

EXPERIMENTAL EVIDENCE FOR HIGH FIELD STRENGTH ELEMENT INCOMPATIBILITY IN TITANIFEROUS PHASES IN EQUILIBRIUM WITH HIGH TITANIUM MARE BASALTS AND PICRITIC GLASS MELTS. N. Dygert, Y. Liang, and P. C. Hess (Department of Geological Sciences, Brown University, Providence, RI 02912, email: nicholas_dygert@brown.edu).

Introduction: Perhaps the most striking feature of the lunar mare basalts and picritic glasses is their wide range in titanium content. Unlike terrestrial oceanic basalts, which rarely exceed 2% TiO_2 , picritic glasses can have more than 16.5% TiO_2 . Mare basalts are typically classified as low Ti (LT, <5% TiO_2) or high Ti (HT, >8% TiO_2) [1]. High titanium contents are generally thought to have originated from the melting or assimilation of late stage titaniferous crystallization products of the lunar magma ocean (LMO), such as ilmenite (FeTiO_3) and/or armalcolite ($(\text{Fe,Mg})\text{Ti}_2\text{O}_5$) [2-4]. It is well known that mare basalts and picritic glass melts are not saturated with ilmenite or armalcolite at their multiple-saturation points [3,4]. This indicates that if ilmenite or armalcolite was present in the source lithology it was melted out completely. Alternatively, Ti could have been assimilated in parent magmas of mare basalts as they were transported through an incompletely overturned Ti rich cumulate layer left over from the LMO [5].

Trace element partitioning behavior, particularly of the high field-strength elements (HFSEs), may allow us to determine the high-Ti source mineralogy and help us understand the bimodal distribution of the mare basalts [3,6]. In this study, we examine the partitioning of HFSEs between titaniferous oxides and lunar high-Ti basalts at high temperatures and pressures. Combined with literature data, we show that the partitioning of HFSEs in ilmenite and perhaps armalcolite depend strongly on the TiO_2 abundance in the coexisting melt. The HFSEs are moderately incompatible in ilmenite coexisting with lunar high-Ti magmas.

Experiments: We conducted ilmenite-melt partitioning experiments at 1350°C and 1 GPa using a 19.2 mm piston cylinder apparatus, following procedures similar to those described in [5]. Our starting composition consists of ilmenite powder composed of unaltered phases (olivine + opx + cpx) picked from a spinel ilmenite xenolith ($\text{Mg}\# = 91$) and natural ilmenite (49.5% TiO_2 , 45.2% FeO , 0.3% MgO , and 3.5% MnO). Fine powdered starting material was first loaded in the graphite capsule and dried in a 200°C vacuum oven for at least 12 hours. The experiments were run for approximately 48 hours to ensure crystal growth sufficient for trace element analysis. The run products were olivine, ilmenite, and high-Ti melt, with major element compositions similar to those reported in [5, see also

Fig. 1]. Both orthopyroxene and clinopyroxene were reacted out during the experiment, resulting in a final melt composition that is on the extensions of lunar picritic glass melt trends (Fig. 1). Major element compositions of coexisting phases were analyzed using the Cameca SX100 electron microprobe at Brown University and trace element abundances were analyzed using a LA-ICP-MS at the Plasma Mass Spectrometry Laboratory at the University of Maryland.

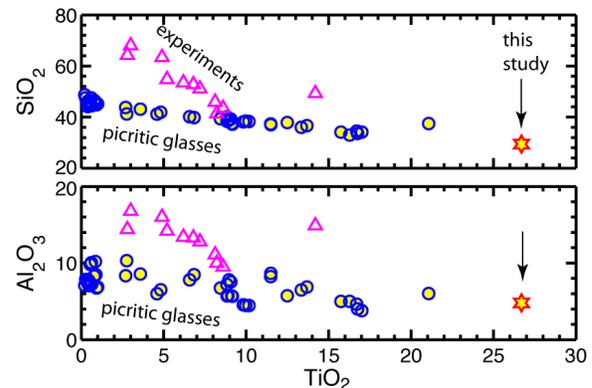


Figure 1. Comparisons of melt compositions (in wt%) between lunar picritic glasses [2] and melts coexisting with ilmenite in the ilmenite-melt partitioning experiments reported in the previous (magenta triangles) [7-11] and present (red star) studies.

Results: Fig. 1 compares selected major element abundances in melts from ilmenite-melt partitioning studies and those in lunar picritic glasses. Note the very high TiO_2 content in the melt used in this study (26.7%, Fig. 1), which compliments previous partitioning studies, although the SiO_2 and Al_2O_3 (MgO and FeO) abundances in the latter melts are considerably higher (lower) than those in lunar basalts. We analyzed ilmenite and melt for HFSEs, transition metals (TM), and REEs + Y, but low REE abundances in ilmenite caused high uncertainties and only K_{DS} for TM, HFSEs, and Y are reported here. We found lower ilmenite HFSE K_{DS} (within error) than nearly all those reported previously (Table 1 and Fig. 2) [7- 12]. K_{DS} for TM are consistent with values reported in [7,8], and the K_{D} for Y falls within the range of values reported in [7] (Fig. 2).

