Experimentally Determined Effects of Olivine Crystallization and Melt Titanium Content on Iron Isotopic Fractionation in Planetary Basalts

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Abstract

Olivine is the most abundant mantle mineral at depths relevant to oceanic crust production through melting. It is also a liquidus phase for a wide range of mafic and ultramafic magma compositions. We have experimentally investigated the effects of olivine crystallization and melt composition on the fractionation of Fe isotopes in igneous systems. To test whether there is a melt compositional control on Fe isotopic fractionation, we have conducted nuclear resonant inelastic X-ray scattering (NRIXS) measurements on a suite of synthetic glasses ranging from 0.4 to 16.3 wt.% TiO_2. The resulting force constants are similar to those of the reduced (fO_2 = IW) terrestrial basalt, andesite, and dacite glasses reported by Dauphas et al. (2014), indicating that there is no measurable effect of titanium composition on Fe isotopic fractionation in the investigated compositional range. We have also conducted olivine crystallization experiments and analyzed the Fe isotopic composition of the experimental olivines and glasses using solution MC-ICPMS. Olivine and glass separates from a given experimental charge have the same iron isotopic composition within error. This result is robust in both the high-Ti glass (Apollo 14 black) and low-Ti glass (Apollo 14 VLT) compositions, and at the two oxygen fugacities investigated (IW-1, IW+2). Additionally, we have determined that Fe loss in reducing one-atmosphere gas-mixing experiments occurs not only as loss to the Re wire container, but also as evaporative loss, and each mechanism of experimental Fe loss has an associated Fe isotopic fractionation.

We apply our results to interpreting Fe isotopic variations in the lunar mare basalts and lunar dunite 72415-8. Our experimental results indicate that neither melt TiO_2 composition nor equilibrium olivine crystallization can explain the observed difference in the iron isotopic composition of the lunar mare basalts. Additionally, equilibrium iron isotopic fractionation between olivine and melt cannot account for the “light” iron isotopic composition of lunar dunite

72415-8, unless the melt from which it is crystallizing was already enriched in light iron isotopes. Our results support models of diffusive fractionation to explain the light iron isotopic compositions measured in olivine from a variety of rock types and reduced (fO_2 = IW-1 to IW+2) igneous environments (e.g., lunar dunite and basalts, terrestrial peridotites and basalts, martian shergottites).

1. Introduction

Analytical developments over the past decade have revealed that igneous rocks and minerals display variations in the isotopic composition of non-traditional stable isotope systems (i.e., not C, H, N, O, S Teng et al., 2017, and references therein). The degree of mass-dependent fractionation between stable isotopes has been attributed to factors such as oxidation state, bonding environment, and volatility. While early studies focused on low-temperature stable isotopic fractionation, a growing number of studies have revealed measurable isotopic fractionations present in high temperature igneous systems (e.g., Beard and Johnson, 2004; Poitrasson et al., 2004; Weyer et al., 2005; Williams et al., 2005; Teng et al., 2008, and subsequent studies). Interpretations of these variations are often hampered by the paucity of equilibrium fractionation factors between coexisting phases, which limits quantitative modeling of the relevant igneous processes.

High-temperature stable isotopic fractionations have been used to elucidate planetary-scale processes, such as the formation of the Moon, as well as smaller scale processes, such as the differentiation of magma. In particular, high-precision studies of stable isotopes have resolved isotopic differences between terrestrial and lunar samples for certain elements (e.g., Wang and Jacobsen, 2016). However, for many isotopic systems, it is difficult to tell whether the Earth and

Moon have different isotopic compositions because the processes of magmatic differentiation, including lunar magma ocean crystallization and later magma generation and crystallization, have imparted stable isotopic variations to lunar rocks that need to be understood and disentangled before a claim can be made regarding the bulk composition of the Earth or Moon. The increased precision of modern isotope analyses has resolved a "dichotomy" present between the bulk stable isotopic compositions of the low-Ti and high-Ti mare basalts on the Moon (Figure 1). Specifically, this dichotomy has been observed for Fe (Wiesli et al., 2003; Poitrasson et al., 2004; Weyer et al., 2005; Craddock et al., 2010; Liu et al., 2010; Sossi and Moynier, 2017), with high-Ti mare basalts being isotopically "heavy" compared to low-Ti basalts ($\delta^{56}\mathrm{Fe}_{\text{high-Ti}} > \delta^{56}\mathrm{Fe}_{\text{low-Ti}}$). The dichotomy was also observed for Mg ($\delta^{26}\mathrm{Mg}_{\text{high-Ti}} < \delta^{26}\mathrm{Mg}_{\text{low-Ti}}$; Sedaghatpour et al., 2013), Li ($\delta^{7}\mathrm{Li}_{\text{high-Ti}} > \delta^{7}\mathrm{Li}_{\text{low-Ti}}$; Day et al., 2016), and Ti ($\delta^{49}\mathrm{Ti}_{\text{high-Ti}} > \delta^{49}\mathrm{Ti}_{\text{low-Ti}}$; Millet et al., 2016). Though the difference in stable isotopic compositions between the high- and low-Ti basalts is well documented analytically, the petrologic processes responsible for the lunar isotopic dichotomy remain elusive.

Despite increasing evidence for high-temperature isotopic fractionation in igneous rocks (e.g., Dauphas and Rouxel, 2006; Dauphas et al., 2017), there is a paucity of experimental studies of isotopic fractionation during magmatic differentiation of mafic compositions. The iron isotopic compositions of igneous rocks have been extensively studied, and the documented isotopic variations in igneous rocks are caused by a combination of partial melting (e.g., Williams et al., 2005; Weyer and Ionov, 2007; Dauphas et al., 2009a; Dauphas et al., 2014; Williams and Bizimis, 2014), equilibrium and fractional crystallization (e.g., Teng et al., 2008; Dauphas et al., 2014; Roskosz et al., 2015), and diffusive fractionation (e.g., Dauphas and Rouxel, 2006; Sio et al., 2013; Oeser et al., 2015; Sio and Dauphas, 2016; Collinet et al., 2017). Experimental studies of equilibrium Fe isotope partitioning at high temperature have investigated metal-silicate systems, fayalite-magnetite fractionation, as well as Fe isotopic fractionation between evolved rhyolitic compositions and sulfides (e.g., Schuessler et al., 2007; Shahar et al., 2008; Poitrasson et al., 2009). Additionally, Dauphas et al. (2014) investigated the Fe bonding structure in a suite of terrestrial volcanic glass compositions ranging from basalt to rhyolite, concluding that Fe isotopic composition is influenced by the redox state of iron and the silica content of the melt.

