



# The earliest Lunar Magma Ocean differentiation recorded in Fe isotopes



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## ABSTRACT

Recent high-precision isotopic measurements show that the isotopic similarity of Earth and Moon is unique among all known planetary bodies in our Solar System. These observations provide fundamental constraints on the origin of Earth–Moon system, likely a catastrophic Giant Impact event. However, in contrast to the isotopic composition of many elements (e.g., O, Mg, Si, K, Ti, Cr, and W), the Fe isotopic compositions of all lunar samples are significantly different from those of the bulk silicate Earth. Such a global Fe isotopic difference between the Moon and Earth provides an important constraint on the lunar formation – such as the amount of Fe evaporation as a result of a Giant Impact origin of the Moon. Here, we show through high-precision Fe isotopic measurements of one of the oldest lunar rocks ( $4.51 \pm 0.10$  Gyr dunite 72415), compared with Fe isotope results of other lunar samples from the Apollo program, and lunar meteorites, that the lunar dunite is enriched in light Fe isotopes, complementing the heavy Fe isotope enrichment in other lunar samples. Thus, the earliest olivine accumulation in the Lunar Magma Ocean may have been enriched in light Fe isotopes. This new observation allows the Fe isotopic composition of the bulk silicate Moon to be identical to that of the bulk silicate Earth, by balancing light Fe in the deep Moon with heavy Fe in the shallow Moon rather than the Moon having a heavier Fe isotope composition than Earth as a result of Giant Impact vaporization.

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## 1. Introduction

Smooth Particle Hydrodynamic (SPH) simulations have been used to support the hypothesis that Earth–Moon system is the product of an ancient catastrophic Giant Impact event. The original simulations suggested that the Moon was made mostly from the impactor material with only minor contributions from Earth (Canup and Asphaug, 2001; Canup, 2008). In contrast, isotopic studies have demonstrated that Earth and Moon are remarkably similar in their isotopic compositions for many elements (e.g., O, Ti, Cr and W isotopic anomalies and Mg and Si stable isotopes) (Armytage et al., 2012; Clayton and Mayeda, 1996; Qin et al., 2010; Touboul et al., 2007; Zhang et al., 2012). This similarity between Earth and Moon is unique in our Solar System when compared to other planetary bodies (such as Mars, Vesta 4 and other asteroids represented by the various classes of meteorites). It provides a fundamental constraint on the theory of the origin of

the Moon; any successful model must properly explain such similarity between Earth and Moon. Thus, a model for Earth–Moon isotopic equilibration subsequent to the Giant Impact was developed (Pahlevan and Stevenson, 2007). In contrast, more recently SPH simulations have been carried out for different scenarios and now appear to show that it is possible to make the Moon primarily out of Earth materials in a Giant Impact scenario if the angular momentum constraint could be lifted (Canup, 2012; Čuk and Stewart, 2012). Here we explore the case of Fe as many previous studies have argued that the Fe isotopic compositions of Earth and Moon are not the same. All published Fe isotope data of lunar materials, show an at least about 50 ppm/a.m.u. (parts per million/atomic mass units) enrichment of heavy Fe isotopes relative to the bulk silicate Earth. This difference is well resolved within the current analytical uncertainties and has been repeatedly reported in samples ranging from mare basalts, highland anorthosites, Mg-suite plutonic rocks, to lunar regolith (Craddock et al., 2010; Liu et al., 2010; Moynier et al., 2006; Poitrasson et al., 2004; Wang et al., 2012a, 2012b; Weyer et al., 2005; Wiesli et al., 2003). It has been debated whether this Fe isotopic difference between Earth and Moon represents a primary signature

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of the Giant Impact due to the evaporative Fe loss (Poitrasson et al., 2004), or of an unidentified mechanism during magma differentiation on the Moon (Craddock et al., 2010; Liu et al., 2010; Weyer et al., 2005).

