

Importance of considering melt activity coefficients and charge-balancing substitution mechanisms when understanding partitioning in olivine. J. K. Anderson¹, S. J. Buhr², R. O. Colson³, L. K. Anderson, E. D. Young, and S. Fetting. Dept of Anthropology and Earth Science, Minnesota State University Moorhead, Moorhead MN 56563, ¹andersojor@mnstate.edu, ²buhrsa@mnstate.edu, ³colson@mnstate.edu

Introduction: Although lattice strain models predict free energy for partitioning reactions as a function of cation size [e.g. 1-6], these models are less well suited to predicting the effects of melt composition. Both melt activity coefficients and charge-balancing substitutions (stoichiometric effects) need to be considered in order to understand melt effects on partitioning [e.g 7]. New results in simple systems in which temperature and crystal composition are held constant yield insights into the effects of stoichiometric considerations. These results suggest that more than one charge-balancing substitution mechanism may operate at a time in olivine.

Experimental Concept: Lattice strain models have been used to predict the partition coefficients for a variety of elements between melt and solid phases [5, 6]. These models can predict free energy for a variety of partitioning reactions, including those that involve a charge-balancing substitution [6]. Lattice strain cannot predict the variation in partitioning resulting from changes in melt activity coefficients with composition, or the changes in activities of charge-balancing components and these have to be measured in real melts. In order to measure the importance of melt composition in modeling partitioning coefficients, this study seeks to identify how variations in melt composition effect partitioning independent of temperature or solid-phase composition. We believe that studies that examine lattice strain energy in the crystal could be better tuned if melt effects were better understood and modeled as done by [8]. Melt composition might effect both the activity coefficient of trace elements in the melt and the activities of components that are involved in a reasonable substitution reaction or a charge-balancing coupled substitution with the trace element.

Because we wanted to focus on melt effects, we did experiments at a single temperature and chose to examine Fe-free systems so that the composition of olivine did not change (pure Forsterite). This is similar to the approach used by [8] in their study of partitioning into plagioclase. We also chose to look mainly at variations in the concentration of Al, anticipating that Al might be important in charge-trivalent cations via a Tschermak-like substitution of Al-for-Si on the tetrahedral site, although we also consider the possibility of a vacancy substitution mechanism as suggested previously [9]. We chose compositions in which we expected both olivine and orthopyroxene on the liquidus, anticipating comparing charge-balancing substitution mechanisms

in the two phases, however, only olivine was present in the experiments reported here.

Experimental: Experiments were run in CO₂ in 1-atm gas mixing furnaces, yielding fO₂ values (calculated from the thermodynamic data of [10]) of between 1.2x10⁻³ and 1.3x10⁻³, depending on temperature. Experimental compositions were mixed from reagent grade oxides (SiO₂-Al₂O₃-CaO-MgO-NiO-Y₂O₃). Compositions were Fe-free (as discussed in previous section). The starting target bulk compositions are given in Table 1. Experimental samples were initially brought up to a melting temperature of 1520°C and left at that temperature for approximately 30 minutes to homogenize the samples. Then, experimental temperatures were dropped 70°C over a period of 24 hours to reach a final experimental temperature ranging from 1444°C to 1452°C. Samples were left in the furnace for an additional 24 to 48 hours once the final experimental temperature was reached. Samples were air quenched. Experimental melt compositions determined by EMP analyses are given in Table 2. Olivine is essentially pure Fo. Partitioning values are reported in Table 3, measured using EMP, employing careful measurement of background counts and long counting times.

Table 1: Target Bulk Compositions (in wt%)

	PAL 1	PAL 2	PAL 3
SiO ₂	58.8	56.7	55.7
Al ₂ O ₃	0.0	4.2	8.0
CaO	10.0	8.0	3.2
MgO	31.2	31.1	33.1
NiO	0.3	0.3	0.3
Y ₂ O ₃	0.3	0.3	0.3

Table 2: EMP Analyses of Melt (wt% oxides), 15kV, 20-100nA

	PAL 1	PAL 2	PAL 3
SiO ₂	60.5	58.5	58.5
Al ₂ O ₃	0.14	5.3	10.4
CaO	11.8	10.0	4.4
MgO	27.7	26.3	26.9
NiO	0.14	0.08	0.09
Y ₂ O ₃	0.36	0.37	0.38

Table 3: D Al (1 sigma uncertainties in value of last digit)

	PAL 1	PAL 2	PAL 3
Ni	5.34(20)	5.36(12)	6.21(10)
Al	0.010(54)	0.00330(12)	0.00420(8)
Y	0.00026(230)	-0.003(5)	0.0125(54)

Discussion: Considering trace element exchange reactions (e.g. Ni²⁺ + Mg₂SiO₄ ↔ Mg²⁺ + MgNiSiO₄) rather than formation reactions (Ni²⁺ + Mg²⁺ + SiO₄ ↔ + MgNiSiO₄) can minimize variations in partitioning due to melt composition effects [11]. From the exchange reaction, we can write a simplified equilibrium

constant as $K = D \cdot X_{\text{Fo}} \cdot \gamma_{\text{XMg}^{2+}} / \gamma_{\text{Ni}^{2+}}$. At constant T, P, and X_{Fo} , any variation in D will be due to variations in $\gamma_{\text{XMg}^{2+}} / \gamma_{\text{Ni}^{2+}}$. Variations in D with X_{Mg} in the melt are shown in Fig 1., suggesting that variations in $\gamma_{\text{Mg}^{2+}} / \gamma_{\text{Ni}^{2+}}$ are small but significant for these compositions.

