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Key Points:

- We constrained the Fe isotope fractionation factor for the silicate mantle up to 30 GPa using a bulk silicate Earth composition
- We present a holistic Fe isotope fractionation model for core formation considering pressure, temperature, composition, and redox state
- Our model shows that core formation can cause the mantle of small planetary bodies to be light in Fe isotopes, but heavy for that of Earth

Supporting Information:

Supporting Information may be found in the online version of this article.

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Planet Size Controls Fe Isotope Fractionation Between Mantle and Core

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Abstract As an element ubiquitous in the Solar system, the isotopic composition of iron exhibits rich variations in different planetary reservoirs. Such variations reflect the diverse range of differentiation and evolution processes experienced by their parent bodies. A key in deciphering iron isotope variations among planetary samples is to understand how iron isotopes fractionate during core formation. Here we report new Nuclear Resonant Inelastic X-ray Scattering experiments on silicate glasses of bulk silicate Earth compositions to measure their force constants at high pressures of up to 30 GPa. The force constant results are subsequently used to constrain iron isotope fractionation during core formation on terrestrial planets. Using a model that integrates temperature, pressure, core composition, and redox state of the silicate mantle, we show that core formation might lead to an isotopically light mantle for small planetary bodies but a heavy one for Earth-sized terrestrial planets.

Plain Language Summary Planetary formation and differentiation are fundamental processes that physically and chemically shaped terrestrial planets. As a major element ubiquitous in terrestrial planets, the isotopic ratios of Fe are found to vary among different planetary reservoirs, reflecting the formation and differentiation processes that occurred on their parent bodies. Deciphering the information behind these variations require experimental and theoretical constraints on how the isotopic ratios of Fe evolve during different planetary processes. Here, we present a systematic model on how Fe isotopes behave during planetary core formation based on high pressure experiments. We show that Fe isotope fractionation between the mantle and core of terrestrial bodies depends strongly on the planet size.

1. Introduction

As the most abundant transition metal element in the Solar System, iron (Fe) plays an important role in almost every stage of formation, differentiation, and evolution of terrestrial planets. Since Fe exists as Fe^0 in the metallic core portion but dominantly Fe^{2+} or Fe^{3+} in the silicate mantle portion of a planet, it has long been thought that Fe isotopes could fractionate between the two reservoirs, hence tracing the core formation process (Poitrasson et al., 2004). Iron isotope measurements of natural samples show substantial variations among different terrestrial and planetary reservoirs, supporting the possibility that some of the variations are due to core formation. Primitive chondritic meteorites, widely accepted as the building blocks of terrestrial planets, have remarkably similar Fe isotope compositions with an average $\delta^{57}Fe$ ($^{57/54}Fe$ ratios relative to the IRMM-014 standard in per mil units) of 0.01 ± 0.02‰ (2 s.e., Craddock & Dauphas, 2010). Differentiated meteorites from Mars (shergottites, nakhlites, chassignites, and ALH 84001) and asteroid 4 Vesta (howardites, eucrites, and diogenites) are found to be approximately chondritic in Fe isotope composition (Anand et al., 2006; Poitrasson et al., 2004; Schoenberg & von Blanckenburg, 2006; Sossi, Nebel, Anand, & Poitrasson, 2016; Wang et al., 2012; Weyer et al., 2005). Angrites and aubrites, however, have Fe isotope compositions heavier ($\delta^{57}Fe = 0.19 \pm 0.02$‰) and lighter ($\delta^{57}Fe = -0.13 \pm 0.10$‰) than chondritic, respectively (Wang et al., 2012, 2014). On the other hand, terrestrial basalts produced at the mid-ocean ridges (MORB) are approximately 0.15‰ heavier than chondritic in their $\delta^{57}Fe$, leading to the early hypothesis that the Earth's mantle is non-chondritic in Fe isotope composition and the fractionation is due to partial vaporization during the Moon-forming giant impact (Poitrasson et al., 2004). Successive studies proposed alternative explanations that the heavy Fe isotope composition of mid-ocean ridge basalts is a result of core formation (Polyakov, 2009), mantle silicate disproportionation (H. M. Williams et al., 2012), or partial melting (Craddock et al., 2013; Dauphas et al., 2009; Weyer & Ionov, 2007).

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Understanding Fe isotopic variations among different terrestrial and planetary reservoirs relies heavily on the knowledge of high-pressure Fe isotope fractionation during core-mantle segregation, a large-scale process universal for terrestrial planets and large asteroids. Early piston-cylinder and multi-anvil experiments at <7.7 GPa yielded limited Fe isotope fractionation between molten metal and silicate (Hin et al., 2012; Poitrasson et al., 2009), but more recent studies show a positive fractionation that correlates with the amount of substitutional impurities in the metal alloy (Elardo & Shahar, 2017; Elardo et al., 2019). On the other hand, knowledge of the fractionation at higher pressures between 40 and 60 GPa (Corgne et al., 2009) relevant to terrestrial core formation primarily comes from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) experiments and theoretical simulations (Liu et al., 2017; Polyakov, 2009; Shahar et al., 2016; Yang et al., 2019). Based on previously published NRIXS spectra, Polyakov (2009) proposed that pressure has a strong impact on the isotopic fractionation factor between lower mantle minerals and iron metal, causing the Earth's mantle to be heavier than chondritic in Fe isotope composition. In subsequent studies, the role of nickel and light elements (H, C, O, Si, and S) in the metal alloy was further investigated and found to also have an effect on silicate-metal fractionation, but the overall fractionation is minimal at the terrestrial core formation conditions (Liu et al., 2017; Shahar et al., 2016).

