OLIVINE - MELT EQUILIBRIA IN LUNAR ULTRAMAFIC MAGMAS: INSIGHTS INTO MELT THERMODYNAMIC PROPERTIES Stephanie M. Brown and Timothy L. Grove

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Experiments on lunar high-Ti melts revealed unusual variability of Fe-Mg partitioning between olivine and melt ($K_{D}^{\text{Fe-Mg}}$). [1], and more recently [2], have shown that is it not clear what causes the non-ideal behavior that leads to the observed $K_{D}^{\text{Fe-Mg}}$ variability. The lunar high-Ti experimental dataset, supplemented by new experiments on the intermediate-Ti ultramafic glasses, isolates the influence of silica activity and suggests that neither silica activity nor NBO/T (# of non-bridging oxygens per # of tetrahedrally coordinated cations) can sufficiently predict $K_{D}^{\text{Fe-Mg}}$. Rather, $K_{D}^{\text{Fe-Mg}}$ variation is due to the complex solution behavior of network modifying Fe-Mg melt components.

The relation between melt components, variable $fO_2$, and the olivine-melt $K_{D}^{\text{Fe-Mg}}$ The observed decrease at low $fO_2$ of the olivine $K_{D}^{\text{Fe-Mg}}$ in high-Ti lunar ultramafic glass experiments means that either the olivine is more forsteritic or the silicate melt has higher (FeO/MgO) [2]. This can be expressed as a reduction in the activity coefficient ratio of the Fe-Mg melt components, $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$. Because olivine is a nearly pure Fe-Mg solid solution with well known thermodynamic properties (i.e. there is a wide range in $K_{D}^{\text{Fe-Mg}}$ for a given olivine composition), the culprit must be the melt.

Thus there must be a change in the speciation of olivine forming silicate melt components under low-$fO_2$ and high TiO$_2$ conditions, resulting in low $K_{D}^{\text{Fe-Mg}}$ and low $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$ values. When $K_{D}^{\text{Fe-Mg}}$ corrected to 1 atm is compared to the $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$ corrected to 1 atm [3], the $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$ ratio decreases with decreasing $fO_2$.

The $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$ ratio is directly dependent on melt speciation: if either component is bonding preferentially with other components in the melt, its activity will be reduced because the formation of such complexes stabilizes these components in the melt phase, reducing their availability for olivine formation. Thermodynamically, this occurs when there is a negative non-ideal free energy excess (-$\Delta S_{\text{mix}}^{\text{excess}}$) to form the melt complexes.

The valence state of titanium is dependent on the $fO_2$ conditions of the experiments: $Ti^{3+}$ is likely being reduced to $Ti^{4+}$ in the low-$fO_2$ Fe capsule experiments [2]. Combining this with the above observation that there are $fO_2$-dependent changes in melt speciation strongly suggests that Fe and $Ti^{3+}$ are complexing more efficiently together at low $fO_2$ to reduce the Fe activity in the melt. An enticing solution is that $Fe^{2+}$, at the expense of Mg, is more efficiently complexing with $Ti^{3+}$ than it did with $Ti^{4+}$ in the melt, effectively increasing the amount of magnesium available for olivine. This type of reaction also predicts that the melt would become more olivine normative, which is observed experimentally by the expanding of the olivine primary phase volume (i.e., deepening of the multiple saturation point): the silicate-forming melt becomes more olivine normative as the Ti/(Fe+Mg) ratio of (Fe,Mg)-Ti melt components increases, thereby increasing the (FeO+MgO)/SiO$_2$ ratio of the remaining liquid [2].

A pair of melt component reactions, similar to the one proposed by [2], can explain all the observed behavior. Reaction 1 is an oxidation-reduction reaction that describes the reduction of $Ti^{4+}$ to $Ti^{3+}$ by dissociation of a preexisting ilmenite (Fe,Mg)TiO$_3$ melt component. The titanium in the ilmenite-like melt component is donated to the armalcolite-like melt component, setting $x = 1$, the new melt component becomes “anosovite” $Ti^{4+}Ti^{3+}O_5$:

$$\begin{align*}
(\text{Fe,Mg})\text{Ti}_x^4\text{O}_5 + x(\text{Fe,Mg})\text{Ti}_5^4\text{O}_3 & \rightleftharpoons \text{Fe,Mg})_{1-x}\text{Ti}_{2x}^3\text{O}_2 + 2x(\text{Fe,Mg})\text{O} + x\text{O}_2, \\
\text{(1)}
\end{align*}$$

Reaction 2 describes the Fe-Mg exchange in the Ti-rich modified armalcolite melt component, setting $x = 0.5$:

$$\begin{align*}
\text{Mg}_{0.5}\text{Ti}_{5}^4\text{O}_3 + \text{FeO} & \rightleftharpoons \text{Fe}_{0.5}\text{Ti}_{1.5}^4\text{Ti}^{3+}\text{O}_5 + \text{MgO}, \\
\text{(2)}
\end{align*}$$

Reaction 2 proceeds to the right as the amount of titanium in the bulk composition increases causing preferential release of MgO into the melt, successfully predicting the decrease in $(\frac{\gamma_{\text{FeO}}}{\gamma_{\text{MgO}}})_{\text{melt}}$ and $K_{D}^{\text{Fe-Mg}}$. In summary, this behavior suggests that the more Fe,Ti-rich modified armalcolite melt component is stable because it has a large excess non-ideal contribution to $\Delta S_{\text{mix}}^{\text{excess}}$ at low $fO_2$. 
Figure 1: The lunar experimental dataset cannot be predicted by the silica activity Fe-Mg $K_{D}^{Fe-Mg}$ model of [3]. Data is from this work and [11, 6, 7, 12, 8, 9, 2].

Predicting $K_{D}^{Fe-Mg}$ Many models exist for predicting $K_{D}^{Fe-Mg}$ [4, 1, 5, 3, etc.]; however, these models cannot account for the range in $K_{D}^{Fe-Mg}$ observed from lunar ultramafic experiments. For example, experiments on the low titanium lunar ultramafic glasses and mare basalts consistently record high olivine Fe-Mg $K_{D}^{Fe-Mg} > 0.35$ [1, 6, 7, 8, 9, 10] than compared to terrestrial rocks [3]. The cause of the $K_{D}^{Fe-Mg}$ variation must also be related to melt speciation. But unlike the lower $(\frac{FeO}{MgO})_{melt}$ of the intermediate - high TiO$_2$ liquids, the low-titanium ultramafic lunar glasses exhibit elevated $(\frac{FeO}{MgO})_{melt}$. Such high values typically correlate with terrestrial liquids that are 8-12 mol% more SiO$_2$ rich [3] than the SiO$_2$ content of the low-titanium lunar ultramafic glasses. Therefore, the high $K_{D}^{Fe-Mg}$ of these low SiO$_2$ melts cannot be explained by a change in silica activity (Figure 1).

Additionally, [5] suggested that the melt polymerization proxy FeO + MgO (wt%), or the equivalent NBO/T, of an ultramafic liquid controlled $K_{D}^{Fe-Mg}$. They found that the $K_{D}^{Fe-Mg}$ reached a maximum at NBO/T = 2, or FeO + MgO $\approx$ 36 wt%. When we superimpose the lunar dataset on top of the [5] data (Figure 2), we find that the lunar data crosscuts this correlation. The true cause of $K_{D}^{Fe-Mg}$ variation in ultramafic glasses is more complex than silica activity or NBO/T.

As an alternative model, we are working on quantifying the role of network modifiers and network formers for predicting $K_{D}^{Fe-Mg}$ as a function of temperature, pressure, $fO_2$, and composition.

References