## 2. Samples and methods

### 2.1. Samples

To better understand the significance of Fe isotopes in the origin of the Moon, we analyzed a variety of lunar materials for Fe isotopes. The lunar dunite 72415 is one of the oldest rocks from the Moon ( $4.51 \pm 0.10$  Gyr with Rb–Sr dating after corrected with the new  $^{87}\text{Rb}$  decay constant of  $1.402 \times 10^{-11} \text{ yr}^{-1}$ , or 4.37–4.52 Gyr with U–Pb dating) (Papanastassiou and Wasserburg, 1975; Premo and Tatsumoto, 1992). It is also one of the most magnesian (Mg#89) rocks from the Moon. It comprises 93% olivine (coarse-grained olivine embedded in fine-grained olivine matrix), 4% plagioclase, and 3% pyroxene (Dymek et al., 1975). It has been debated whether it is a deep-origin cumulate of the primary differentiation of the Moon (Dymek et al., 1975), or a cumulate in a shallow intrusion (Ryder, 1992). This shallow-origin argument rests on two observations: the slightly zoned olivines (Fo<sub>86–89</sub>) and relatively high CaO contents (0.05–0.12%) in 72415, which neither is a reliable indicator of depths, as that there are counter examples in terrestrial mantle xenoliths (see Supplementary Materials). A recent experimental petrology study suggests that dunite 72415 was most likely formed from a partial melting of the hybridization of a rising solid diapir of low-density early cumulates of Lunar Magma Ocean (LMO), KREEP and plagioclase components at the base of the crust (Elardo et al., 2011; Shearer et al., 2014). This dunite belongs to the lunar Mg-suite of plutonic rocks (including dunites, troctolites, norites and gabbronorites), which are likely relicts of the earliest cumulates of LMO differentiation or mostly derived from these cumulates. No Fe isotopic composition of this dunite and other Mg-suite rocks (except of one norite) (Poitrasson et al., 2004) has been previously reported. In addition, nearly all the literature data (but one) (Wang et al., 2012a) are from analysis of Apollo samples. They are collected in a very limited lunar near-side area close to the Procellarum KREEP Terrane, which is actually a compositional anomaly. In contrast, lunar meteorites which are random samplings of both the near-side and far-side of the Moon provide a better estimate of the average lunar composition (Korotev et al., 2003). Hence, here we analyzed Fe isotopic compositions of additional Apollo lunar samples (dunite 72415, troctolite 76535, basalt 15555, ilmenite, olivine, and pyroxene mineral separates from basalts 15555, 12021, and 10062), and lunar meteorites (NWA 479, 6221, 6570, 6950, 7007, 7493, Dhofar 1627, and Shisr 166; one basalt, two gabbrors and five feldspathic breccias).

### 2.2. Sample preparation and chemical purification of iron

Apollo samples, lunar meteorites and terrestrial geostandards were prepared in a clean room. A few milligrams chips of whole-rock samples were directly dissolved in 10 mL MARSXpress high-pressure reaction vessels with a CEM MARS 6 microwave digestion system through a two-step procedure (first step: 0.5 mL HF + 2 mL HNO<sub>3</sub> + 1 mL HCl; second step: 0.5 mL HNO<sub>3</sub> + 1.5 mL HCl + 1 mL H<sub>2</sub>O; Power 400 W; Temperature 230 °C; 15 min ramping + 45 min holding + 30 min cooling). Fully digested samples were dried with heat lamps in ultrapure nitrogen environment and then loaded to 1 mL Bio-Rad AG1-X8 (200–400 mesh) anion-exchange resin chromatography columns in 6 N HCl. Matrix elements were eluted in 6 N HCl and iron were recollected in 0.4 N HCl. This process was repeated again to further purify Fe. The purification

of Fe using anion-exchange chromatography is following an established protocol (Strelow, 1980). Detailed reviews of this technique are previously presented (Craddock and Dauphas, 2011; Dauphas et al., 2009, 2004).

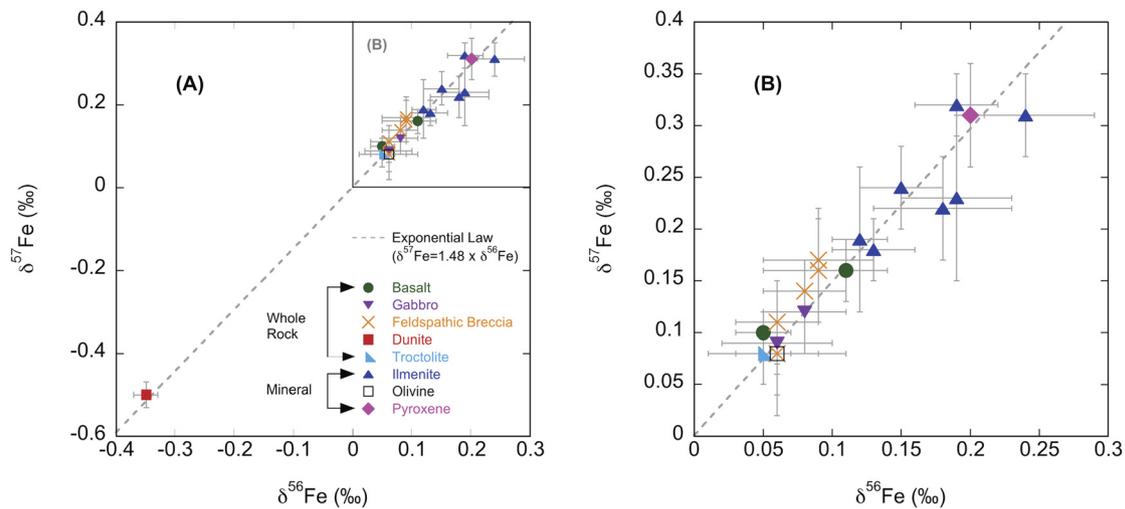
### 2.3. Iron isotopic analyses with MC-ICP-MS