The previous NRIXS studies either used mantle crystalline phases, such as ferropericlase, post-perovskite (Polyakov, 2009), and bridgmanite (Shahar et al., 2016), or a basaltic glass (Liu et al., 2017) as analogs to the liquid silicate magma ocean during core formation. It is widely accepted, however, that the Earth's mantle has an ultramafic, pyrolitic composition (McDonough & Sun, 1995) that better represents magma ocean silicate composition during accretion. Furthermore, recent experimental and theoretical work showed that the valence state of iron in the silicate mantle of a terrestrial planet could vary as a function of its oxygen fugacity and magma ocean depth (Armstrong et al., 2019; Deng et al., 2020; Hirschmann, 2022). The potential implications of magma ocean $Fe^{3+}/\sum Fe$ on Fe isotope fractionation during core formation, however, has not yet been investigated. Therefore, understanding Fe isotope fractionation during core formation for terrestrial planets requires two-fold information on (a) the isotopic fractionation factor between pyrolitic melts and metal alloys as a function of pressure and (b) its dependence on the valence state of iron in the melt. In this study, we report new NRIXS experimental data up to 30 GPa on pyrolitic glasses synthesized with varying Fe^{3+} contents. Our data are then combined with previously published high pressure experiments on Fe-rich alloys to assess Fe isotope fractionation during core formation for terrestrial planets from a holistic point of view. For the first time we are able to model iron isotope fractionation during core formation by integrating pressure, temperature, composition, and redox state. With the new model, we show that Fe isotope fractionation between mantle and core varies significantly as a function of the size of a planetary body.

2. Materials and Methods

2.1. Synthesis of ^{57}Fe-Enriched Pyrolitic Glasses

To synthesize the pyrolitic glasses, reagent grade oxides and carbonates were weighed, mixed and grinded in an agate mortar under ethanol three times to achieve a homogeneous mixture. An $^{57}Fe_2O_3$ powder from American Elements was used as the source of Fe for the starting glasses. The mixture was subsequently decarbonated in a box furnace at 1000°C for 24 hr. Approximately 20 mg of the decarbonated powder mixture was pressed into each pellet in preparation for laser levitation. The pyrolitic glasses were fused using the aerodynamic levitation heating furnace at IPGP, Paris, in which a spherical sample was levitated by a gas mixture from a conical nozzle and heated with a 125 W CO_2 laser that has a spot diameter of ~5 mm. All the pelleted samples were first heated at 1900 ± 50°C for 30 s in pure O_2 to achieve complete melting and quenched to glass. The glassed samples were then equilibrated again under different gas mixtures to impose the desired oxygen fugacities to the glasses (Table S1 in Supporting Information S1). The re-equilibrium step was done at 1900 ± 50°C for approximately 60 s, before being quenched at high rates of ~800°C/s to below the glass transition temperature by switching off the power to the laser. The glass products were crushed into pieces for experiments. Fragments of the synthesized glass beads were verified to be crystal-free by X-ray diffraction (Figure S1 in Supporting Information S1). Their chemical compositions were also found to be homogeneous using electron microprobe analysis.

Major element compositions of the synthetic glasses were measured using a JEOL 8530 F electron microprobe at the Earth and Planets Laboratory of the Carnegie Institution for Science and the average compositions are reported in Table S2 in Supporting Information S1. The $Fe^{3+}/\sum Fe$ ratios of the glasses were determined by conventional Mössbauer spectroscopy using a sinusoidal motion Mössbauer spectrometer with a Rh matrix ^{57}Co

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source at the Argonne National Laboratory. Data were collected over 1,024 channels and calibrated using an α-Fe foil. Original spectra and the fitting are plotted in Figure S2 in Supporting Information S1. Detailed fitting parameters are reported in Table S3 in Supporting Information S1.

2.2. Diamond Anvil Cell Preparation and Synchrotron NRIXS Experiments

In situ NRIXS experiments on the ^{57}Fe-enriched pyrolitic glasses at room pressure and up to 30 GPa in diamond anvil cells (DAC) were conducted at sector 3ID-B of the Advanced Photon Source of the Argonne National Laboratory. Ambient pressure experiments were done by taping a 20–30 μm chip of the sample glass on the tip of a capillary tube, which is subsequently fixed on a motorized stage for alignment. For each high-pressure experiment, a sample approximately ∼40 μm in thickness and 40–50 μm in diameter was loaded into a panoramic DAC with flat culets ∼300 μm in diameter. A beryllium gasket with a diameter of 3 mm was first indented to ∼100 μm in thickness. Subsequently, 80% of the indented area was drilled and embedded with a powder mixture of cubic boron nitride and epoxy as the gasket insert. The powder-filled Be gasket was indented again and a chamber with a diameter similar to the sample was drilled in the insert before loading the sample. Two or three ruby spheres were also loaded into the sample chamber as the pressure calibrant. The pressure gradient across the sample was estimated to be within 10%. A schematic diagram of the experiment setup is shown in Figure S3 in Supporting Information S1 for reference. Note that the sample compression was conducted at room temperatures and no heating was involved. Each NRIXS spectra was collected by scanning around the nuclear transition energy of ^{57}Fe at 14.4125 keV with a step size of 0.25 meV and an acquisition time of 1–3 s per energy step. To improve the statistics of the inelastic signals, 4–6 scans and 16–43 scans were collected and combined for the room pressure and high-pressure experiments, respectively. The energy range scanned for the spectra collection was from −110 to +140 meV for room pressure experiments and −100 to +120 meV for high-pressure experiments (Figure S4 and Table S4 in Supporting Information S1). Details about the data reduction are reported in Text S1 in Supporting Information S1.