Discussion: Our results demonstrate that HFSEs are more incompatible in ilmenite in equilibrium with the very high TiO_2 melt than in other ilmenite-melt partitioning experiments (Fig. 2). TiO_2 in our melt (26.7%) is significantly greater than in experiments

of [7], most of which were between 3% and 8%. Although limited in the number of partitioning data, there appears to be a negative correlation between K_{DS} of HFSE and TiO_2 abundance in the melt. This negative correlation is well defined for Zr (Fig. 3) and Hf (not shown) that have more partitioning data, and somewhat less well defined for Nb and Ta where only 4 additional data points were reported in the literature [7]. In a companion study, we show that partition coefficients of REE between opx and basaltic melts also depend strongly on the TiO_2 abundance in the melt [13].

Table 1. Selected Ilmenite-melt Partition Coefficients

| | | | |
|----|-----------|----|------------|
| Sc | 0.88±0.12 | Y | 0.014±0.01 |
| V | 4.5±0.3 | Zr | 0.23±0.04 |
| Cr | 7.1±0.6 | Nb | 0.42±0.03 |
| Co | 2.3±0.6 | Hf | 0.29±0.28 |
| Cu | 0.57±0.20 | Ta | 0.66±0.09 |
| Zn | 1.4±0.2 | | |

The decrease in HFSE K_{DS} with the increase of TiO_2 in the melt may be understood in terms of substitution of HFSE cations for Ti^{4+} (possibly charge balanced by a trivalent cation such as Al^{3+} , e.g., $Nb^{5+} + Al^{3+} = 2Ti^{4+}$) in the Ti rich species in high Ti melts. As TiO_2 abundance in the melt increases, the activities of the HFSE in the melt increase. This is consistent with the experimental study of [14], regarding the partitioning of Nb and Ta between rutile and peraluminous melts.

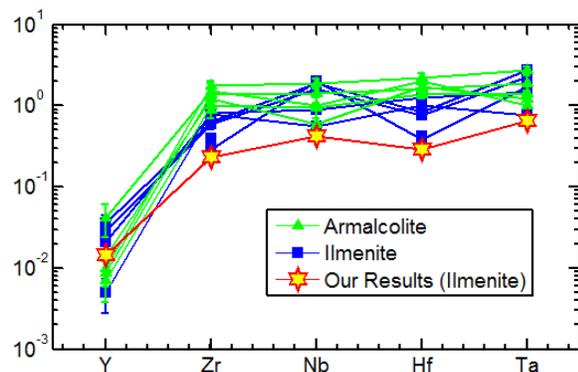


Figure 2. Mineral-melt HFSE + Y K_{DS} for armalcolite and ilmenite from several earlier studies [7-11], and our results.

Though our melt is more Ti rich than lunar picritic glasses, it falls on their high Ti extension in oxide vs. TiO_2 space (Fig. 1). Therefore, our K_{DS} may provide a lower bound for trace element partitioning between ilmenite and high Ti picritic glasses (thought to be parental to the mare basalts) under lunar mantle conditions. In comparison, melts in experiments of [7] all have SiO_2 abundances > 49%, Al_2O_3 contents 12.8%-16.8%, and Na_2O > 2.7% (Fig. 1). The picritic glasses fall outside these compositional ranges and the high HFSE K_{DS} reported by [7] may not be

appropriate for modeling magma generation in the lunar mantle. Our results are more consistent with those reported in [10] ($Zr = 0.339$, $Hf = 0.409$), whose melt composition is similar to mare basalt with 8.6% TiO_2 .

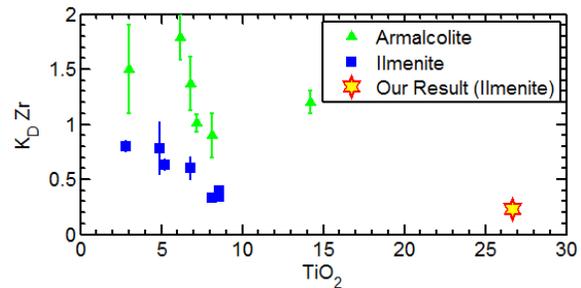


Figure 3. $K_D Zr$ vs. wt % TiO_2 in melt from [7-11] and our study. Ilmenite $K_D Zr$ may decrease exponentially with increasing TiO_2 before its slope moderates near 10% TiO_2 . While Zr is clearly more compatible in armalcolite than ilmenite, the dependence of armalcolite $K_D Zr$ on Ti in melt may follow a similar trend, though the data is more scattered.

A recent phase equilibrium study shows that ilmenite is stable in a pyroxene-free dunite over a large range of pressures in the lunar mantle, and at depths greater than 280 km in a harzburgite host, whereas armalcolite is more stable at depths less than 280 km, but these stability fields are dependent on the chemistry of coexisting phases [5]. Figs. 2 and 3 compare the published armalcolite-melt partition coefficients (all at 1 bar) with those of ilmenite. The more compatible behaviors of the HFSE in armalcolite than in ilmenite may be attributed in part to the differences in crystal structure and the higher Al_2O_3 abundance in the armalcolite. The presence of Al^{3+} in armalcolite or ilmenite helps to charge balance HFSE, in a manner similar to those described in [14]. Clearly more work is needed to expand the ilmenite and armalcolite-melt partitioning data over the entire range of Ti abundances in the mare basalts.

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