THE EFFECT OF MELT TiO$_2$ ON Fe-Ti OXIDE-PICRITIC BASALT HFSE PARTITIONING: PARAMETERIZED MODELS, LUNAR APPLICATIONS. Dygert, N. Liang, Y. and Hess, P. C. (Department of Geological Sciences, Brown University, Providence, RI 02912, email: nicholas_dygert@brown.edu).

Introduction: Picritic glass melts, thought to be parental to the mare basalts, fall into three distinct compositional groups: very-low Ti (VLT, <1\% TiO$_2$), low Ti (LT, ~1-5% TiO$_2$), and high-Ti (HT, >8\% TiO$_2$) [1]. Elevated TiO$_2$ abundances suggest that an Fe-Ti oxide (ilmenite, FeTiO$_3$, armalcolite, FeTi$_2$O$_5$, or both) plays a role in picritic glass melt petrogenesis. Workers have argued that Fe-Ti oxides are assimilated by upwelling melts of the lunar cumulate mantle [2] or are present in the melt source region [3]. A third hypothesis proposes that negatively buoyant cpx and Fe-Ti oxide melts sink, metasomatizing the picritic glass melt source [4].

Because their charge and ionic radii are similar to those of Ti, HFSE are sensitive to the presence or absence of Fe-Ti oxides in the melting region and ideal tracers for investigating picritic glass melt petrogenesis. It is well known that melt TiO$_2$ has a strong effect on olivine-melt Fe-Mg partitioning [e.g., 5-7], and based on limited experimental results, we proposed that melt TiO$_2$ also has a significant effect on ilmenite-melt and armalcolite-melt $D_{HFSE}$ [8]. Here we report 8 additional experiments conducted to investigate the effect of melt TiO$_2$ on HFSE partitioning, and parameterized ilmenite and armalcolite HFSE partitioning models developed from the experimental results.

![Figure 1](image)

**Figure 1** (a), $D_{Zr}$ vs. melt TiO$_2$, (b) Ilmenite and armalcolite $D_{HFSE}$ Ratios vs. TiO$_2$ demonstrate that although partitioning trends are qualitatively similar among HFSE, they are not parallel, particularly for ilmenite.

Methods: Experiments were conducted in a 19.1 mm piston cylinder apparatus in graphite lined Mo capsules at 1050-1350°C and 1-2GPa. A wide range of lunar relevant starting compositions (2.6 to 28% TiO$_2$, Fig. 1) prepared from mineral separates [8] and/or oxide powders were used. A conditioned REE+HFSE mixture was added to most experiments to reduce analytical uncertainty. Major elements were analyzed on the Cameca SX-100 microprobe at Brown University. Trace elements were measured using laser ablation inductively coupled mass spectrometry (LA-ICP-MS) at the University of Rhode Island. One experiment was also analyzed at the Plasma Mass Spectrometry Laboratory at the University of Maryland and the analyses from the two labs are nearly identical.

Results: Ilmenite and armalcolite $D_{HFSE}$ decrease with increasing melt TiO$_2$ (Fig. 1a). The negative correlation between $D_{Zr}$ and melt TiO$_2$ moderates significantly between 5.6 and 6.8\%. Above 6.8\%, $D_{Zr}$ is effectively constant. Although $D_{Ni}$, $D_{Nb}$, and $D_{Ta}$ are higher than $D_{Zr}$ at all TiO$_2$ abundances for both minerals, their partitioning trends are similar and semi-parallel to Zr. However, $D_{Zr}/D_{Ni}$ and $D_{Nb}/D_{Ta}$ vary as a function of melt TiO$_2$ (Fig. 1b). The difference between our ilmenite partition coefficients and those from the literature at low melt TiO$_2$ may be due to different melt compositions of [9] which are rhyolitic. Our experimental melts are compositionally similar to the lunar picritic glasses (e.g., [8]), and our partition coefficients are directly applicable to lunar petrogenetic modeling.

Discussion: We attribute the dependence of HFSE partitioning on melt TiO$_2$ to the formation of Fe-O-Ti melt species at elevated melt TiO$_2$ (e.g., [7]). As the normative ilmenite content of a melt increases, trace elements which substitute into the Ti site of an Fe-Ti oxide but are of slightly different charge or ionic radius than Ti are more readily accommodated by Fe-O-Ti melt species, which are more structurally relaxed than their crystalline counterparts. As melt TiO$_2$ content increases, the activity coefficients of HFSE in melt decrease and the oxide-melt $D_{HFSE}$ also decrease. The negative correlation between $D_{HFSE}$ and melt TiO$_2$ moderates when melts are effectively depolymerized near 6\% TiO$_2$ (Fig. 1a).