3. Results

3.1. Force Constants of Iron Bonds in Pyrolitic Glasses

Silicate glasses of bulk silicate Earth (BSE) composition synthesized using a laser levitation furnace were used to simulate the liquid silicate magma ocean during core formation. The relative amounts of Fe_2O_3 and FeO in the glasses were adjusted by controlling the oxygen fugacity of the levitation gas mixture. Mössbauer spectroscopy analysis shows that the three glasses synthesized at oxygen fugacities of 6.7, 3.1, and 1.4 logarithmic units above the iron-wüstite (IW) buffer have $Fe^{3+}/\sum Fe$ ratios of 0.57, 0.21, and 0.087, respectively. The measured $Fe^{3+}/\sum Fe$ ratios are also consistent with a recent calibration between $Fe^{3+}/\sum Fe$ ratio and oxygen fugacity for pyrolitic glasses (Sossi et al., 2020). NRIXS spectra obtained on these glasses loaded in a diamond anvil cell (see Materials and Methods) show that the average force constant of iron bonds in the synthesized pyrolitic glasses depends strongly on the ferric iron content (Figure 1). Note that pressurization of the pyrolitic glasses is performed at room temperatures, therefore the $Fe^{3+}/\sum Fe$ ratio of each glass remains constant because thermally activated charge transfer between Fe^{2+} and Fe^{3+} is unlikely to occur at such low temperatures (Mao et al., 2014). The dependence on ferric iron content is reflected in two ways. Under ambient pressure, the force constant of iron in pyrolitic glasses increases with increasing $Fe^{3+}/\sum Fe$ ratio, indicating that more ferric Fe in the glass leads to stronger iron bonding in the silicate structure. This observation is consistent with previous studies on basaltic, andesitic, dacitic, and rhyolitic glasses, which all show a positive effect of ferric Fe content on iron force constants at room pressure (Dauphas et al., 2014). On the other hand, the pyrolitic glass with higher $Fe^{3+}/\sum Fe$ ratio demonstrates smaller pressure dependence for the Fe force constant compared with those with lower $Fe^{3+}/\sum Fe$ ratios (Figure S5 in Supporting Information S1). More quantitatively, the average force constant of Fe $\langle F \rangle$ in the pyrolitic glass is a linear combination of the Fe^{2+} and Fe^{3+} force constants, which are themselves linear functions of pressure, so that the dependency on $Fe^{3+}/\sum Fe$ ratio and pressure (P) can be expressed as:

$$\langle F \rangle = \frac{Fe^{2+}}{\sum Fe}(a_1 + a_2 P) + \frac{Fe^{3+}}{\sum Fe}(b_1 + b_2 P). \quad (1)$$

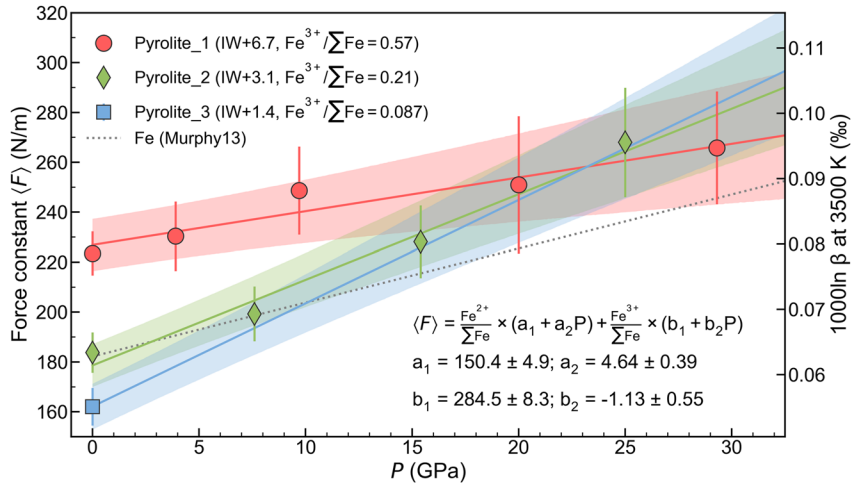

Figure 1. Force constants of Fe bonds in synthesized pyrolitic glasses with various ferric Fe content measured at pressures of up to 30 GPa. Those of hexagonal close-packed iron (hcp Fe) from Murphy et al. (2013) are also plotted in dashed curve for comparison. The corresponding reduced partition function ratios (1000lnβ) at 3500 K for y-axis are calculated using Equation 2. All 10 force constant measurements were simultaneously fit using Equation 1 assuming that the force constant depends linearly on $Fe^{3+}/\sum Fe$ and pressure. The results and 2σ errors of the fit are shown on the right bottom corner of the figure. The solid red, green, and blue curves show the projections of the fit results for Pyrolite_1, Pyrolite_2, and Pyrolite_3, respectively. The colored regions represent 95% confidence interval of the fit.