Except for five additional analyses of the dunite 72415, all other samples were analyzed for Fe isotopic ratios with the Neptune Plus MC-ICP-MS in the Department of Earth and Planetary Sciences at Washington University in St. Louis, using the same procedures previously described (Wang et al., 2012a, 2012b). The Neptune Plus MC-ICP-MS was used in medium resolution mode to resolve the different peaks of Fe and argide species. Samples were introduced into the plasma ion source with a 100  $\mu\text{L}/\text{min}$  PFA MicroFlow nebulizer and a SSI (Stable Sample Introduction) cyclonic/scott dual quartz spray chamber. All measurements with the Neptune Plus were conducted in the medium ( $M/\Delta M \sim 8500$ ) resolution on the peak shoulder in order to resolve isobaric interference of  $^{40}\text{Ar}^{14}\text{N}$  (on  $^{54}\text{Fe}$ ),  $^{40}\text{Ar}^{16}\text{O}$  (on  $^{56}\text{Fe}$ ), and  $^{40}\text{Ar}^{16}\text{O}^1\text{H}$  (on  $^{57}\text{Fe}$ ). The interference of  $^{54}\text{Cr}$  on  $^{54}\text{Fe}$  is corrected by measuring  $^{53}\text{Cr}$  intensities. The correction is up to 0.01‰ for one Cr-rich dunite sample and negligible for other samples. These results are calculated with sample-standard bracketing and expressed as conventional delta notations, that  $\delta^x\text{Fe} = [(^x\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^x\text{Fe}/^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$ , where  $x = 56$  or  $57$ . Uncertainties are reported as 2SE (standard errors) of repeated measurements. All the data from the Neptune Plus are plotted in a  $\delta^{56}\text{Fe}$ – $\delta^{57}\text{Fe}$  space (see Fig. 1) and all the samples fall on a mass-dependent fractionation line, expressed as the exponential law.

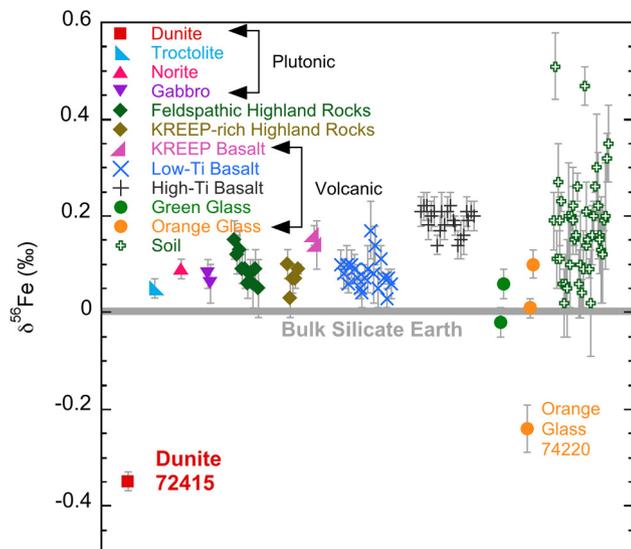
The dunite 72415 first measured with the Neptune Plus shows a surprising value compared to all the lunar samples previously reported. To confirm the validity of this negative value, we dissolved four more chips of this dunite sample (dunite #2 to dunite #5; mass varies from 0.6 to 6.2 mg). The five additional measurements were conducted with a GV Instruments IsoProbe P MC-ICP-MS at the Cosmochemistry Laboratory in the Department of Earth and Planetary Sciences at Harvard University. The IsoProbe utilizes a hexapole collision cell to remove argide-based interferences. Samples were introduced into the plasma source using an APEX-IR spray chamber and ACM desolvator system and a 100  $\mu\text{L}/\text{min}$  PFA MicroFlow nebulizer. By introducing 1.5 mL/min Ar and 1.5 mL/min H<sub>2</sub> collision gases into the hexapole collision cell, the interferences of  $^{40}\text{Ar}^{14}\text{N}$  (on  $^{54}\text{Fe}$ ) and  $^{40}\text{Ar}^{16}\text{O}$  (on  $^{56}\text{Fe}$ ) were removed, and the interference of  $^{40}\text{Ar}^{16}\text{O}^1\text{H}$  (on  $^{57}\text{Fe}$ ) was reduced, however, not entirely removed. Blank solutions were measured immediately before each sample/standard, and blank subtractions were applied to remove such residual signals of  $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ . Even though with such remedy, the data quality for  $^{57}\text{Fe}/^{54}\text{Fe}$  is not as good as those from the Neptune Plus. All IsoProbe P measurements were done on the peak centers of  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$ . The interference of  $^{54}\text{Cr}$  on  $^{54}\text{Fe}$  is corrected by measuring the  $^{53}\text{Cr}$  intensity. The correction is up to 0.01‰ of  $\delta^{56}\text{Fe}$  for Cr-rich dunites, which is within the error bar. The final results were calculated with sample-standard bracketing and expressed as delta notations. The standards BHVO-1 and San Carlos olivine were also analyzed with the IsoProbe P in the same sessions with dunite samples to monitor the quality of measurements. The  $\delta^{56}\text{Fe}$  data are similar to those measured with the Neptune Plus.