Evidence for mineralogical, compositional, and redox controls on Fe isotope partitioning in igneous rocks highlights the importance of experimentally quantifying mineral-melt fractionations for major rock-forming minerals. Olivine is a ubiquitous mineral on rocky, differentiated planetary bodies. Even a small (<0.1‰) olivine-melt Fe isotopic fractionation could significantly fractionate the Fe isotopes in mantle reservoirs during planetary differentiation; for example, an olivine-melt fractionation $\delta^{56}Fe_{olivine}$ - $\delta^{56}Fe_{melt}$ = -0.05‰ would increase the $\delta^{56}Fe$ of a magma ocean by 0.1‰ after 50% fractional crystallization of olivine. The measured iron isotopic compositions of olivine separates are often used to interpret olivine-melt fractionations (e.g., Williams et al., 2005; Wang et al., 2015). Yet, naturally occurring minerals have complex crystallization-cooling histories, and inferring an equilibrium fractionation factor from such measurements is fraught with difficulties. The use of natural samples to determine olivine-melt equilibrium iron isotopic fractionations is complicated by diffusion-driven, kinetic iron isotopic fractionations (e.g., Teng et al., 2008; Teng et al., 2011; Sio et al., 2013). In terrestrial igneous rocks, both Fe^{2+} and Fe^{3+} coexist, which can cause equilibrium isotopic fractionation between melt and olivine (i.e., Teng et al., 2008; Dauphas et al., 2009a). Redox-driven fractionation on Earth may obscure the existence of equilibrium iron isotopic fractionation between olivine and Fe^{2+} in silicate melt. On the other hand, large Fe isotopic fractionations exist among lunar basalts in an environment relatively free of Fe^{3+}. The absence of Fe^{3+} on the Moon supports mechanisms of mineral fractionation, melt composition, and/or diffusive re-equilibration as cause for the observed iron isotopic variation between the low- and high-Ti mare basalts. The iron isotopic fractionations associated with these equilibrium and kinetic processes need to be well-characterized in order to distinguish the effects of each process on the resulting iron isotopic compositions of igneous rocks.

To investigate the effects of melt composition and olivine crystallization on Fe isotopic fractionation, we have experimentally determined the olivine-melt equilibrium partitioning of Fe isotopes for a compositional suite of synthetic lunar volcanic glasses. We have implemented a dual approach, combining independent techniques (MC-ICPMS and NRIXS) for determining equilibrium Fe isotopic fractionations between high temperature phases. In focusing our experimental study on compositions and oxygen fugacities relevant for lunar differentiation, we investigated Fe isotopic fractionation in the case where Fe^{3+} is of negligible abundance. Furthermore, in experimentally examining the Fe isotope dichotomy between high-Ti and low-Ti lunar mare basalts, we have examined whether the bulk titanium content of a melt exhibits a compositional control on the resulting Fe isotope signature of the basalt.

2. Methods

We have investigated the equilibrium fractionation of Fe isotopes between olivine and melt using two independent techniques. To determine the melt compositional control on Fe isotopic fractionation between lunar melts and olivine, we have conducted nuclear resonant inelastic X-ray scattering (NRIXS) measurements on a suite of synthetic glasses ranging from 0.4 to 16.3 wt.% TiO_2. To evaluate the magnitude of iron isotopic fractionation at equilibrium between olivine and melt, we have conducted olivine crystallization experiments and analyzed the Fe isotopic composition of the experimental olivines and glasses using solution MC-ICPMS. Direct olivine crystallization experiments were conducted using two bulk compositions: a synthetic glass similar to Apollo 14 VLT (very low Ti), and a synthetic Apollo 14 black glass (Table 1). Both of these compositions have olivine as a liquidus phase at one atmosphere pressure.

In comparing the results of both the NRIXS and direct crystallization experimental methods, we have determined the effect of equilibrium olivine crystallization and melt titanium content on Fe isotopic fractionation during high-temperature igneous processes. Additionally, the reducing experimental run conditions minimize Fe^{3+} content in the olivine and glass, making our results directly applicable to lunar oxygen fugacity conditions (IW-2 to IW+1; Sato, 1973).

2.1. Starting materials

For the NRIXS measurements, synthetic lunar ultramafic volcanic glass compositions were prepared from oxide powders to match the Apollo 16 green (0.39 wt.% TiO_2), Apollo 14 yellow (4.58 wt.% TiO_2), Apollo 17 orange (8.63 wt.% TiO_2), and Apollo 14 black (16.4 wt.% TiO_2) glass compositions given in Delano (1986) (Table 1). These glasses were chosen to span the range of TiO_2 content in the picritic lunar glass suite. Sodium and potassium were added to the mixtures as carbonates (Na_2CO_3, K_2CO_3), calcium was added as $CaSiO_3$, and all other components were added as single element oxides. In order to perform the NRIXS measurements, which are only sensitive to the Mössbauer isotope ^{57}Fe, ^{57}Fe-enriched Fe_2O_3 powder (96.64% ^{57}Fe, Cambridge Isotopes) was used. Oxides were mixed by hand under isopropanol in an agate mortar and pestle for 20 minutes.

For the olivine crystallization experiments, the starting materials were prepared to be similar in composition to the synthetic Apollo 14 VLT (green) and Apollo 14 black glasses in Delano (1986) (Table 1). Calcium was added as $CaCO_3$ for the green glass, and $CaTiO_3$ for the black glass. Compositions used for the olivine crystallization experiments contained natural Fe isotope abundances and were mixed without the addition of Cr, Na, or K. Oxides, silicates, carbonates, and titanates were mixed under isopropanol in a silicon-nitride ball mill for 3 hours. Polyvinyl alcohol was added as a binding agent to the starting material mixtures for both the NRIXS and olivine crystallization techniques. Once dry, 75 mg aliquots of each mixture were pressed into cylindrical pellets of 4 mm diameter and 2 mm height in preparation to be melted in the gas-mixing furnace. Great care was exercised to ensure that no cross-contamination took place between the experiments involving enrichment in ^{57}Fe and those with natural Fe isotopic abundances. However, select experiments did exhibit slight enrichments in ^{57}Fe (as detailed in the Supplementary Material). By focusing on δ^{56}Fe, we minimize any potential effects of ^{57}Fe contamination.

2.2. Experimental Methods

Lunar volcanic glass syntheses and olivine crystallization experiments were conducted in vertical gas-mixing furnaces at Washington University in St. Louis. Sample pellets were fused to rhenium loops and hung by a Pt wire thread in the furnace hot spot for the run duration. Experimental samples were then quenched rapidly by melting the Pt hanging wire and dropping the sample from within the furnace into a beaker of deionized water. The ^{57}Fe-doped glass syntheses were conducted for approximately 3 hours at 1400°C and an oxygen fugacity corresponding to the iron-wüstite buffer (Table 2). Olivine crystallization experiments were conducted at fO_2 values of IW-1 and IW+2 for durations of 6 hours, 1 day, and 4 days (Table 2). The temperatures for the olivine crystallization experiments ranged from 1262 to 1269°C, with

±1°C variation during a given experimental run (Table 2). These temperatures were optimal for producing low modal abundances (10-20 wt.%) of large olivine crystals.