As shown in Figure 1, a multilinear regression using Equation 1 reproduces all $\langle F \rangle$ data well with $a_1 = 150.5 \pm 4.9$, $a_2 = 4.65 \pm 0.39$, $b_1 = 284.5 \pm 8.3$, and $b_2 = -1.18 \pm 0.55$. The errors represent 95% confidence interval of the fit. Similar results were also obtained if the $\langle F \rangle$ data for each pyrolite glass were fit separately with a linear function (Figure S5 in Supporting Information S1). According to the fitting results, at ambient pressure, a pyrolitic glass with purely ferrous iron would have an $\langle F \rangle$ of 151 N/m for Fe, while that with purely ferric iron would have an $\langle F \rangle$ of 285 N/m. Due to the different pressure dependence, however, the two glasses are expected to reach the same $\langle F \rangle$ of 257 N/m at 23 GPa. Compared to the force constant of pure Fe metal (Murphy et al., 2013), a pyrolitic glass with low $Fe^{3+}/\sum Fe$ ratio has a smaller force constant at ambient pressure, but its force constant becomes larger than Fe metal as the pressure increases. On the other hand, a pyrolitic glass with high $Fe^{3+}/\sum Fe$ ratio has a larger force constant than pure Fe metal at ambient pressure, but the difference diminishes at high pressures (Figure 1). The different pressure dependence of Fe^{2+} and Fe^{3+} force constants might be related to how Fe^{2+}-O and Fe^{3+}-O bonds respond to pressure differently. More specifically, it depends on how the bond distance and coordination number for Fe^{2+}-O and Fe^{3+}-O change as a function of pressure. A quantitative understanding of the observed difference requires dedicated techniques to measure the bond distance and coordination number of Fe-O at different pressures, which is beyond the scope of this study. A recent molecular dynamic simulation work on iron-bearing $MgSiO_3$ melts, however, demonstrated that the Fe^{2+}-O coordination number becomes higher than that of Fe^{3+}-O at ~20 GPa (Ghosh & Karki, 2020), supporting the reverse of force constant for ferrous and ferric Fe observed at 23 GPa in this study.

3.2. Iron Isotope Fractionation Between Pyrolitic Melt and Iron Metal

With the force constant of iron bonds determined for pyrolitic glasses, the reduced partition function ratios (i.e., β-factors) for $^{57}Fe/^{54}Fe$ as a function of temperature (T) can be deduced via the following equation (Dauphas et al., 2012):

$$1000\ln\beta = 1000\left(\frac{1}{M_{54}} - \frac{1}{M_{57}}\right)\frac{\hbar^2}{8k_B^2T^2}\langle F\rangle = 4281\frac{\langle F\rangle}{T^2}, \quad (2)$$

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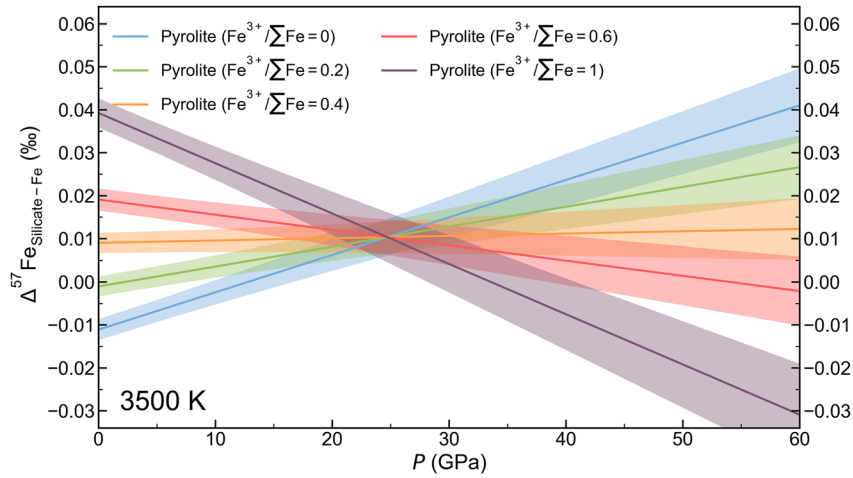

Figure 2. Calculated Fe isotope fractionation factors at 3500 K between pyrolitic melts and pure Fe metal as a function of pressure. Pyrolitic melts with $Fe^{3+}/\sum Fe$ ratios of 0, 0.2, 0.4, 0.6, and 1 are plotted in different colors. β-Factors for pure Fe metal are calculated based on force constant data reported in Murphy et al. (2013). Ferric iron content in the pyrolitic melts controls how the silicate-metal isotopic fractionation changes as a function of pressure.