## 3. Result

The results of our measurements are given in Tables 1 and 2. The  $\delta^{56}\text{Fe}$  values ( $[(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{standard}} - 1] \times 1000$ ) for the standards BHVO-1 and San Carlos olivine show excellent agreement for both instruments. The San Carlos



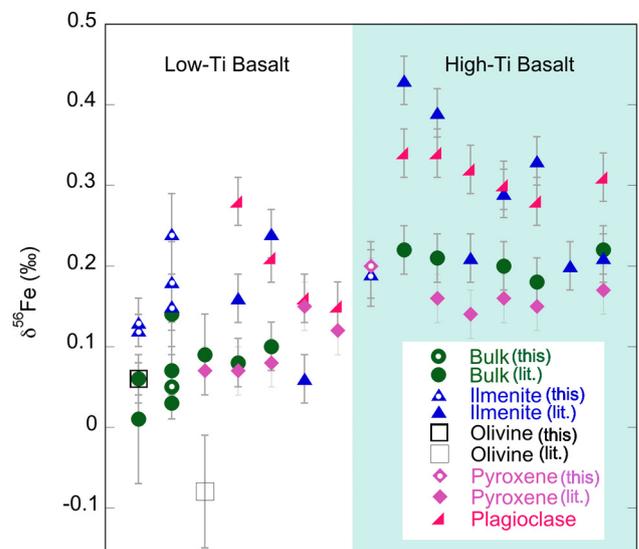
**Fig. 1.** Iron isotope compositions of Apollo lunar whole rock samples and mineral separates, and lunar meteorite whole rock samples measured in this study. The data are given as  $\delta^{56}\text{Fe}_{\text{IRMM-014}}$  and  $\delta^{57}\text{Fe}_{\text{IRMM-014}}$  values relative to the IRMM-014 standard. The dashed line is the exponential law fractionation curve ( $\delta^{57}\text{Fe} = 1.48 \times \delta^{56}\text{Fe}$ ). All the data are consistent with this fractionation curve. The upper right corner of panel A is expanded in panel B.



**Fig. 2.** All published iron isotope compositions ( $\delta^{56}\text{Fe}$ ) of whole-rock lunar samples from this study and literature (Craddock et al., 2010; Liu et al., 2010; Moynier et al., 2006; Poitrasson et al., 2004; Weyer et al., 2005; Wiesli et al., 2003).

olivine data agree well with literature values:  $0.02 \pm 0.03\text{‰}$  (Weyer et al., 2005);  $0.01 \pm 0.03\text{‰}$  (Sossi et al., 2015);  $0.03 \pm 0.04\text{‰}$  (Sio et al., 2013). The BHVO-1 measurements also agree well with reported values:  $0.11 \pm 0.01\text{‰}$  (Craddock and Dauphas, 2011). The data are plotted in Fig. 2 together with other existing Fe isotope data on lunar rocks. Fig. 3 shows  $\delta^{56}\text{Fe}$  values of mineral separates from lunar basalts from this study and the literature. The highest  $\delta^{56}\text{Fe}$  value ( $+0.24\text{‰}$ ) was found in a high-purity ilmenite separate of 1555 and the lowest value in the lunar dunite ( $-0.43\text{‰}$ ; the average of five measurements of individual olivine grains is  $-0.35 \pm 0.02\text{‰}$ ). Data of lunar meteorites are similar to those from Apollo samples which both continue to display  $\sim +0.1\text{‰}$  higher than the bulk silicate Earth value (Craddock et al., 2013) and confirm previous studies.