All experimental run products were synthesized at oxygen fugacities that bracket the oxygen conditions inferred for the Moon. These reducing conditions minimize the presence of Fe^{3+}, which has been demonstrated to affect Fe isotope partitioning (e.g., Dauphas et al., 2014). A controlled flow of H_2 and CO_2 gases buffered the oxygen fugacity throughout each experiment. The fugacity was monitored with a Ca-doped zirconia oxygen probe using air as the reference gas. The fO_2 was found to vary between 0.01 to 0.15 log units (1σ standard deviation) during a given experiment (Table 2).

Long experimental run durations aided in crystal growth, allowing for clean mechanical separation of olivine grains for MC-ICPMS work. Olivine grains from our four-day experiments exhibited a range in grain diameter from 20 to 100 μm, compared to the 5 to 50 μm grain diameter range for the one-day experiments (Figure 2). However, Fe loss from an experimental charge increases with increased run duration (Table 2, Figure 3a). Thus, a four-day run duration was deemed optimal for the olivine crystallization experiments needed to minimize Fe loss from the experiment, while providing experimental olivines large enough to hand-separate for MC-ICPMS measurements. To ensure that clean olivine and glass could be retrieved for MC-ICPMS work, olivine and glass were separated from the four-day experiments. Quantitative analysis of the Fe loss in these experiments is presented in Section 4.1.

2.3. Approach to equilibrium

The experimentally produced olivines are compositionally homogenous and do not exhibit compositional zoning within the grains (Figure 2), and electron microprobe compositional analyses show low standard deviations amongst all analyzed grains in a given sample (Table 3). Mineral-liquid Fe-Mg exchange coefficients ($K_D^{Fe\text{-}Mg}$, Table 2) for our olivine-bearing experiments are a function of melt Ti content (0.32-0.34 for 0.06 wt.% TiO_2; 0.23-0.26 for 18 wt.% TiO_2) and are consistent with the results of Krawczynski and Grove (2012). In addition, a time series of experiments was conducted for each experimental starting composition (Apollo 14 VLT green glass, Apollo 14 black glass) at each experimental oxygen fugacity (IW-1, IW+2) in order to evaluate the effect of experimental Fe loss on the olivine-melt equilibrium. Experimental iron loss increases with increased run duration and decreased oxygen fugacity (Table 2). Thus, the lowest oxygen fugacity (fO_2 = IW-1) experiments experienced significant (up to 18%) Fe loss during the four-day experiments (see discussion in Section 4.1). Despite the increased Fe loss, the mineral-liquid Fe-Mg exchange coefficients for the four-day experiments are the same as those calculated for the shorter duration experiments (Table 2), indicating that olivine-melt equilibrium was maintained.

2.4. Analytical Methods

2.4.1. Electron Microprobe Analysis

Experimental run products were analyzed for major element abundances using the JEOL JXA-8200 electron microprobe at Washington University in St. Louis. Standardization was performed with a beam diameter of 20 μm on natural and synthetic glass and mineral samples. We used the mean atomic number (MAN) method (Donovan et al., 2016) for wavelength dispersive spectrometer background correction and measured the following elements: Si, Al, Ti, Cr, Fe, Mn, Mg, Ca, Na, K. Each quantitative analysis used a 15 kV accelerating potential and 25 nA beam current. Glass compositions were analyzed with a 20 μm beam diameter, and olivine compositions were analyzed with a focused beam (~1 μm diameter). Each compositional data point was reduced using *Probe for EPMA* software. Averages of the analyzed glass and olivine compositions are reported in Table 3. Only analyses with totals 98.5-101.5 weight percent (wt.%) are included in the reported averages (with the exception of experiment J021, for which the analytical totals were on average 96.75 wt.% likely due to incomplete degassing of the carbonates in the starting material). Olivine analyses were filtered to include only those with olivine stoichiometry (cation total between 2.98-3.02 for 4 oxygen atoms). The same calibration was used for the compositional analysis of the experimental wires, with pure Re, Fe, and Pt metal samples added as analytical standards. The Re experiment wires were analyzed from core to rim with a 2 μm beam diameter.

2.4.2. Nuclear Resonant Inelastic X-ray Scattering Spectroscopy (NRIXS) Methods

Nuclear resonant inelastic X-ray scattering spectroscopy (NRIXS) was used to probe the excitation modes of iron atoms and derive quantities needed to calculate equilibrium fractionation factors. From the phonon excitation probability function, *S(E)*, or the partial phonon density of states, *g(E)*, (itself derived from *S*), the force constant for the iron sublattice can be extracted (e.g., Dauphas et al., 2012; Dauphas et al., 2014; Liu et al., 2017) (also see Polyakov et al., 2007 for a different approach based on the kinetic energy). Assuming that the bonds are harmonic and given the high temperatures involved in magmatic processes, the reduced partition function ratio, or β-factor is calculated as a function of temperature from the mean force constant of the iron bonds, $\langle F \rangle$ in N/m (the higher order terms needed to calculate iron β-factors at low temperature are given in Table 4):

$$1000 \, ln \, \beta = 2904 \, \frac{\langle F \rangle}{T^2} \tag{1}$$

At a given temperature, the equilibrium stable isotopic fractionation factor (e.g., $\alpha_{\text{mineral-melt}}$) between two phases is related to the β-factor and Fe isotopic composition (δ^{56}Fe) for each phase through:

$$1000\, ln\alpha_{mineral-melt} = \delta^{56}Fe_{mineral} - \delta^{56}Fe_{melt} = 1000\, ln\beta_{mineral} - 1000\, ln\beta_{melt} \tag{2}$$

Using the measured force constants for synthetic lunar glasses and olivine (Dauphas et al., 2014), the equilibrium fractionation factor between olivine and melt can be theoretically determined using equation (2), assuming that the iron force constant in the glass is not significantly different from that of a melt of the same composition.

2.4.3. Multicollector-Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) Methods

The quenched experimental samples were crushed, and then individual phases were hand separated for Fe isotopic analysis with a Thermo Scientific Neptune MC-ICPMS in the Origins Lab at the University of Chicago. The instrument was upgraded in the course of its life by addition of an OnToolBooster Jet pump, bringing it to specifications on par with the Neptune Plus model. Olivine grains were hand-picked from the experimental samples under an optical microscope using cross-polarized light to distinguish the birefringent olivines from the isotropic glass. Separated olivine grains ranged between 30 and 100 μm in diameter and contained minor amounts of glass, present as thin layers on the edge of the grains. Glass separates were approximately 50-150 μm in diameter, and the transparency of the glass allowed for separation of glass pieces that were free of olivine grains.

