the bead to dry at room temperature for at least 6 hours, anorthite crystals were grown in slow crystallization ($2^\circ\text{C}/\text{hr}$) experiments. This approach gives large crystals for ion probe analysis, and maximizes the opportunity for slow growth and interface equilibrium partitioning. Trace element data are available for the 224 composition based on electron microprobe analysis. D values of final mineral and melt compositions were corrected for fractional crystallization according to the procedure of [7].

Results: Figure 1 compares Onuma curves parameterized (Table 1) from experimental divalent element partitioning data for 224 experiments with Blundy and Wood composition 90-6 [1] and composition 91-4 from Bindeman et al. [8]. D values from the three 224 experiments agree well. The Blundy and Wood end-member anorthite extrapolation (not shown) predicts

that the Young's Modulus, E , of the plagioclase crystal lattice site increases with An content, which narrows the Onuma curve, enhancing the differences between the 224 and Blundy-Wood curve. This strain parameter is related to the bulk modulus (K) of the crystal by Poisson's ratio. If anorthite is assumed to be an approximate Poisson solid, then $E \approx 1.5 K$, where K = bulk modulus [9].

	CAI An _{99.7} [this study]	Extrapolated An ₁₀₀ [1]	90-6 An ₈₉ [1]	94-1 An ₇₇ [7]
D_{Ca}	0.71 (<1)		0.89	1.709
D_{Sr}	1.01 (25)		0.914(17)	1.572
D_{Ba}	0.26(1)		0.118(12)	0.226(0.011)
D_{Mg}	0.083(1)		0.05	0.032
D_o	1.045	1.118	1.089	1.939
r_o (Å)	1.229	1.196 (18)	1.194	1.183
E kbar	941.3	1245 (148)	1082	982

If crystal chemistry were the only factor in element partitioning, one would expect agreement of the Onuma curve of CAI melt-equilibrated anorthite with the extrapolated An₁₀₀ curve of [1], or at least identical shapes. Instead, the curves differ, with a lower strain parameter describing the curve fitting the 224 partitioning data. At identical P-T conditions, anorthite crystals of different melt systems do not possess different internal strengths, which would suggest that melt composition may be responsible for the variable shapes of end-member anorthite curves. Although the temperatures of the 224 data range from 1200-1300°C, such temperature differences have limited influence on



D as described by the Blundy-Wood model. Between 1200 and 1350°C, calculated D_{Ba} increases by only 0.02 for An₁₀₀ in the Blundy and Wood and CAI melt systems. This indicates that temperature alone cannot explain differences between the divalent element partitioning curves of these different melt systems. Curves were parameterized and ionic radii were taken from Shannon [10] for VIII-fold coordination. Blundy and Wood [1] commented that adoption of VI- or VII-fold

coordination for the plagioclase M site had no material effect on their results.

The limited amount of data at present restricts interpretation of the curves and corresponding melt compositions, though a few strong correlations emerge from the data. D_o directly correlates with the molar sum of tetrahedrally coordinated network-forming cations Si^{+4} , Ti^{+4} , and Al^{+3} in the melts. This strong positive relationship suggests that higher concentrations of network-formers in melts may somehow enhance the ability of a growing crystal to fill the M plagioclase site with cations close to its ideal radius, such as Ca^{2+} . However, a complementary decrease in the presence of modifying cations in the melt with increasing D_o is not observed.

Blundy and Wood use D_{Mg} in their parameterization, but this isn't correct because Mg has been shown to substitute into tetrahedral sites [7,11]. Thus Mg has not been used in the fits of Figure 1. Re-parameterization of the 90-6 divalent element partitioning curve without D_{Mg} brings its shape slightly closer to that of 224. Figure 1 shows a 224 D_{Mg} higher than predicted by the divalent Onuma curve for that melt composition, but the Mg compositions in the anorthite of 90-6, and 91-4 in particular, fall below the divalent Onuma curves for the M site. A fourth D_i value is clearly desirable to better constrain the curves, but Mg appears an inappropriate selection for the plagioclase M site.

Conclusions: Variation of D_o , r_o , and E from the Blundy-Wood model for different melt systems suggests that melt has a significant effect relative to crystal chemistry on divalent element partitioning between anorthite and a coexisting liquid phase. Preliminary results indicate that D_o is directly correlated with the molar sum of network-forming cations Si, Ti, and Al in the melt. Greater understanding of melt influence on partitioning will enable further refinement of lunar anorthosite parent melt calculations and provide better constraints on magma ocean modeling.

References: [1] Blundy, J. A. and Wood, B. J. (1994) *Nature*, 372, 452-454. [2] Wood, B. J. and Blundy, J. A. (1997) *Contr. Min. Petr.*, 129, 166-181. [3] Onuma, N. et al. (1968) *EPSL*, 5, 47-51. [4] Brice, J. C. (1975) *J.Cryst.Growth*, 28, 249-253. [5] Ghiorso, M. S. and Sack, R. O. (1995) *Contr. Min. Petr.*, 119, 197-212. [6] Simon, S. B. et al. (1994) *GCA*, 58, 1507-1523. [7] Peters, M. T. et al. (1995) *GCA*, 59, 2785-2796. [8] Bindeman, I. N. et al. (1998) *GCA*, 62, 1175-1193. [9] Wood, B. J. et al. (1999) *GCA*, 63, 1613-1620. [10] Shannon, R. D. (1976) *Acta Cryst. Ser. A*, 32, 751-767. [11] Longhi, J. et al. (1976) *LPS VII*, 1281-1300.