in which M_{54} and M_{57} are the molar masses of ^{54}Fe and ^{57}Fe, $\hbar$ is the reduced Planck constant, and k_B is the Boltzmann constant. The above reduced partition function ratios can then be combined with those for iron metal alloys to calculate the equilibrium isotope fractionation factor for $^{57}Fe/^{54}Fe$ between silicate and metal:

$$\Delta^{57}Fe_{Sil-Met} = \delta^{57}Fe_{Sil} - \delta^{57}Fe_{Met} = 1000\,(\ln\beta_{Sil} - \ln\beta_{Met})\,. \quad (3)$$

Applying the measured force constants of pyrolitic glasses at room temperature to core formation conditions (e.g., between 40 and 60 GPa and ~3500 K for Earth, Corgne et al., 2009) assumes that these glasses have the same structure as their corresponding liquids at high temperatures. This assumption is supported by in situ structural measurements of amorphous silicates under static and dynamic compressions to the core-mantle boundary pressures, which showed that silicate glasses and melts of mantle compositions share similar structures at high pressures (Morard et al., 2020).

The silicate-metal Fe isotopic fractionation factor calculated at 3500 K using Equations 2 and 3 are plotted versus pressure in Figure 2. The results generally reflect the same effect of $Fe^{3+}/\sum Fe$ ratio on $^{57}Fe/^{54}Fe$ ratio as for the Fe force constant. Pyrolitic melts with low ferric Fe are expected to be isotopically lighter when equilibrated with Fe metal at low pressures, but heavier as the pressure increases. On the other hand, pyrolitic melts with high ferric Fe contents could be up to 0.04‰ heavier in $^{57}Fe/^{54}Fe$ than the equilibrated iron metal at room pressure, but the direction of fractionation inverses at ~30 GPa (Figure 2). A pyrolitic melt with ~40% ferric iron demonstrates minimal pressure dependence for its Fe isotope fractionation with Fe metal, at approximately 0.01‰ from 0 to 60 GPa. From another perspective, the calculated Fe isotope fractionation factors in Figure 2 indicate that ferric iron content in the mantle affects the direction of mantle/core Fe isotope fractionation differently for small planetesimals and Earth-sized terrestrial planets. For a small planetesimal, its mantle is expected to be lighter in $^{57}Fe/^{54}Fe$ than its core if it contains less than 20% ferric iron in the mantle. While for a terrestrial planet of the Earth's size, low ferric iron in the mantle leads to a heavier $^{57}Fe/^{54}Fe$ ratio than the core because of the stronger pressure effect (Figure 2).

4. Discussion

4.1. Modeling Fe Isotope Fractionation During Planetary Core Formation

Equilibrium iron isotope fractionation between silicate and metal during planetary core formation has been shown to be dependent on temperature, pressure, as well as metal and silicate compositions. Starting with a pyrolitic silicate mantle, in Figure 3 we show a way to model Fe isotope fractionation during planetary core formation as a function of pressure, core composition, and ferric iron content of the mantle. Solidus and liquidus

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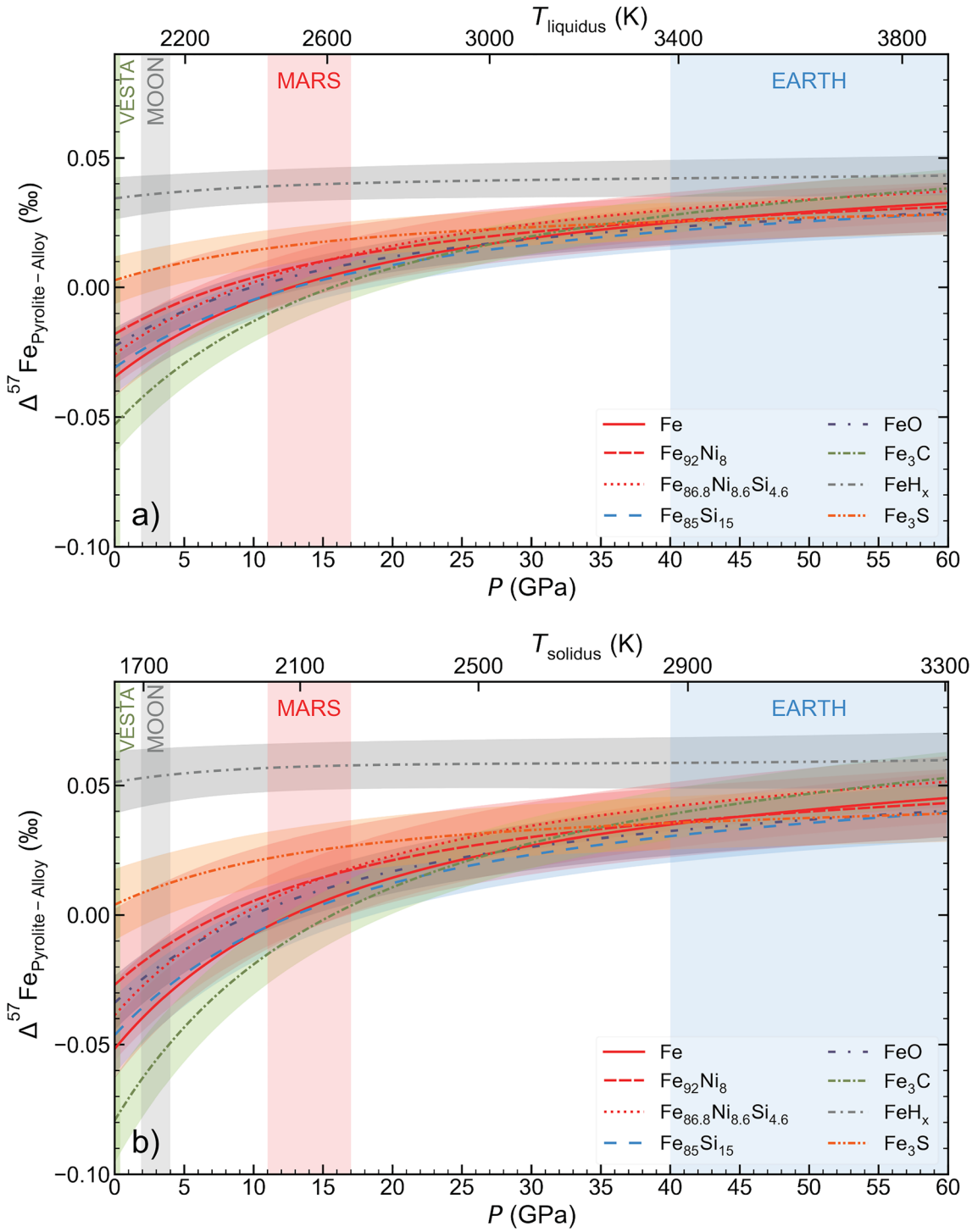