However, the most surprising result from this study is that the dunite 72415 shows a significant light Fe isotope enrichment ( $-0.35 \pm 0.02\text{‰}$ ). Such negative  $\delta^{56}\text{Fe}$  values have not been observed in any other lunar samples except for one measurement of an orange pyroclastic glass (Moynier et al., 2006) ( $-0.24 \pm 0.05\text{‰}$ ; Fig. 2). This value of the orange glass was explained as due to



**Fig. 3.** Comparison of our  $\delta^{56}\text{Fe}$  values of mineral separates from lunar basalts with literature data (Craddock et al., 2010; Liu et al., 2010; Poitrasson et al., 2004). Only the olivine separated from basalt 12045 shows enrichment in light Fe isotopes. With a few exceptions, ilmenites have heavier Fe isotope compositions than other minerals.

the light-isotope enriched vapor condensed on the surface of these glass beads based on its coupled light Fe, Cu and Zn isotope compositions (Moynier et al., 2006). Also note that two measurements of the same orange glass from two other studies (Poitrasson et al., 2004; Weyer et al., 2005) show a normal lunar  $\delta^{56}\text{Fe}$  value (Fig. 2).

In order to confirm this surprising result of the lunar dunite 72415 first measured with a Neptune Plus, we have analyzed this and four additional grains separated from this dunite 72415 with a different MC-ICP-MS (IsoProbe). The IsoProbe method is very different from the Neptune Plus method. With the IsoProbe, we remove the Ar-based polyatomic interference on Fe isotopes with a hexapole collision gas cell, while the Neptune Plus relies on pseudo-high-resolution to resolve the Ar-based polyatomic peaks from the Fe peaks. The average of the five new samples of dunite 72415 measured with the IsoProbe gives an exact average value ( $-0.35\text{‰}$ ) with the one measured by Neptune Plus. However, the five new data from the IsoProbe do show variability between the five grains separated from the dunite 72415. The variability is

**Table 1**  
Iron isotope compositions of Apollo Lunar rocks and minerals in this study.

Sample	Description	Mass (mg)	$\delta^{56}\text{Fe} \pm 2\text{SE}^{\text{a}}$ (‰)	$\delta^{57}\text{Fe} \pm 2\text{SE}^{\text{a}}$ (‰)	$n^{\text{b}}$	Instrument
<i>APOLLO SAMPLES</i>						
72415	Dunite #1 (Neptune Plus)	1.1	$-0.35 \pm 0.02$	$-0.50 \pm 0.03$	11	Neptune Plus
	Dunite #1–5 Average (Isoprobe P)		$-0.35 \pm 0.20$	$-0.58 \pm 0.45$	55	Isoprobe P
	Dunite #1	1.1	$-0.41 \pm 0.04$	$-0.64 \pm 0.12$	11	Isoprobe P
	Dunite #2	6.2	$-0.23 \pm 0.04$	$-0.29 \pm 0.13$	11	Isoprobe P
	Dunite #3	1.4	$-0.25 \pm 0.05$	$-0.43 \pm 0.17$	11	Isoprobe P
	Dunite #4	1.2	$-0.43 \pm 0.03$	$-0.80 \pm 0.07$	11	Isoprobe P
	Dunite #5	0.6	$-0.43 \pm 0.05$	$-0.78 \pm 0.12$	11	Isoprobe P
76535	Troctolite	4.2	$0.05 \pm 0.02$	$0.08 \pm 0.03$	9	Neptune Plus
12021-17	Ilmenite #1 (high purity)	3.3	$0.13 \pm 0.03$	$0.18 \pm 0.03$	8	Neptune Plus
12021-17	Ilmenite #2	8.8	$0.12 \pm 0.02$	$0.19 \pm 0.07$	7	Neptune Plus
12021-17	Olivine	6.0	$0.06 \pm 0.03$	$0.08 \pm 0.06$	9	Neptune Plus
10062-33	Ilmenite #1 (high purity)	1.2	$0.19 \pm 0.03$	$0.32 \pm 0.03$	9	Neptune Plus
10062-33	Ilmenite #2	8.6	$0.19 \pm 0.04$	$0.23 \pm 0.08$	7	Neptune Plus
10062-33	Pyroxene	7.6	$0.20 \pm 0.01$	$0.31 \pm 0.05$	8	Neptune Plus
15555-139	Ilmenite #1 (high purity)	3.2	$0.24 \pm 0.05$	$0.31 \pm 0.04$	9	Neptune Plus
15555-139	Ilmenite #2	4.0	$0.18 \pm 0.05$	$0.22 \pm 0.05$	7	Neptune Plus
15555-139	Ilmenite #3	9.3	$0.15 \pm 0.03$	$0.24 \pm 0.04$	7	Neptune Plus
15555-139	Olivine-normative basalt	5.3	$0.05 \pm 0.04$	$0.10 \pm 0.02$	7	Neptune Plus

<sup>a</sup> Standard errors (SE = standard deviation divided by the square root of the total number of measurements).

<sup>b</sup> Number of measurements.

