

THE ROLE OF DIFFERENTIATION PROCESSES IN MARE BASALT IRON ISOTOPE SIGNATURES.

K. B. Williams¹, M. J. Krawczynski¹, N. X. Nie², N. Dauphas², H. Couvy¹, M. Y. Hu³, and E. E. Alp³, ¹Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, 1 Brookings Dr., St. Louis, MO 63130 (k.b.williams@wustl.edu), ²Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, ³Advanced Photon Source, Argonne National Laboratory.

Introduction: A distinct dichotomy exists between the bulk Fe-isotopic compositions of the high titanium and low titanium mare basalts [1-5]. High-Ti basalts have an average $\delta^{56}\text{Fe} = +0.191 \pm 0.020\%$, while low-Ti basalts have an average $\delta^{56}\text{Fe} = +0.073 \pm 0.018\%$ [4]. To date, there is no satisfactory explanation for the difference in Fe-isotopic composition, and the question remains as to which high-temperature processes could lead to such large fractionation. Here, we assess the potential role of igneous differentiation processes in producing the observed Fe-isotope dichotomy.

Isotopic compositions of olivine and ilmenite mineral separates were measured previously in lunar basalts, dunites, and troctolites [5,6]. [5] found $\delta^{56}\text{Fe}_{\text{ilmenite}}$ to be between +0.16 to +0.24 ‰ for low-Ti basalts, and +0.20 to +0.42 ‰ for high-Ti basalts. Comparison of the isotopic compositions from each ilmenite sample and its bulk rock shows that $\sim 2/3$ of the ilmenites measured by [5] are isotopically “heavy” ($\delta^{56}\text{Fe}_{\text{ilmenite}} > \delta^{56}\text{Fe}_{\text{bulk}}$), while the remaining 1/3 of the analyzed ilmenites are isotopically “light” ($\delta^{56}\text{Fe}_{\text{ilmenite}} < \delta^{56}\text{Fe}_{\text{bulk}}$). [6] measured similar isotopic compositions for lunar ilmenites ($\delta^{56}\text{Fe}_{\text{ilmenite}} = +0.18$ to +0.32 ‰), however all ilmenites are isotopically heavy compared to the bulk sample composition. In contrast, previous Mössbauer studies of ilmenite and basalt vibrational properties predict ilmenite to be isotopically light [7]. Olivines from lunar dunites analyzed in [6] have $\delta^{56}\text{Fe}_{\text{olivine}}$ between -0.43 to -0.23 ‰, and are considerably lighter than the mare basalts. These values, if representative of equilibrium fractionation from a mare basalt-like parent melt, differ significantly from the predicted Fe-isotope fractionation determined by Nuclear Resonant Inelastic X-ray Scattering (NRIXS) in [8], which found no significant fractionation between olivine and basaltic melt at lunar-like $f\text{O}_2$.

The results from [5-8] suggest crystallization of olivine and ilmenite changes the isotopic composition of the residual melt. This fractionation may explain the iron isotope dichotomy between high-Ti and low-Ti basalts if each experienced different degrees of ilmenite and/or olivine fractionation. However, the discrepancy between mineral separate analyses and NRIXS interpretations generates uncertainty as to *how* the melt would evolve with the crystallization of each mineral.

The major distinction between high-Ti and low-Ti basalts is Ti content; this suggests the dichotomy may

Table 1. Force constant, $\langle F \rangle$ (N/m), and 2σ error derived from NRIXS data in this work.

	$\langle F \rangle$	error
Green Glass	189	9
Yellow Glass	195	12
Orange Glass	203	11
Black Glass	191	11
Ilmenite	156	10
Fe _{0.82} Olivine ^[8]	197	10

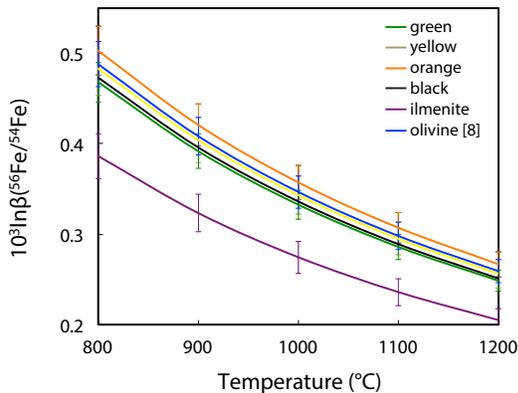
be an effect of melt composition. In order to investigate the effect of melt composition on Fe-isotope fractionation, we have obtained NRIXS data on synthetic lunar volcanic glasses. We have combined our results with those of previous studies to model fractionation of ilmenite and olivine from lunar melt compositions.

Experimental and Analytical Methods: We synthesized lunar volcanic glasses from oxide powders according to the Apollo green, yellow, orange, and black glass compositions in [9]. In order to perform the NRIXS measurements, we used ⁵⁷Fe-enriched Fe₂O₃ powder (96.64% ⁵⁷Fe). Samples were fused to rhenium loops and glassed at 1400°C for 3 hours in a vertical gas-mixing furnace using a controlled flow of H₂ and CO₂ gases to buffer the oxygen fugacity at IW-0.06. Each glass sample composition was confirmed by electron microprobe analysis at Washington University in St. Louis. The NRIXS method measured the inelastic X-ray scattering of nuclear energy transitions in ⁵⁷Fe, giving information about the vibrational properties of the iron in each sample. With NRIXS we obtain the force constant, which quantifies the strength of the bonds holding iron in position. [8], [10], and [11] have previously characterized the force constants in mineral and glass phases using NRIXS spectra.