Figure 3. Iron isotope fractionation between mantle and core as a function of planetary core formation pressure and core composition based on Nuclear Resonant Inelastic X-ray Scattering data. (a) Liquidus and (b) solidus of the pyrolitic mantle are used to constrain the temperature based on core formation pressure. The $Fe^{3+}/\sum Fe$ ratio of the silicate mantle is calculated as a function of pressure and temperature using the model of Deng et al. (2020) (Figure S6 in Supporting Information S1).

(Andrault et al., 2012; Fiquet et al., 2010) of the peridotite mantle are used to represent the temperature range for core formation as a function of pressure (Badro et al., 2015; Righter & Chabot, 2011). Force constant data from previous NRIXS studies (Liu et al., 2017; Murphy et al., 2013; Shahar et al., 2016) and this study are used

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to calculate the isotope fractionation factors for Fe in the core and the silicate magma ocean (see Text S2 in Supporting Information S1).

Figure 3 shows the modeled Fe isotope fractionation between mantle and core as a function of planetary core formation pressure, taking into consideration the effects of temperature and ferric Fe content (which both co-evolve with pressure), and core composition. The modeled trend for isotopic fractionation in Figure 3 demonstrates systematic changes as the final pressure of core formation (i.e., planetary size) increases. Taking pure Fe as the composition of the core, for example, the mantle is estimated to be 0.03–0.05‰ lighter in δ^{57}Fe relative to the core when equilibrated at ambient pressure. As pressure increases, the fractionation gradually decreases, because the force constant of the Fe^{2+}-dominated pyrolitic melt has a stronger pressure dependence than that of the pure Fe (Figure 2). At ~15 GPa, the sign of the fractionation inverses and the pyrolitic mantle becomes heavier than the core in δ^{57}Fe as a result of the pressure effect. The pressure effect becomes even stronger at higher pressures despite the increasing temperature and ferric Fe content of the silicate mantle, leading to a silicate mantle 0.03–0.06‰ heavier in δ^{57}Fe than the core (Figure 3).

The effect of core composition on the predicted isotopic fractionation is also demonstrated in Figure 3. Overall, the modeled fractionation trend is relatively similar when the core is an Fe-rich alloy of Fe-Ni, Fe-Si, Fe-Ni-Si, or Fe-O. If the core is alloyed with C, isotopic fractionation during core formation could potentially cause the mantle to be light by as much as 0.05–0.08‰ at <1 GPa. If alloyed with S or H, on the other hand, the mantle is expected to be enriched in the heavy isotopes of Fe during low pressure core formation. This is especially the case with Fe-H alloys, which could potentially lead to a mantle 0.04–0.05‰ heavier than the core regardless the size of the body.

4.2. Implications for Earth, Mars, and Other Planetary Bodies

The modeled trends in Figure 3 clearly demonstrate the change in weights of different factors on Fe isotope fractionation during core formation for planetary bodies of different sizes. It should be noted here that the net isotopic composition of the magma ocean (Figure 3) is calculated using a single-stage core formation model that averages the cumulative differentiation process to a single average pressure and temperature of formation. While physically unrealistic, especially for larger planets, we do not expect significant impact on our results and conclusions, because the curves in Figure 3 are smooth and slowly varying. For a planet the size of Earth, the net Fe isotopic composition of the mantle should be the normalized integral of the curves in Figure 3; but it is clear from the shape of those curves that this should be in essence quite close to the final single-stage value.