**Table 2**  
Iron isotope compositions of Lunar meteorites and terrestrial standards in this study.

Sample	Description	Mass (mg)	$\delta^{56}\text{Fe} \pm 2\text{SE}^{\text{a}}$ (‰)	$\delta^{57}\text{Fe} \pm 2\text{SE}^{\text{a}}$ (‰)	$n^{\text{b}}$	Instrument
<i>LUNAR METEORITES</i>						
NWA 479	Basalt	3.8	$0.11 \pm 0.03$	$0.16 \pm 0.03$	8	Neptune Plus
NWA 6950	Gabbro	6.2	$0.08 \pm 0.03$	$0.12 \pm 0.04$	9	Neptune Plus
NWA 7007	Gabbro	4.3	$0.06 \pm 0.04$	$0.09 \pm 0.03$	8	Neptune Plus
Dhofar 1627	Feldspathic breccia	4.3	$0.09 \pm 0.04$	$0.17 \pm 0.05$	6	Neptune Plus
NWA 6221	Feldspathic breccia	2.3	$0.06 \pm 0.03$	$0.11 \pm 0.04$	9	Neptune Plus
NWA 6570	Feldspathic breccia	7.9	$0.08 \pm 0.03$	$0.14 \pm 0.03$	9	Neptune Plus
NWA 7493	Feldspathic breccia	8.3	$0.06 \pm 0.05$	$0.08 \pm 0.04$	6	Neptune Plus
Shisr 166	Feldspathic melt breccia	3.6	$0.09 \pm 0.04$	$0.16 \pm 0.05$	8	Neptune Plus
<i>TERRESTRIAL</i>						
San Carlos Ol.	Mantle lherzolite	3.3	$0.01 \pm 0.04$	$0.02 \pm 0.05$	9	Neptune Plus
		3.3	$-0.03 \pm 0.03$	$0.17 \pm 0.02$	11	Isoprobe P
BHVO-1 <sup>c</sup>	Basalt	9.6	$0.09 \pm 0.01$	$0.17 \pm 0.02$	42	Neptune Plus
		9.6	$0.09 \pm 0.03$	$0.14 \pm 0.05$	49	Isoprobe P

<sup>a</sup> Standard errors (SE = standard deviation divided by the square root of the total number of measurements).

<sup>b</sup> Number of measurements.

<sup>c</sup> Geostandard BHVO-1 was repeatedly measured with each sample session to monitor the data quality.

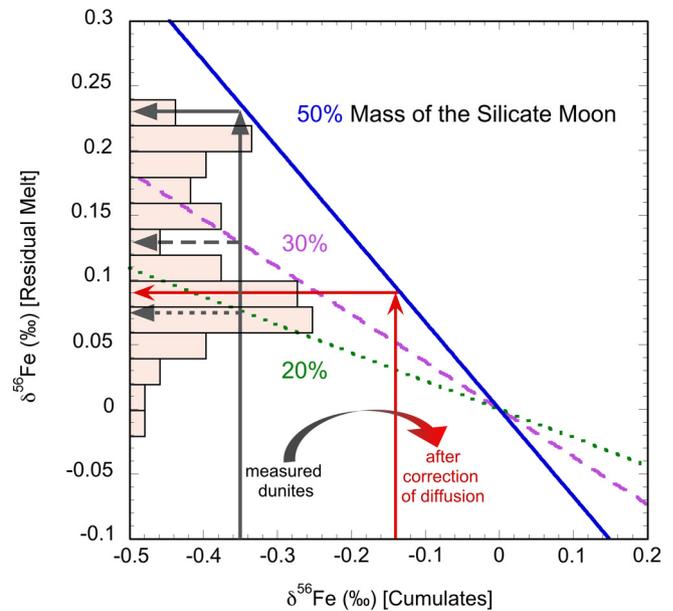
likely due to minor amounts of other mineral grains (clinopyroxene and spinel) sticking to the surfaces of these olivine grains. These grains were handpicked under a microscope as individual olivine grains from the dunite, but minor amounts of other minerals were visible and could not be cleaned off from their surfaces. Also their chemical compositions (see Supplementary Materials) show that they are not 100% pure olivines. However, all these five dunite olivine grains consistently show a significantly lighter Fe isotope composition than any other lunar samples, and this has never been observed before.