Olivine and glass separates were then dissolved for MC-ICPMS analysis. The starting material powders, used experiment wires, and "total samples" (experimental sample left after minor glass and olivine separate removal) were also dissolved and measured to aid in interpretation of the measured isotopic compositions (see Section 4.1). Following the routine sample dissolution protocol of the Origins Lab (e.g., Dauphas et al., 2009b; Craddock and Dauphas, 2011), we digested 10-40 mg of each sample through hot-plate acid dissolution with mixtures of concentrated HF-HNO_3-$HClO_4$ and HCl-HNO_3-$HClO_4$. An additional dissolution step using aqua regia (3:1 ratio of HCl-HNO_3) was used for the starting material powders, Re wires, and "total samples". This step was repeated three times to ensure all of the Fe had been dissolved from the samples. However, a white residue (rich in TiO_2 and Al_2O_3), remained after two weeks of dissolution for the starting material powders and "total samples". Analysis of the white residues by electron dispersive spectroscopy confirmed that there was no Fe present, indicating that the dissolution effectively removed all Fe from the samples despite the remaining white residue. After the heated dissolution steps, each sample was dried out (the samples with visible residues were centrifugated and the supernatants were used), then dissolved in 6M HCl in preparation for Fe column chemistry.

The sample solutions were purified for Fe through column chemistry following the routine methods of the Origins Lab at the University of Chicago (e.g., Dauphas et al., 2004; Dauphas and Rouxel, 2006; Dauphas et al., 2009b). The iron isotopic compositions of the sample solutions were measured using the standard-bracketing method of Dauphas et al. (2009b), and are reported as δ^{56}Fe relative to IRMM-524, whose isotopic composition is identical to IRMM-014 (Craddock and Dauphas, 2011).

3. Results

Here we report experimentally determined mean force constants of iron bonds in synthetic glass samples and iron isotopic compositions of synthetic olivine and glass separates. Iron isotopic fractionation factors determined from the force constants and iron isotopic compositions demonstrate an absence of resolvable iron isotopic fractionation during olivine crystallization in reducing (fO_2 = IW-1 to IW+2) conditions.

3.1. NRIXS Results

The force constants calculated from NRIXS spectra on our synthetic lunar glasses show that within error, the lunar glasses have the same force constant, averaging to a value of 195 ± 22 N/m (Table 4). This similarity in force constants over the 0.4 – 16.3 wt.% TiO_2 range of our synthetic glasses suggests that Fe isotopic fractionation is not a function of melt Ti content (Figure 4). Further, the mean force constants of our synthetic suite of lunar glasses are similar to the force constants generated for reduced (fO_2 = IW) terrestrial basalts (197 ± 8 N/m) in Dauphas et al. (2014). The force constants from the synthetic lunar glasses are also similar to the previously determined iron force constant for olivine (Fo_{86} , Fe^{3+} absent) of 197 ± 10 N/m (Dauphas et al., 2014).

3.2. Olivine Crystallization Experiments

The measured Fe isotopic compositions of the experimental glass and olivine separates indicate that there is no measurable fractionation between olivine and glass (Table 5). The isotopic difference between the starting material, experiment wire, and olivine and glass separates can be explained by the fractionation of Fe isotopes during experimental Fe loss to the Re wire and through evaporation (Section 4.1). The iron isotopic composition of the starting material powders

(Table 5) is controlled by both the iron isotopic composition of Fe_2O_3 (used in all starting compositions) and Fe metal sponge (used only in starting compositions #010 and #011) (Appendix Table 1). To further illustrate the isotopic relationship among all experimental parts, the measured Fe isotopic compositions have been plotted in Figure 5. For each experiment, the olivine Fe isotopic composition is indistinguishable from that of the glass. The measured compositions thus indicate that olivine does not significantly fractionate iron isotopes when crystallizing from lunar melt compositions at lunar-like fO_2.

4. Discussion

4.1. Quantitative analysis of experiment iron loss

The four-day olivine crystallization experiments experienced up to 18% total Fe loss (Table 2). We estimated the amount of total Fe loss using a mass balance of the measured phase compositions and the bulk starting composition of the experiment (Krawczynski and Olive, 2011). A rhenium wire was used in all of the experiments to minimize the diffusive Fe loss to the metal loop at reduced oxygen fugacities (Borisov and Jones, 1999). The experimental runs at fO_2 = IW+2 experienced less Fe loss than those at fO_2 = IW-1 (9% vs. 18% Fe loss, Table 2). The total amount of iron lost from our experiments under reducing conditions is consistent with the estimated loss in experiments ran at similar conditions by Borisov and Jones (1999). Electron microprobe analyses of the Re wires after completion of the experiments (Figure 3b, Appendix Table 2) yield Fe concentrations within the range of those measured in Re wires from Borisov and Jones (1999). The Re wire is always enriched in the light isotopes of iron, which is consistent with the fact that transport through the wire is diffusive, and light isotopes of iron diffuse faster than heavier ones (Mullen, 1961; Roskosz et al., 2006; Dauphas, 2007; Richter et al., 2009; Van Orman and

Krawczynski, 2015). However, the Fe mass balance between the wire and sample cannot account for all of the sample Fe loss.

To account for the effect of Fe loss on the measured Fe isotopic compositions of the samples, we measured the Fe isotopic compositions of the bulk starting material, experiment wire, and the sample material remaining after olivine and glass separates were removed (Table 5). Owing to their similar Fe isotopic compositions, removal of minor olivine and glass fractions from the sample did not change the bulk isotopic composition of the remaining sample material (un-separated glass and olivine, hereafter referred to as "total sample"). For each of the olivine crystallization experiments, the isotopic compositions (δ^{56}Fe) of the total sample were higher than that for the bulk starting material. Open system behavior of Fe and isotopic fractionation between the bulk starting material and the total sample can be explained by Fe loss to the Re wire and evaporative Fe loss in the gas-mixing furnace. Using the measured iron isotopic compositions of the bulk starting material, experiment wire, and the total sample, we were able to quantify the mass of Fe lost and the associated Fe isotopic fractionation for both mechanisms of Fe loss occurring during an experimental run.

The incorporation of Fe into Re wire during the experiment induced some Fe isotopic fractionation, with the wire having a lighter iron isotopic composition than the total sample (Table 5, Figure 5). Roskosz et al. (2006) demonstrated that experimental iron loss to Pt wires fractionates iron isotopes. In that study, kinetic fractionation of Fe isotopes produced an isotopically light Pt wire (relative to the experimental sample) in short duration experiments. In longer duration experiments, Fe isotopes equilibrated between the Pt wire and experimental charge producing an isotopically heavier Pt wire, which presumably represented the equilibrium partitioning of stable Fe isotopes between Pt and melt. Similar to the Pt wire results of Roskosz et al. (2006), the Re wires from our experiments are isotopically lighter than the experimental samples. This is most likely associated with diffusive transport of iron, as it is well-documented in a variety of systems that light isotopes diffuse faster than heavier ones (e.g., Richter et al., 2009; Van Orman and Krawczynski, 2015), resulting in light isotope enrichment in the reservoir that experiences net Fe gain (i.e., the Re wire) relative to the source (i.e., the silicate melt). Owing to this kinetic fractionation, iron isotopes are more fractionated between the Re wire and total sample in the experiments that experienced less iron loss (fO_2 = IW+2). That is, as more Fe diffuses into the Re wire, the fractionation between the wire and the sample decreases. Only one sample (H055) has a Re wire iron isotopic composition that is heavier than the iron isotopic composition of the bulk starting material, however the wire is still isotopically lighter than the glass. Owing to the presence of a thin glass coating on the H055 wire, it is possible that a minor amount of experimental glass was dissolved along with the wire during preparation for iron isotope measurement. This would result in a measured iron isotopic composition for the wire that is heavier than the iron isotopic composition of the wire without glass.