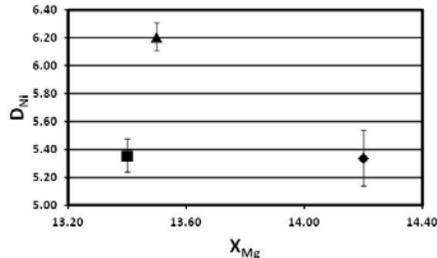


Figure 1: Variation in D_{Ni} with mole fraction Mg in the melt. Since temperature and olivine composition are constant, unexplained variation in D is associated with how the activity coefficient of Mg changes in relation to the activity coefficient of Ni.

Partitioning of trivalent cations into olivine (Al) requires a charge-balancing coupled substitution. Two possible substitution reactions were considered. The first was a “Tschermaks type” substitution: $2\text{Al}(\text{m}) + \text{Fo} \leftrightarrow \text{Mg}(\text{m}) + \text{Si}(\text{m}) + \text{MgAlAlO}_4$ ($K_{\text{T,P}} = (\text{constant}) \cdot D [(a_{\text{Mg}} \cdot (a_{\text{Si}})/(a_{\text{Al}}))]$). The second was a vacancy substitution reaction: $\text{Al}(\text{m}) + \text{Fo} \leftrightarrow 1.5\text{Mg}(\text{m}) + [(\text{Mg}_{0.5}, \square_{0.5}), \text{Al}] \text{SiO}_4$ ($K_{\text{T,P}} = (\text{constant}) \cdot D \cdot [a_{\text{Mg}}]^{1.5}$). In order to make a first-order evaluation of whether either of these mechanisms explains the observed variation in partitioning with melt composition, we applied a simple ideal-solution activity model in which cations (Mg, Al) mix with other similar cations, either network modifiers or network formers. Mg activity = $a_{\text{Mg}} \equiv X_{\text{Mg}} / (X_{\text{Mg}} + X_{\text{Ca}} + X_{\text{Fe}} + X_{\text{Ni}})$. Al activity (or Si analogously) = $a_{\text{Al}} \equiv X_{\text{Al}} / (X_{\text{Al}} + X_{\text{Si}})$.

Fig. 2 shows that the vacancy model cannot account for the variation in D_{Al} . The magnitude is right but in the wrong direction.

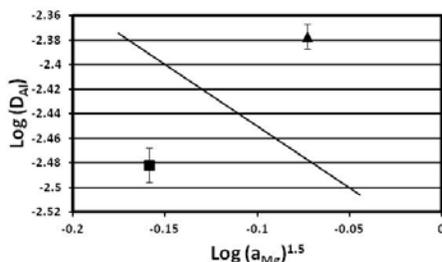


Figure 2: Observed variation in D_{Al} compared to variation expected for a vacancy substitution, given a simplified ideal solution model.

Fig. 3, shows that the “Tschermaks type” substitution can explain the direction of the variation in D, but not the magnitude. Variation is less than half of what is expected.

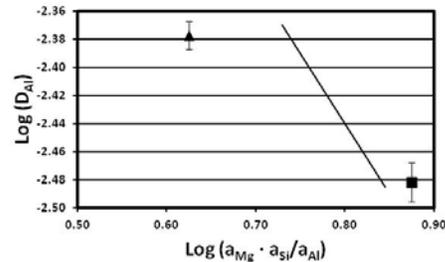


Figure 3: Observed variation in D_{Al} compared to variation expected for the Tschermaks-like substitution, given a simplified ideal solution model.

Fig. 4 shows the variation in D_{Al} against the sum of variations expected from the two substitution reactions. Considering that we used a simple ideal-solution model, the fit to the observed variation in D is quite good, suggesting that both substitution reactions may be significant. If multiple substitution reactions are important in more complex systems, it might explain why partitioning models that do not take melt composition or charge balancing reactions into account have been successful—as melt composition changes enough to diminish one mechanism, another rises to dominance. Even so, understanding the effect of melt composition might be important in natural melts.

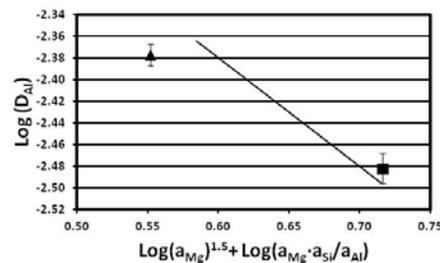


Figure 4: Observed variations in D_{Al} compared to variations expected if both substitution reactions are taking place.

Conclusions: Both variations in melt activity and charge-balancing substitution mechanisms may be important in understanding partitioning. Experiments that hold T and solid-phase composition constant in order to examine the effects of melt composition alone may yield useful insights into how melt activities affect partitioning and the type of charge-balancing substitutions occurring in the solid phase.

References:

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