#### 4. Discussion and conclusion

The fact that the lowest  $\delta^{56}\text{Fe}$  value ( $-0.35\text{‰}$ ) among all lunar rocks is observed in the old lunar dunite is very important. Terrestrial peridotites averaging in  $\delta^{56}\text{Fe} \sim 0\text{‰}$ , have been argued to define the bulk silicate Earth value (Craddock et al., 2013) and thus the bulk Moon is expected to have this value as shown in many isotopic systems. Light Fe isotope compositions in some terrestrial dunitites have also been reported (down to  $-0.38\text{‰}$ ) (Williams et al., 2005). These low values have been argued to be the result of the kinetic isotopic fractionation due to high-degree mantle metasomatic activities (exchanging Fe with  $\text{H}_2\text{O}$  or  $\text{CO}_2$  rich-fluids or silicate melts) (Poitrasson et al., 2013; Zhao et al., 2010). The light  $\delta^{56}\text{Fe}$  value of lunar dunite 72415 is unlikely caused by the metasomatism on the Moon. First, there is no petrological and mineralogical evidences for any  $\text{H}_2\text{O}$  or  $\text{CO}_2$  rich-fluids metasomatism have been reported on the Moon. Secondly, even though there are some arguments of silicate melts-based metasomatism (Elardo et al., 2012; Lindstrom et al., 1985, 1984; McCallum, 1983; Neal and Taylor, 1991, 1989; Snyder et al., 1994; Treiman et al., 2014), none of these has been reported for the dunite 72415. In contrast, all other lunar samples (with or without silicates melt metasomatism) show similar heavier Fe isotopic compositions relative to that of the dunite 72415.

Alternatively, the light Fe isotope enrichment in dunite 72415 could be explained by chemical diffusion-driven kinetic disequilibrium fractionation between olivine and melt (Dauphas et al., 2010). Such effect has been previously proposed for the light Fe isotope enrichment displayed in strongly zoned ( $\text{Fo}_{70-89}$ ) olivine grains separated from the basalts in the Kilauea Iki lava lake, Kilauea volcano, Hawaii (Sio et al., 2013; Teng et al., 2011) and from Germany and Canary Islands (Weyer and Seitz, 2012). However, this mechanism cannot single-handedly create the observed fractionation in dunite 72415 according to the quantitative modeling of the Fe isotopic fractionation during the Fe–Mg inter-diffusion in olivine (contributing up to  $\sim 0.21\text{‰}$ ; see Supplementary Materials) due to 72415 olivine's larger grain size, weaker zoning and lower oxygen fugacity in the Moon relative to Earth. Also while it is easy to understand how such an effect may apply to olivines embedded in basalts from lava lakes; it is not clear that this mechanism would be important in dunite formation in the lunar magma ocean.

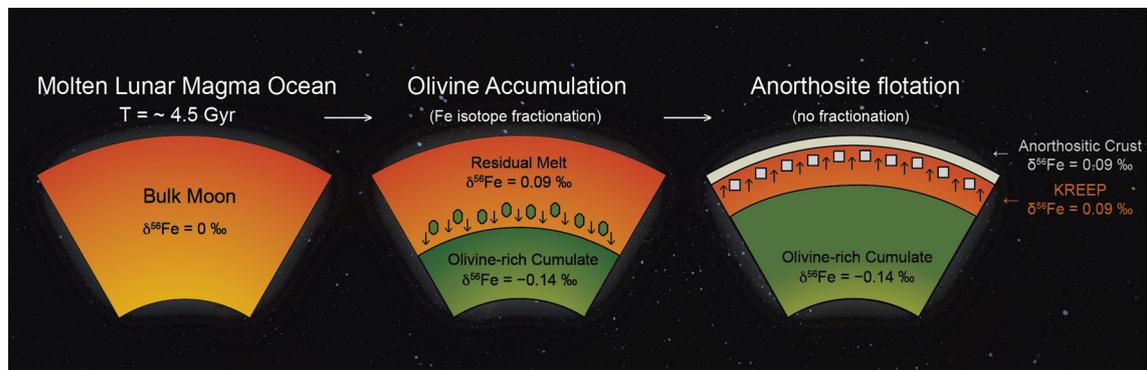
After removing the maximum possible imprint by this effect, dunite 72415 is still significantly different from all other lunar samples and is at least  $\sim 0.14\text{‰}$  lower than the bulk silicate Earth in term of  $\delta^{56}\text{Fe}$ . Therefore, this light Fe isotope enrichment of dunite 72415, likely represents a primary signature of the earliest differentiation event in the LMO. Mg-rich olivines were the first minerals to crystallize and cumulate from the LMO. After 50% crystallization of the LMO, the cumulates are composed primarily of a dunitic composition with  $\sim 90\%$  olivine with smaller amounts of orthopyroxene, and/or garnet and spinel (Elardo et al., 2011). If these dunitic cumulates were enriched in light Fe isotopes as recorded in dunite 72415, the residual melt after this first accumulation, which later formed the anorthosite flotation crust and a