Although loss of Fe to the Re wire fractionates Fe isotopes and produces a heavier Fe isotopic composition for the total sample relative to the bulk starting material, the total amount of Fe incorporated into the wire cannot account for the magnitude of Fe isotopic fractionation between the two, nor the bulk Fe loss. Similar to Fe loss to the Re wire, evaporative Fe loss would preferentially deplete the experiments in lighter Fe isotopes, resulting in greater δ^{56}Fe for the olivine, glass, and total sample compared to the bulk starting material.

To assess the extent of both evaporative Fe loss and Fe loss to the Re wire, we calculated an isotopic mass balance of the measured experiment parts (starting material, wire, and total sample) and, by difference, the Fe that evaporated during the experiment. For example, using the isotopic measurements (Table 5) for each part of experiment H056 we can estimate a δ^{56}Fe for the Fe lost by evaporation:

$$\delta^{56}Fe_{starting\ material} = \sum_{i}(X_{Fe}^{i} \times \delta^{56}Fe_{i}) \tag{3}$$

where *i* denotes a reservoir of the experiment (wire, total sample, gas), where X_{Fe} represents the mass fraction of the initial Fe present in each reservoir, $\delta^{56}Fe_{starting\ material}$, $\delta^{56}Fe_{total\ sample}$, $\delta^{56}Fe_{wire}$ are measured values, and $\delta^{56}Fe_{gas}$, X_{Fe}^{wire}, $X_{Fe}^{total\ sample}$, X_{Fe}^{gas} can then be calculated from mass balance constraints (results presented in Figure 6). $X_{Fe}^{total\ sample}$ is equivalent to one minus the percent total Fe loss estimated from mass balance of the measured phases and the experimental starting composition (Krawczynski and Olive, 2011). For H056, which experienced 18% total Fe loss, $X_{Fe}^{total\ sample} = 0.82$ (Figure 6b). X_{Fe}^{wire} is calculated using the ICP-MS Fe concentration measurement of the dissolved wire (μg, Table 5) and the estimated mass of Fe in the starting material (75 mg pellet, wt.% FeO for starting composition, Table 1). For H056, $X_{Fe}^{wire} = 0.04$. Following this, X_{Fe}^{gas} can be calculated assuming $X_{Fe}^{total\ sample} + X_{Fe}^{wire} + X_{Fe}^{gas} = 1$. Thus, for H056, $X_{Fe}^{gas} = 0.14$. From this calculation, we conclude that 14% of the initial Fe in the starting material was lost by evaporation during the experiment.

The last unknown of equation (3) is the “iron isotopic composition” of the Fe lost through evaporation ($\delta^{56}Fe_{gas}$), or rather the net isotopic fractionation that resulted from the evaporation. To estimate the evaporative fractionation, we solve equation (3) for $\delta^{56}Fe_{gas}$ using the X_{Fe} values calculated above (Figure 6b) and the measured δ^{56}Fe values for the experiment parts (Table 5). For H056, the resulting isotopic composition associated with the evaporated gas is $\delta^{56}Fe_{gas}$= -2.01‰, and the bulk isotopic fractionation factor is $\alpha_{experiment\text{-}vapor} = 1.0028$. Our estimates of the evaporative isotopic fractionation based on the mass balance of our measured experimental run products (bulk $\alpha_{\text{experiment-vapor}}$) range from 1.0002 to 1.0028, with the smallest fractionation between experiment and vapor (1.0002) existing for experiment J012, the high-Ti (black glass) composition conducted at IW+2. The experiment-vapor fractionation in our gas-mixing furnace experiments is smaller than that in a vacuum furnace because the Fe vapor pressure is higher, which dampens the isotopic fractionation (Richter et al., 2002; Richter, 2004; Dauphas and Rouxel, 2006; Richter et al., 2007; Richter et al., 2009; Dauphas et al., 2015). Most likely, the evaporative Fe loss proceeded through a Rayleigh distillation. Using the $\alpha_{\text{experiment-vapor}}$ calculated for each experiment, we have modeled the change in the iron isotopic composition of the experimental sample as iron is lost by evaporation (Figure 7).

For experiments conducted at fO_2 = IW-1, on average 5% of the Fe starting material was lost to the Re wire (average $X_{Fe}^{wire} = 0.05$), while this value is negligible at IW+2 (Figure 6b). Additionally, 13% of the Fe starting material was lost via evaporation at IW-1 (average $X_{Fe}^{gas} = 0.13$) and 8% of the starting material Fe was lost by evaporation at IW+2 (average $X_{Fe}^{gas} = 0.08$). In one-atmosphere gas-mixing furnace experiments, Fe loss has generally been considered as loss to the container (e.g., Re or Pt wire), while volatile element loss (e.g., Na, K) has been attributed to vaporization (Corrigan and Gibb, 1979; Donaldson and Gibb, 1979; Grove, 1981; Borisov and Jones, 1999). Our results indicate that at IW-1, ~75% of the estimated Fe loss occurred via evaporation, and only 25% of the Fe loss can be attributed through loss to the Re wire. At IW+2, the estimated Fe loss is due to ~95% evaporative loss and ~5% loss to the Re wire.

To further assess the potential for evaporative isotopic fractionation at our experimental run conditions, we have calculated the evaporative flux of Fe (J_{Fe}) from the sample using the Hertz-Knudsen equation:

$$J_{Fe} = \frac{\alpha_{Fe}\,(P_{Fe}^{v} - P_{Fe}^{a})}{\sqrt{2\pi M_{Fe}RT}} \tag{4}$$

in which J is the evaporative flux in moles cm^{-2} s^{-1}, α is the evaporation coefficient, M is molecular weight, P^{v} is equilibrium vapor pressure for the element considered, P^{a} is the ambient pressure for the element considered, R is the universal gas constant (J mol^{-1} K^{-1}), and T is temperature (K). Following the methods outlined in Fedkin et al. (2006), we calculated the equilibrium vapor pressure of Fe assuming both Fe and FeO species exist in the gas, and the only contribution of Fe to the furnace gas atmosphere is from the experimental sample:

$$P_{Fe}^{v} = P_{Fe}^{sample} = P_{FeO} + P_{Fe} \tag{5}$$

The partial pressures of the gases evaporated from the molten experimental sample are then calculated from the volatilization reactions:

$$FeO_{(l)} \rightarrow FeO_{(g)} \tag{6}$$

$$FeO_{(l)} \rightarrow Fe_{(g)} + \frac{1}{2} O_{2\ (g)} \tag{7}$$

The equilibrium constants, k, for reactions (6) and (7) are constructed from the thermodynamic data in the JANAF tables (Chase, 1996) and used to calculate the equilibrium vapor pressure of Fe:

$$P_{Fe}^{sample} = k_6 a_{FeO} + \frac{k_7 a_{FeO}}{\sqrt{fO_2}} \tag{8}$$

where a_{FeO} is the activity of FeO in the molten experimental sample, and fO_2 is the oxygen fugacity of the experiment. We used the rhyolite-MELTS code (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Gualda et al., 2012) to calculate the activity of FeO in the silicate liquid for each experimental starting composition at the experimental temperature and oxygen fugacity. Using equation (8), we calculate P_{Fe}^{sample}, which is then used to calculate the evaporative flux, J_{Fe}, from equation (4). Assuming the gas flow in our furnace is efficient in removing any Fe gas that is released into the furnace from the sample, we set the ambient vapor pressure of Fe (P^a) equal to 0. Then, the only unknown needed to solve for the evaporative flux (J_{Fe}) using equation (4) is the Fe evaporation coefficient (α_{Fe}). The evaporation coefficients we used in equation (4) to calculate evaporative Fe loss that matches the estimated evaporative Fe loss from our samples are $\alpha_{\mathrm{Fe}} = 2.5\mathrm{x}10^{-3}$ at IW-1, and $\alpha_{Fe} = 6.3\mathrm{x}10^{-2}$ at IW+2 (see Supplementary Material for additional detail).

Through isotopic measurement and mass balance calculations of our experiments, we have demonstrated that isotopic fractionation during evaporation and loss to the experimental container are essential considerations for experimental studies of isotope partitioning. Despite this open system behavior, the olivine and glass phases were always in equilibrium, as diffusion in the melt is fast (at 1265°C, anhydrous basaltic melt $D_{\mathrm{Fe}} \sim 10^{-11}$ m^2/s; Zhang et al., 2010), and 10-50 μm diameter olivine grains would diffusively equilibrate at the experimental run temperature and duration. For example, at experimental conditions of 1265°C and IW+2, a 50 μm olivine grain would equilibrate with respect to Fe and Mg in approximately 50 hours (McDougall and Harrison, 1999; Dohmen and Chakraborty, 2007). The olivine and glass separates showed deviation from the starting material, but had identical isotopic composition to that of the "total sample" which diffusively maintained equilibrium. Thus, the measured Fe isotopic compositions of the olivine and glass can accurately be compared to interpret the olivine-melt Fe isotopic fractionation during olivine crystallization.

4.2. Factors controlling iron isotopic fractionation on the Moon

We have applied our results to test whether the lunar iron isotope "dichotomy" observed between the high- and low-Ti basalts can be explained by olivine crystallization or melt titanium content.

From our complementary NRIXS and olivine crystallization experiments, we have concluded that any equilibrium fractionation of iron isotopes between olivine and melt at lunar-like oxygen fugacities is not resolvable within analytical uncertainties. Olivine-melt Fe isotopic fractionation factors for the lunar volcanic glasses were determined from our measured force constants on the glass suite and the olivine NRIXS results from Dauphas et al. (2014) (Figure 8). Our result from the MC-ICPMS olivine crystallization study is consistent with the Fe isotopic fractionation factors predicted by the NRIXS measurements on olivine (Dauphas et al., 2014) and the suite of lunar volcanic glasses (this study), in that there is not a resolvable iron isotopic fractionation. Some major element variations in lunar mare basalts can be attributed to differences in source compositions having experienced varying degrees of olivine fractionation (Shearer et al., 2006, and references therein). Additionally, extensive crystallization of the lunar magma ocean involving significant fractionation of olivine has been previously hypothesized as a mechanism for generating the isotopically heavy source regions for the high-Ti basalts (Wang et al., 2015). However, because olivine does not fractionate iron isotopes to a measureable extent, varying degrees of equilibrium olivine crystallization can be eliminated as a potential mechanism for generating the mare basalt iron isotope dichotomy. The fractionation of phases other than olivine, such as clinopyroxene and ilmenite, are likely more important in interpreting both the major element and isotopic compositions of the lunar mare basalt suites.

Both of our experimental approaches indicate that the difference in melt titanium content between low-Ti and high-Ti mare basalts cannot explain the observed iron isotope dichotomy. Partitioning of Fe into olivine has been shown to be a function of Ti content (Longhi et al., 1978; Xirouchakis et al., 2001; Krawczynski and Grove, 2012). Titanium influences the coordination environment of Fe^{2+} in silicate melt by forming Fe-Ti complexes, and as a result, Fe is preferentially incorporated into the melt relative to olivine (Krawczynski and Grove, 2012). However Fe isotope partitioning does not appear to correlate with melt titanium content, as demonstrated by our NRIXS force constant measurements (Table 4, Figure 4) and our olivine crystallization experiments from both the low-Ti and high-Ti glass compositions. Despite the different coordination of Fe2+ for different Ti contents. Though the major element partitioning of Fe into olivine is affected by Fe^{2+}-Ti complexes in silicate melt, the isotopic partitioning of Fe is not affected by melt titanium content. We conclude that Fe^{2+} coordination in silicate melts has a minimal effect on iron isotopic fractionation. In contrast, Dauphas et al. (2014) demonstrated that melt compositional parameters such as silica content and the redox state of iron (i.e., Fe^{3+} content) influence the Fe bonding structure, and consequently, the iron isotopic composition, in a suite of terrestrial volcanic glass compositions ranging from basalt to rhyolite.

4.3. Iron isotopic composition of lunar dunite 72415

Olivines from lunar dunite 72415 are considerably lighter than the mare basalts ($\delta^{56}Fe_{dunite} = -0.35 \pm 0.20‰$, Wang et al., 2015; Sossi and Moynier, 2017). These values, if representative of equilibrium fractionation from a parent melt isotopically similar to the mare basalts ($\delta^{56}Fe = 0‰$

to +0.2‰), differ from the predicted Fe isotopic fractionation of this study. The absence of resolvable equilibrium iron isotopic fractionation between olivine and lunar melts in our experiments supports a non-equilibrium model for generating the light iron isotopic composition of the lunar dunite.

As Fe begins to diffuse into olivine, the isotopes of Fe with lighter mass will be preferentially enriched, creating a "light" iron isotopic composition (Teng et al., 2008; Dauphas et al., 2010; Teng et al., 2011; Sio et al., 2013; Sio and Dauphas, 2017). The lunar dunite is highly magnesian ($Fo_{84} – Fo_{89}$, Dymek et al., 1975), and any Fe that diffuses into the olivine will greatly affect the mass balance of Fe isotopes in the dunite. Diffusive iron isotopic fractionation modeling that reproduces the observed Fe-Mg zoning profiles in lunar dunite olivine grains, can produce iron isotope signatures as low as δ^{56}Fe = -0.21‰ and -0.3‰ (Wang et al. 2015). Further, kinetic isotopic fractionation models of Fe-Mg interdiffusion and olivine crystallization (Teng et al., 2008; Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015; Collinet et al., 2017; Sio and Dauphas, 2017) reproduce isotopic fractionations as large as 1‰ observed in olivine grains.