For small differentiated planetary bodies such as the extinct asteroid 4 Vesta, with a center pressure of <0.4 GPa (Righter & Drake, 1996) and a core mantle boundary pressure of ~0.15 GPa (Warren, 1985), core formation is expected to occur at relatively low pressures. The case is similar for large asteroids Pallas and Ceres, which are estimated to have pressures of approximately 0.15 and 0.5 GPa at the core-mantle boundary (Warren, 1985), respectively. Depending on the light elements in the core, core formation at low pressures can potentially cause the silicate mantle to be 0.02–0.08‰ lighter than the core in δ^{57}Fe, unless the core is alloyed with dominantly hydrogen or sulfur (Figure 3). This result differs from the previous understanding based on NRIXS data that core formation fractionates Fe isotopes by <0.02‰ for Vesta (Liu et al., 2017). The main reason for the difference is the use of a basaltic glass to represent the silicate mantle in the previous study, which has a higher force constant compared with that of the pyrolitic glass due to the compositional difference (Figure S7 in Supporting Information S1). The case is similar for the Moon, whose core formation pressure can be estimated to be approximately 2–4 GPa, assuming a magma ocean depth of 400–1,000 km (Lin et al., 2020). For a Moon-sized planetary body, the estimated isotopic fractionation decreases slightly compared with the large asteroids due to the combined effects of higher pressure and temperature, with the silicate mantle being 0.01–0.06‰ lighter than the core (Figure 3). Formation of the Moon by an energetic impact might have led to its core formation at super-liquidus temperatures of >2650 K (Steenstra et al., 2020), which could further decrease the isotopic fractionation by 30%–50%. Such an effect might be common for moons but is less important for large asteroids and terrestrial planets.

At the conditions for Martian core formation (14 ± 3 GPa, Righter & Chabot, 2011), Fe isotope fractionation is reduced to be ±0.02‰ between its mantle and core. On one hand, the increasing pressure leads to an inverse of the direction of Fe isotope fractionation between Fe^{2+}-dominated pyrolitic melt and metal. On the other hand, the

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increasing temperature further suppressed the magnitude of isotopic fractionation. At even higher pressures of 40–60 GPa for the terrestrial core formation, the pressure effect continues to increase and cause the mantle to be 0.03–0.04‰ heavier than the core at liquidus temperatures (Figure 3a) and 0.04–0.06 ‰ heavier than the core at solidus temperatures (Figure 3b). The corresponding high temperatures at terrestrial core formation pressures partially suppressed the pressure effect and reduced the effect of core composition (Figure 3). The slight increase in Fe^{3+} concentrations of the silicate magma ocean by disproportionation (Figure S6 in Supporting Information S1) also contributed to reducing the fractionation at high pressures, because of the weaker pressure dependence of force constants for Fe^{3+}-bearing pyrolite melts. Such an effect by disproportionation, however, only plays a small role in the model as the $Fe^{3+}/\sum Fe$ ratio predicted for a magma ocean at 40–60 GPa is only ∼1% based on the model by Deng et al. (2020).

Overall, our model predicts the mantle of Vesta and the Moon to be 0.02–0.08‰ lighter in $\delta^{57}Fe$ than the core, depending on the light elements it is alloyed with. Mars is expected to have minimal isotopic fractionation (within ±0.02‰) during core formation. On the other hand, the mantle of Earth is expected to be 0.03–0.04‰ heavier than the core at liquidus temperatures and 0.04–0.06‰ heavier at solidus temperatures. Since in most cases, the majority of iron of a planetary body is in its core, mass balance calculations suggest that the effect of core formation on Fe isotope fractionation is primarily inherited by the silicate mantle (Elardo & Shahar, 2017; Jordan et al., 2019). The only exception here is the Moon, whose core is only 1.5–2 wt% of its bulk mass (Righter et al., 2017; J. G. Williams et al., 2014). Assuming that the bulk Moon started with a BSE Fe concentration of 6.26 wt% (McDonough & Sun, 1995) and has a core composition of $Fe_{80}Ni_{20}$ (Steenstra et al., 2020), 75%–80% of the Moon's iron would be in its mantle. As a result, the lunar mantle only inherits 20%–25% of the mantle-core Fe isotope fractionation by mass balance, which can be translated to a fractionation of <0.02‰ from the bulk lunar $\delta^{57}Fe$ value.

When applying our modeling results to natural samples, the predicted 0.03–0.06‰ $\delta^{57}Fe$ fractionation for Earth supports the emerging view in literature that the BSE is slightly heavier than chondritic. For example, Sossi, Nebel, and Foden (2016) estimated the $\delta^{57}Fe$ composition of the Earth mantle to be 0.05 ± 0.01‰ based on the selected measurements of pristine lherzolites in literature. Silicate samples of extraterrestrial origin, however, are often partial melting products of the parental mantle, causing a difficulty in directly applying the model results. Martian basalts are chondritic in $\delta^{57}Fe$ on average (e.g., Sossi, Nebel, & Foden, 2016), which match the model prediction of ±0.02‰ fractionation during core formation if they are representative of the martian mantle. Iron isotope measurements of the mare basalts show a clear dichotomy for the low-Ti and high-Ti basalts, which complicate the interpretation of Fe isotope composition for the lunar mantle. Alternative approaches were pursued in literature studies to use either picritic green glass (Elardo & Shahar, 2017) or the Mg-suite (Sossi & Moynier, 2017) as proxies for the lunar mantle, which are near-chondritic or slightly heavier than chondritic (0.07 ± 0.02‰) in $\delta^{57}Fe$. Our prediction of <0.02‰ $\delta^{57}Fe$ change for the lunar mantle favors the slightly super-chondritic value for the bulk silicate Moon, but other effects such as partial melting and the Moon-forming giant impact have to be further evaluated before reaching a definitive conclusion. Mafic rocks from Vesta (eucrites and diogenites) have $\delta^{57}Fe$ compositions averaged chondritic in composition, which cannot be solely explained by core formation because the bulk silicate mantle of Vesta is expected to be 0.02–0.08‰ lighter than chondritic based on our model.