NRIXS results: Table 1 presents the force constants calculated from the NRIXS spectra on our synthetic lunar glasses. Additionally, we have obtained NRIXS spectra on a synthetic ilmenite to supplement the Mössbauer derived data in [7]. Within error, the lunar glasses have the same force constant, suggesting the Fe-isotope fractionation is not a function of melt composition. Furthermore, the force constants for the lunar glasses are similar to the force constants generated for reduced ($f\text{O}_2 = \text{IW}$) terrestrial basalts in [8].

Comparison of Equilibrium Isotope Partition Coefficients: Using the force constants in Table 1, we predict the equilibrium fractionation factors (α) for

Figure 1. β -factors calculated as a function of temperature from the measured force constants for synthetic Apollo glasses, ilmenite, and olivine [8].



olivine and ilmenite crystallization from each lunar volcanic glass [8]. Our results suggest ilmenite would be isotopically light compared to the parent melt composition (Figure 1). In contrast, olivine shows no significant fractionation. Both of these results conflict with the Fe-isotope fractionations interpreted from analyses of mineral separates [i.e., 6].

To model the isotopic evolution during near-fractional crystallization, we used an olivine-melt Fe-Mg partitioning coefficient (K_D) of 0.3 and an average ilmenite-melt K_D of 1.78 [12,13]. We defined an initial $\delta^{56}\text{Fe}_{\text{melt}}$, and then tracked the $\delta^{56}\text{Fe}_{\text{melt}}$, $\delta^{56}\text{Fe}_{\text{olivine}}$, and $\delta^{56}\text{Fe}_{\text{ilmenite}}$ during crystallization using the equation:

$$\alpha_{(\text{mineral-melt})} = (\delta^{56}\text{Fe}_{\text{mineral}} + 1000) / (\delta^{56}\text{Fe}_{\text{melt}} + 1000) \quad (3)$$

and α values calculated from [5], [6], and this work. Mass balance is considered in each fractionation step of our closed-system model. Figure 2 illustrates the effect of $\alpha_{(\text{mineral-melt})}$ on the isotopic evolution of the residual melts. Our data indicate mineral fractionation will slightly change the residual melt Fe-isotopic composition, but not to the magnitude needed to reach the heavy values of the high-Ti mare basalts.

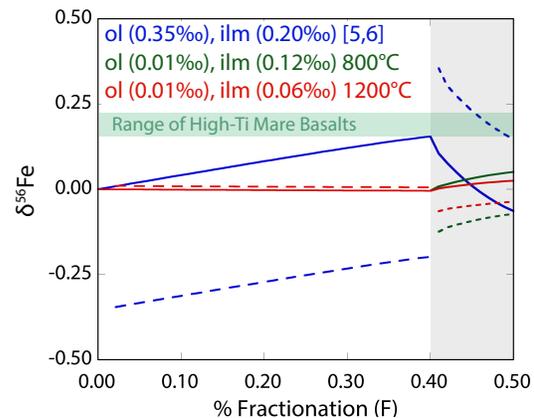
Ongoing Investigation: Experimental work is being conducted to verify the equilibrium fractionation factors predicted by the NRIXS measurements. In addition, dynamic crystallization experiments are investigating possible kinetic controls on the isotopic fractionation between olivine, ilmenite, and basalt.

NRIXS measurements indicate olivine is not a likely source for the Fe-isotope dichotomy between the low- and high-Ti basalts. However, the NRIXS measurements were taken on glass phases, which may not accurately reflect the iron bonding properties in a high-temperature melt structure. Different degrees of ilmenite fractionation between the two basalt types presents

a more likely alternative; but, the fractionation factors predicted by NRIXS measurements do not produce the magnitude of heavy Fe-isotope enrichment observed in the high-Ti basalts and lunar ilmenite separates. It also seems unlikely that the measured heavy isotope values in ilmenite, a mineral that appears late in the crystallization sequence of mare basalts, represent equilibrium fractionation from a parent melt with mare basalt isotope composition. Ilmenite may be in equilibrium with a significantly fractionated melt prior to crystallization, and may also be affected by diffusive re-equilibration subsequent to crystallization.

Quenched phases in our experimental samples are crushed, sieved, and then hand separated for Fe-isotopic analysis with a Thermo Scientific Neptune Plus MC-ICPMS in the Origins Lab at the University of Chicago. When combined with the isotopic data from mare basalts, the results from these experiments will better constrain the lunar magmatic history and chemical differentiation processes that created the observed Fe-isotope dichotomy.

Figure 2. $\delta^{56}\text{Fe}$ evolution of a high-Ti basalt liquid during near-fractional crystallization of olivine ($F < 0.4$) and ilmenite ($F > 0.4$). $\delta^{56}\text{Fe}$ calculated using α values in [5,6] (blue), and NRIXS-based α for 800°C (green) and 1200°C (red).



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