Models of lunar dunite (72415-72418) petrogenesis detail the potential petrologic processes involved in generating a kinetic origin for the isotopically light dunite signature. Early petrologic investigations of the lunar dunite identified it as an early lunar magma ocean cumulate (e.g., Dymek et al., 1975). In contrast, Ryder (1992) concluded that the lunar dunite crystallized at shallow depths less than 1 km. The early lunar magma ocean cumulate hypothesis was invoked by Wang et al. (2015) to explain the isotopically light iron isotopic compositions of the dunite. If the lunar dunite is an early lunar magma ocean cumulate, then, assuming equilibrium conditions, the composition from which the dunite is crystallizing must already be isotopically light; δ^{56}Fe = -0.35 ± 0.20‰.

One way an isotopically light dunite source composition could potentially be generated is by an early core formation and metal-silicate partitioning. Experimental and analytical studies of metal-silicate iron isotope partitioning have suggested that metal is isotopically heavier ($\Delta^{56}Fe_{metal-silicate} \approx +0.1‰$) than coexisting silicate (Poitrasson et al., 2005; Shahar et al., 2015; Elardo and Shahar, 2017). However, a number of investigations (e.g., Schuessler et al., 2007; Poitrasson et al., 2009; Hin et al., 2012; Shahar et al., 2016; Liu et al., 2017) have concluded that no significant iron isotopic fractionation occurs between metal and silicate in equilibrium. The disagreement results from the significant differences in starting compositions, phases, capsule materials, and experimental conditions between studies. Assuming an equilibrium iron isotopic fractionation did exist between metal and silicate, if the dunite source were once deep enough to be in isotopic equilibrium with the lunar core, it would have a relatively light iron isotopic composition. However, the estimates for the bulk mantle iron isotopic composition of the Moon after core formation (e.g., minimum $\delta^{56}Fe = -0.15‰$; Elardo and Shahar, 2017), still cannot explain the magnitude of light iron isotopic compositions measured in the lunar dunite by equilibrium metal-silicate fractionation alone.

Another alternative method of generating isotopically light olivine in the lunar dunite is partial melting. Iron isotope studies of terrestrial peridotites, which are the residues of partial melting and depletion, show a correlation between iron isotopic compositions and depletion, becoming lighter at higher extents of partial melting (Williams et al., 2005; Weyer and Ionov, 2007; Williams et al., 2009; Williams and Bizimis, 2014). It is possible that the iron isotopic composition of the lunar dunite is a result of partial melting, however the existing models of lunar dunite petrogenesis (i.e., Dymek et al., 1975; Ryder, 1992; Shearer et al., 2015) identify the dunite as being of cumulate origin, not an ultra-depleted residue of partial melting.

Considering the potential models for lunar dunite petrogenesis, kinetic fractionation via Fe-Mg interdiffusion seems likely to have occurred, and this mechanism could easily explain the light Fe isotopic compositions measured in the lunar dunite olivines. Regardless of whether the lunar dunite is a deep magma ocean cumulate (Dymek et al., 1975) or shallow cumulate (Ryder, 1992; Shearer et al., 2015), the Mg-rich nature of the dunite ensures it would have interacted with a higher Fe/Mg melt before and/or during its ascent to the lunar surface/sub-surface. In this way, iron diffusion into the dunite is a plausible occurrence during every proposed model of dunite formation. Iron diffusion into the Fe-poor olivine of the lunar dunite would decrease the δ^{56}Fe composition, producing the negative δ^{56}Fe values measured by both Wang et al. (2015) and Sossi and Moynier (2017).

4.4 Considerations for High-Temperature Iron Isotopic Fractionation on Earth and Mars

The results of our olivine crystallization experiments indicate that the absence of a measureable equilibrium iron isotopic fractionation between olivine and melt is robust over fO_2 = IW-1 to IW+2 in both the low-Ti (green glass) and high-Ti (black glass) compositions. Thus, we can apply our results for the synthetic lunar glass compositions to olivine-bearing systems on Earth and Mars with a similar range in oxygen fugacity, keeping in mind that there could be melt compositional controls in addition to that of TiO_2 determined in this work.

Estimations for the oxygen fugacity of Earth's upper mantle from spinel peridotites lie within QFM±2 (IW+1.5 to IW+5.5 at magmatic temperatures), with select abyssal peridotites and peridotite massifs extending to QFM-3 (~IW+0.5) (Frost and McCammon, 2008, and references therein). Garnet peridotites are more reducing than spinel peridotites, with the majority of fO_2 estimations falling between IW-1 and IW+2 (Frost and McCammon, 2008). Additionally, the oxygen fugacity of martian basalts is estimated to be QFM-3 to QFM-1 (~IW to IW+3) (Herd et al., 2002). Considering these estimates of magmatic oxygen fugacity, the IW-1 to IW+2 range of our experiments is relevant to garnet peridotites, as well as the most reduced spinel peridotites and martian basalts.

Iron isotopic compositions of terrestrial peridotites are δ^{56}Fe = -0.1‰ to +0.15‰ (Dauphas et al., 2017). The range of peridotite iron isotopic compositions are considered to be a result of melt extraction based on the correlation between iron isotopic composition and depletion, with iron isotopic compositions of residues becoming lighter at higher extents of partial melting (Williams et al., 2005; Weyer and Ionov, 2007; Williams et al., 2009; Williams and Bizimis, 2014). Alternatively, the heavy isotopic enrichment in the melt relative to the residue may be a result of Fe^{3+} in the melt (Dauphas et al., 2009a; Dauphas et al., 2014). For instance, the difference between the iron isotopic compositions of spinel and garnet peridotites has been attributed to the contrasting behavior of Fe^{3+} during melting (Williams et al., 2005). Experimental determinations of mineral-melt iron isotopic fractionations for additional minerals (i.e., pyroxene, spinel) are needed in order to fully model the evolution of iron isotopic compositions during partial melting, as there exists experimental evidence for equilibrium iron isotopic fractionation between spinel and olivine (Shahar et al., 2008; Roskosz et al., 2015).