Comparing our modeling results to measurements of natural samples in general, a conundrum emerges because our model predicts that core formation would cause the silicate mantle to be near-chondritic or lighter than chondritic in Fe isotope composition for planetary bodies smaller than Mars in size, while mantle-derived planetary silicates are mostly near-chondritic or heavier than chondritic in $\delta^{57}Fe$. This general observation agrees well with interpretations based on metal-silicate equilibrium experiments (e.g., Elardo et al., 2019; Shahar & Young, 2020). Such a mismatch calls for more measurements of mantle-representative extraterrestrial samples, as well as a better understanding of other planetary processes that might cause Fe isotope fractionation, including partial melting, magma differentiation and evaporation.

4.3. The Effect of FeO Disproportionation in a Deep Magma Ocean

A major improvement of our Fe isotope fractionation model over previous studies comes from accounting for ferrous iron disproportionation for planets with a deep magma ocean. Recent experimental and *ab initio* studies (Armstrong et al., 2019; Deng et al., 2020) demonstrated that the Fe_2O_3 melt component has greater

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compressibility than that of FeO at pressures, leading to the increasing stability of ferric iron in silicate melts at high pressures. As a result, the FeO component of the silicate melts would disproportionate to Fe_2O_3 plus metallic iron in a deep magma ocean. According to our results, Fe_2O_3 component in a pyrolitic melt produced by disproportionation weakens its pressure dependence of the iron force constant, therefore partially compensates the effect of increasing pressure on mantle-core isotope fractionation (Figures 2 and 3). The magnitude of this effect of FeO disproportionation depends on the consequential $Fe^{3+}/\sum Fe$ ratios it produced in the silicate magma ocean, which is still a matter of debate. The model by Deng et al. (2020) adopted in this study predicts an $Fe^{3+}/\sum Fe$ ratio on the low end of ~0.01, which indicates limited effects of disproportionation on Fe isotope fractionation during core formation. Another model by Armstrong et al. (2019), on the other hand, was not directly used in this study because it was primarily developed to reproduce their experimental data to 23 GPa and was not meant to be extrapolated to higher pressures. Doing so would wrongly predict a magma ocean with $Fe^{3+}/\sum Fe = 1$ at pressures above ~40 GPa due to the use of a negative partial molar volume change of the disproportionation reaction, as later being pointed out by Deng et al. (2020) and Hirschmann (2022). In the more recent study by Hirschmann (2022), a new model was calibrated based on existing experiments and first principles studies, which predicts an $Fe^{3+}/\sum Fe$ ratio of 0.034–0.10 in the deep terrestrial magma ocean. To further test the potential effect of Fe disproportionation, we scaled the Armstrong et al. model to a maximum $Fe^{3+}/\sum Fe$ ratio of 0.1 (see Text S2 in Supporting Information S1), and applied it to our Fe isotope fractionation model for core formation (Figure S8 in Supporting Information S1). The results show that with 10% ferric Fe in the terrestrial magma ocean, Fe isotope fractionation during core formation would be suppressed by ~0.01‰ and the silicate mantle would be 0.02–0.05‰ heavier in $\delta^{57}Fe$ than the core. Overall, more experiments are still needed for an improved understanding of the FeO disproportionation reaction in deep magma oceans, but our study provides a model that can actively incorporate the role of disproportionation as our knowledge on the reaction develops.

5. Conclusions

To conclude, our new NRIXS data on pyrolitic glasses provide a better proxy for the silicate mantle to calculate Fe isotope fractionation during planetary core formation. By utilizing an Fe isotope model that integrates the effects of temperature, pressure, Fe^{2+} disproportionation, and core composition, we found that core formation is expected to cause the mantle to be 0.02–0.08‰ lighter in $\delta^{57}Fe$ than the core for Vesta and Moon-sized planetary bodies, depending on the core composition. For larger planetary bodies that are similar to Mars in size, the larger pressure for core formation results in similar $\delta^{57}Fe$ compositions for mantle and core when equilibrated with each other. At even higher pressures that are relevent to terrestrial core formation, the pressure effect leads to an increasingly heavier mantle than core in Fe isotopic composition and predicts a terrestrial mantle $\delta^{57}Fe$ value that is 0.03–0.06‰ heavier than chondritic, consistent with more recent studies that favor a superchondritic Fe isotopic composition for the BSE.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data used in this study have been deposited at https://doi.org/10.5281/zenodo.6285970.

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