Partitioning Model: The lattice strain model [10] is often used to parameterize trace element partitioning. Unknown parameters in the model are the effective Young’s modulus ($E$), ideal ionic radius of the lattice site ($r_0$), and partition coefficient for strain free substitution ($D_0$) and are typically estimated by non-linear least squares regression of an array of experimentally determined partition coefficients for a group of elements of the same charge. Because measurably abundant 4+ and 5+ cations in Fe-Ti
oxides are limited to Ti and the HFSE, the model is under-constrained.

However, because $D_{\text{HFSE}}$ are highly correlated with melt TiO$_2$ content (Fig. 1a), and HFSE have charge and ionic radii similar to Ti, and the solubility of oxides in melt is well known at a given melt TiO$_2$, we can reasonably assume $D_{\text{Ti}} = D_{\text{Zr}}$ and $r_{\text{Ti}} = r_{\text{Zr}}$, yielding the solubility weighted partitioning model:

$$
D_{\text{HFSE}}^{\text{weight}} = D_i \exp \left(\frac{-\Delta_g EN_A}{RT} \left(\frac{r_{\text{HFSE}}}{r_i} \left(\frac{r_i}{r_{\text{HFSE}}} - \frac{1}{3} \right) \right) \right)
$$

(1)

For HFSE$^{5+}$, $E^{\text{rm}}_{\text{Ti}}$ and $E^{\text{rm}}_{\text{Zr}}$ were determined by nonlinear least squares regression using $D_{\text{Ti}}$, $D_{\text{Zr}}$, and $D_{\text{HFSE}}$ measured in our experiments and the literature. Parameterized $E$ models (GPa) are presented below:

$$
E^{\text{rm}}_{\text{Ti}} = 1.169(\pm 0.075) \times 10^3 - 6.813(\pm 3.50) \times 10^1 X_{\text{Al}}
$$

(2)

where $X_{\text{Al}}$ is the fraction of Al in the ilmenite chemical formula, and

$$
E^{\text{rm}}_{\text{Zr}} = 1.111(\pm 0.048) \times 10^1 - 0.0054(\pm 0.001) \times 10^1 M_g^{\text{iss}}
$$

(3)

where $E_{\text{Zr}}^{\text{rm}}$ depends on Mg# of the melt.

Because the Nb$^{5+}$ and Ta$^{5+}$ have identical ionic radii, (1) is not applicable to $D_{\text{HFSE}}^{5+}$. However, $\ln(D_{\text{HFSE}}^{5+})$ are linearly correlated with $\ln(D_{\text{Ti}})$. As a preliminary model, we fit ilmenite and armalcolite $D_{\text{HFSE}}^{5+}$ from our data and the literature using linear regressions, producing $D_{\text{HFSE}}^{5+}$ partitioning models which will be presented elsewhere. Fig. 2 demonstrates excellent agreement between experimentally determined and predicted $D_{\text{HFSE}}$.

**Lunar Applications:** Lunar armalcolite are classified as three distinct types [11]. Type 1 is thought to crystallize from HT mare basalts, while workers argued Type 2 and 3 crystallized from LT aluminous basalts. We calculated equilibrium melts for representative armalcolite compositions using our partitioning models and experimentally determined partition coefficients. While Type 1 armalcolite equilibrium melts resemble HT basalts, Type 2 and 3 equilibrium melts have Zr abundances approaching 1%, and Type 3 melts have Y on the order of 10%. The melt compositions are not KREEPy and inconsistent with aluminous LT basalts. Type 2 and 3 armalcolite formation mechanisms should be reinvestigated.

**Figure 2.** Predicted vs. measured $D_{\text{HFSE}}$. Dotted blue lines are 2:1 and 1:2 and solid blue line is 1:1. Error bars are $\pm 2\sigma$.

Batch melting models of an ilmenite bearing lherzolite. An ilmenite free harzburgite melting trend and an ilmenite fractionation trend are also presented. Large mare basalt symbols are isotope dilution data [12], smaller symbols are solution ICP-MS [13].

Melting trends for high- and low-Ti basalts produced from an ilmenite bearing lherzolite. An ilmenite free harzburgite melting trend and an ilmenite fractionation trend are also presented. Large mare basalt symbols are isotope dilution data [12], smaller symbols are solution ICP-MS [13].

Batch melting models of an ilmenite bearing lherzolite overlie HT mare basalt data in Nb/Ta vs. Zr/Hf space (Fig. 3). A LT melt produced by the same lithology trends toward LT mare basalts because HFSE partition coefficient ratios are not constant in melt TiO$_2$ space (Fig. 1b). Harzburgite melting trends are roughly perpendicular to those produced by ilmenite bearing lithologies, and lower degree harzburgite melts, which should be more Ti rich, trend toward LT mare basalts. Source lithologies with armalcolite plot between the HT and LT ilmenite melting trends (not pictured), consistent with Fig. 1b. These observations suggest an Fe-Ti oxide may be present in the HT (and possibly LT) source region. Assimilation of a KREEPy component can explain intermediate HFSE ratios, and fractionation of ilmenite from HT basalt may explain data which fall above the HT melting trend.

**References:**