5. Conclusion

Olivine separates are often enriched in lighter iron isotopes relative to coexisting minerals and the bulk rock (e.g., terrestrial peridotites, Beard and Johnson (2004); Poitrasson et al. (2004); Williams et al. (2005); terrestrial basalts, Teng et al. (2008); Teng et al. (2010); Sio et al. (2013); lunar basalts, Poitrasson et al. (2004); Wang et al. (2012); Wang et al. (2015); martian basalts, Collinet et al. (2017)). Considering the olivine-melt fractionation results presented in this work, the only known mechanism capable of fractionating iron isotopes to a measureable degree is diffusive fractionation (Dauphas et al., 2010; Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015; Sio and Dauphas, 2016; Collinet et al., 2017). Thus, the olivine grains enriched in light Fe isotopes in mafic rocks are not a result of primary igneous crystallization, but rather a diffusive fractionation, potentially related to re-equilibration (Teng et al., 2011; Sio et al., 2013; Oeser et al., 2015) or simultaneous Fe diffusion and crystal growth (Sio and Dauphas, 2016; Collinet et al., 2017). A diffusive fractionation mechanism is further supported by existing isotopic disequilibrium between coexisting mineral pairs in peridotite samples (Beard and Johnson, 2004; Roskosz et al., 2015). This disequilibrium in peridotites has been hypothesized as a result of multiple phases of melt extraction, melt percolation, melt-rock reaction, or metasomatism (Beard and Johnson, 2004; Williams et al., 2005; Macris et al., 2015; Roskosz et al., 2015; Zhao et al., 2017). If the light iron isotopic compositions of terrestrial peridotites can conclusively be attributed to metasomatism, then the light iron isotopic composition of the lunar dunite (discussed in Section 4.3) may also be a result of metasomatism, as metasomatism has been invoked to explain chemical trends and petrographic textures observed in the lunar dunite (Shearer et al., 2015).

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Figure Captions

Figure 1. Iron isotopic compositions plotted as a function of TiO_2. Red points represent terrestrial basalts and andesites, and blue points represent lunar basalts. The terrestrial suite is similar in Fe isotopic composition to the low-Ti basalts, however high-Ti basalts have greater δ^{56}Fe values. The observed fractionation between low- and high-Ti lunar mare basalts appears to be bi-modal, although it is uncertain if this modality is due to sampling bias, as basalts with intermediate Ti concentrations have not been frequently measured. Compositions and isotope measurement errors (95% confidence interval) are from (Wiesli et al., 2003; Poitrasson et al., 2004; Weyer et al., 2005; Teng et al., 2008; Dauphas et al., 2009b; Schuessler et al., 2009; Craddock et al., 2010; Liu et al., 2010; Wang et al., 2015; Sossi and Moynier, 2017).

Figure 2. Back scattered electron image of two olivine crystallization experiments. Both experiments were conducted at fO_2 = IW+2. Experiment durations were 1 day (left) and 4 days (right). Experimental olivine crystals (dark gray) in the 4-day experiment (~50 μm diameter) are larger than those grown in the 1-day experiment (~20 μm). Additionally, the olivine grains are compositionally homogenous, i.e., there is no visible Fe zoning within the grains at the ± 0.5 wt.% FeO level.

Figure 3. a) Back scattered electron image of two Re wires. The wires were mounted in epoxy post-experiment and polished to create a measureable cross section. Both wires were used in experiments conducted at fO_2 = IW-1. Experiment durations were 6 hours (left) and 4 days (right). Experimental Fe loss to the Re wire increases with time, producing a thicker Fe-enriched layer (dark gray) while the core of the Re wire remains Fe-free (light gray).

b) Electron microprobe core-to-rim Fe (wt.%) profile in a Re wire from a 4-day experiment conducted at fO_2 = IW-1.

Figure 4. Force constants from a suite of melt compositions plotted as a function of TiO_2 content. Red points represent the reduced (fO_2 = IW) terrestrial basalt, andesite, and dacite glasses from Dauphas et al. (2014), and blue points represent the synthetic lunar volcanic glass compositions measured in this work. There is no correlation between force constants and TiO_2 content within the investigated 0.4 - 16.3 wt.% TiO_2 compositional range.

Figure 5. Iron isotopic compositions for each experiment part from Table 5 reported as $\Delta^{56}Fe_{\text{part – total sample}}$ ($\delta^{56}Fe_{\text{part}} - \delta^{56}Fe_{\text{total sample}}$). Error bars represent 95% confidence interval. Green symbols indicate a synthetic green glass starting composition, and black symbols indicate a synthetic black glass starting composition. Olivine and glass pairs from a given experiment are highlighted.

Figure 6.

a) A schematic diagram illustrating the Fe mass and isotope distributions detailed in Section 4.1 for experiment H056. The labeled percent values at each branch represent the percent of the initial Fe attributed to a given experiment reservoir. Measured iron isotopic compositions of each experiment reservoir are mass balanced to explain the effect of Fe loss on the iron isotopic composition of the total sample. Iron isotopic compositions and fractionations in italics indicate calculated (not measured) values. Percent initial Fe for olivine and glass separates is calculated using the olivine and glass proportions given in Table 2 (83% glass, 17% olivine for H056) and the calculated percent initial Fe for the total sample ($X_{Fe}^{\text{total sample}} = 1 - X_{Fe}^{\text{loss}}$). A similar calculation was performed for each experiment using the measured iron isotopic compositions for all the experiment reservoirs (starting material, olivine, glass, total sample, experiment wire).

b) A stacked bar graph indicating the X_{Fe} calculated for each Fe reservoir for each experiment. The bracketed labels below the experiment names indicate the oxygen fugacity of the experiment (IW-1 or IW+2). Additionally, the legend identifies which reservoirs constitute Fe loss (wire, gas) and "total sample" Fe (olivine, glass).

Figure 7. The iron isotopic evolution of an experimental sample as evaporative Fe loss proceeds through Rayleigh distillation, as calculated using $\alpha_{\text{experiment-vapor}}$ for each experiment. The iron isotopic composition is reported as $\Delta^{56}Fe_{\text{sample*} - \text{starting material}}$ ($\delta^{56}Fe_{\text{sample*}} - \delta^{56}Fe_{\text{starting material}}$) using $\delta^{56}Fe_{\text{starting material}}$ from Table 5. $\delta^{56}Fe_{\text{sample*}}$ represents the iron isotopic composition of the "total sample" after accounting for the iron isotopic fractionation associated with Fe loss to the Re wire (Section 4.1, Figure 6). This correction was performed to isolate the effect of evaporation on the heavy iron isotopic enrichment that occurs during the experiment, however both losses (to wire, to vapor) would occur simultaneously throughout the experiment. Green symbols indicate a synthetic green glass starting composition, and black symbols indicate a synthetic black glass starting composition. The shape of the symbols reflects the fO_2 of each experiment as indicated in the legend. Each modeled line is labeled with the corresponding $\alpha_{\text{experiment-vapor}}$ used in the Rayleigh distillation equation.

Figure 8. Equilibrium mineral-melt fractionation of iron isotopes for olivine plotted as a function of temperature. The blue line represents the difference between the average beta factor calculated

from the NRIXS mean force constants for our synthetic lunar glasses and the beta factor for olivine (Fo_{82}) from Dauphas et al. (2014). The blue shading represents the error associated with the calculated beta factors. The difference between the iron isotopic compositions of olivine and glass separates in each crystallization experiment (Table 5) are plotted with the associated measurement errors (95% confidence interval). Green symbols indicate a synthetic green glass starting composition, and black symbols indicate a synthetic black glass starting composition. The inset in the bottom right is the same data plotted in the main figure, with the x-axis expanded on the experiment run temperatures. There is no resolvable difference between olivine and the synthetic lunar glass suite under equilibrium conditions, as evidenced by our experimental results from both the NRIXS and ICPMS approaches.

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