

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_2O_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.

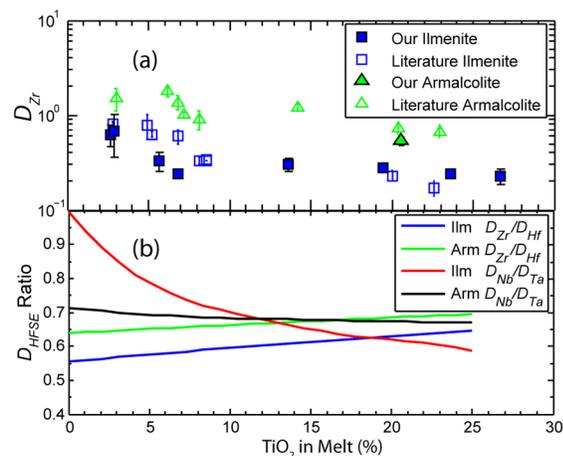


Figure 1 (a). D_{Zr} vs. melt TiO_2 . (b) Ilmenite and armalcolite D_{HFSE} ratios vs. TiO_2 demonstrate that although partitioning trends are qualitatively similar among HFSE, they are not parallel, particularly for ilmenite.

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_{Hf} , 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, $D_{\text{Zr}}/D_{\text{Hf}}$ and $D_{\text{Nb}}/D_{\text{Ta}}$ 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.

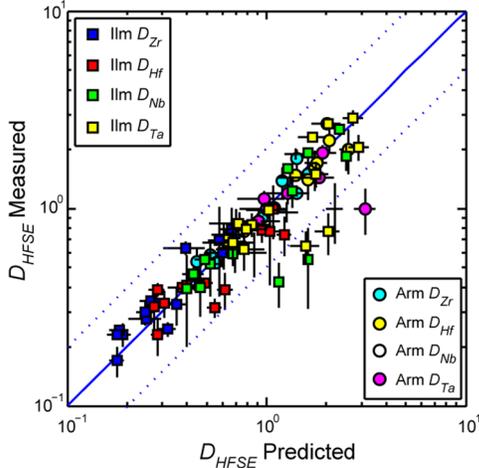


Figure 2. Predicted vs. measured D_{HFSE} . Dotted blue lines are 2:1 and 1:2 and solid blue line is 1:1. Error bars are 2σ .

However, because D_{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 $D_0 = D_{Ti}$ and $r_0 = r_{Ti}$, yielding the solubility weighted partitioning model:

$$D_i^{oxide-melt} = D_{Ti} \exp\left(\frac{-4\pi EN_A}{RT} \left(\frac{r_{Ti}}{2}(r_{Ti} - r_i)^2 - \frac{1}{3}(r_{Ti} - r_i)^3\right)\right) \quad (1)$$

For $HFSE^{4+}$, E^{ilm} and E^{arm} were determined by nonlinear least squares regression using D_{Ti} , D_{Zr} , and D_{Hf} measured in our experiments and the literature. Parameterized E models (GPa) are presented below:

$$E^{ilm} = 1.169(\pm 0.075) \times 10^3 - 6.813(\pm 3.50) \times 10^3 X_{Al} \quad (2)$$

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

$$E^{arm} = 1.111(\pm 0.048) \times 10^3 - 0.0054(\pm 0.001) \times 10^3 Mg\#^{melt} \quad (3)$$

where E^{arm} depends on $Mg\#$ of the melt.

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

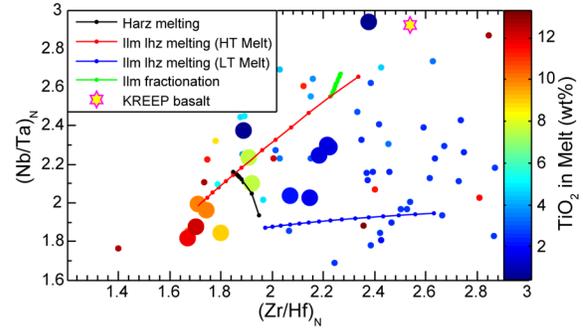


Figure 3. HFSE ratios in mare basalts and representative melting trends for high- and low-Ti basalts produced from an ilmenite bearing lherzolite. An ilmenite free harzburgite melting trend and an ilmenite fractionation trend are also presented. Large mare basalt symbols are isotope dilution data [12], smaller symbols are ion probe data [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 KREEP component can explain intermediate HFSE ratios, and fractionation of ilmenite from HT basalt may explain data which fall above the HT melting trend.

References: [1] Neal and Taylor (1992) *GCA* 56, 2177-2211. [2] Wagner and Grove (1997) *GCA* 61, 1315-1327. [3] Singletary and Grove (2008) *EPSL* 268, 182-189. [4] Van Orman and Grove (2000) *Meteor. & Planet. Sci.* 35, 783-794. [5] Longhi, Walker, and Hays (1978) *GCA* 56, 2235-2251. [6] Delano (1980) *Proc. 11 LSC* 251-288. [7] Jones (1988) *Proc. 19 LSC* 561-562. [8] Dygert, Liang, and Hess (2011) *Proc. 42 LSC* 1956. [9] Klemme, Gunther, Hametner, Prowatke, and Zack (2006) *Chem. Geol.* 234, 251-263. [10] Wood and Blundy (1997) *CMP* 129, 166-181. [11] Haggerty (1973) *Proc. 4 LSC* 777-797. [12] Münker (2010) *GCA* 74, 7340-7361. [13] Neal (2001) *JGR* 106, 27865-27885.