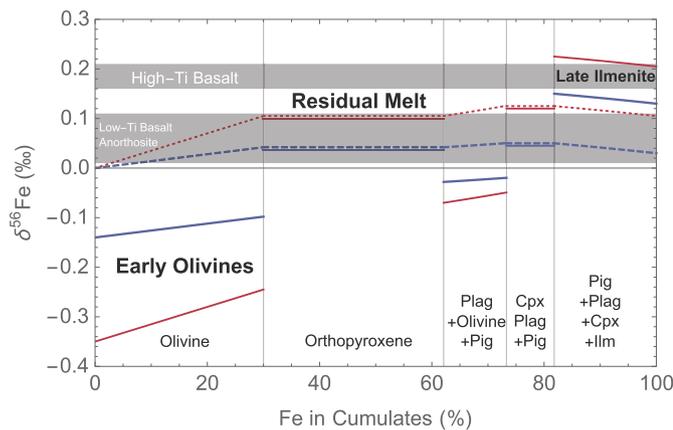
**Fig. 4.** Modeled  $\delta^{56}\text{Fe}$  values of the cumulates and residual melt after 50% lunar magma ocean crystallization. The vertical black arrow shows the average measured dunite  $\delta^{56}\text{Fe}$  value while the vertical red arrow is the value after correction for the maximum possible diffusion effect. The histogram ( $N = 66$ ) on the y axis shows all measured lunar samples except for the lunar dunite 72415, orange glass 74220 and all soils. The blue line show Fe mass-balance between the cumulates and residual melt at 50% crystallization of the Moon (model is from Elardo et al., 2011). Two additional models (20% and 30% crystallization) are shown by dotted and dashed lines. Note that the balance between the light olivine-rich cumulates and heavy residual melts would make the Moon identical to the Earth in terms of the Fe isotope composition. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

leftover KREEP-rich intermediate layer, would have been enriched in heavy Fe isotopes. This model is demonstrated with a simple mass-balance calculation in Fig. 4 that shows the modeled iron isotope compositions of the cumulates and residual melt after 50%, 30% or 20% LMO crystallization. The dark grey line on the x axis is the measured dunite range and the red line is the range after correction of the maximum diffusion effect. The histogram on the y axis represents all measured lunar samples except for the lunar dunite 72415, one orange glass 74220 and all soils. Fig. 5 illustrates the model of the Fe isotopic fractionation during dunitic accumulation shortly after the formation of the Moon.

The simple mass-balance calculation above shows that the early dunitic cumulates could have caused enough Fe isotopic fractionation to explain the higher Fe isotopic compositions of lunar samples compared to Earth. We further modeled the Fe isotope evolution during the entire Lunar Magma Ocean fractionation (Fig. 6). It agrees well with the result from the simple mass-balance consideration that the early olivine accumulation is the single most important factor to enrich the heavy Fe isotopes in the residual melt. Further details are also revealed with this evolution curve. In addition to olivine accumulations, it also shows that the late-stage ilmenite mineral crystallization would provide a heavy Fe isotope source for high-Ti basalts. The importance of ilmenite mineral fractionation to the higher Fe isotope composition in lunar high-Ti basalts has been previously suggested (Craddock et al., 2010; Liu et al., 2010). It has been empirically shown that ilmenites are enriched in heavy Fe isotopes compared to other minerals (see Fig. 3), even though high quality Fe isotopic fractionation factors for ilmenites are still needed (Krawczynski et al., 2013). This lunar Fe isotope evolution curve could effectively explain 1) the general trend of the higher Fe isotope composition of lunar samples (except of dunitites) compared to the Earth; and 2) the fractionation



**Fig. 5.** Cartoon illustrating how accumulation of light olivine shortly after the formation of the Moon may result in the observed Fe isotopic fractionation among lunar samples, with the other lunar rocks being heavy. The modeled values are from the mass balance calculations in Fig. 4 (red line). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)



**Fig. 6.** Equilibrium fractionation model of the evolution of  $\delta^{56}\text{Fe}$ -values during the lunar magma ocean differentiation. Abbreviations: Plag – plagioclase, Pig – pigeonite, Cpx – clinopyroxene, Ilm – ilmenite. The blue and red lines represent calculations based on two different olivine-melt fractionation factors (0.14 and 0.35‰, respectively). The ilmenite fractionation factor of 0.2‰ is estimated based on (Craddock et al., 2010) and this study. Fractionation of Fe isotopes among other minerals was neglected. The solid and dashed lines show evolution of Fe isotope compositions of cumulates and residual melts, respectively. When olivine and/or ilmenite are missing from crystallization sequence (30–62.1% and 73.3–81.8% cumulates) there is no isotopic difference between the cumulate and residual melt; here, for the sake of presentation, the solid and dashed lines are shown with a small displacement relative to each other. This model calculation is based on the Fe partitioning during magma ocean crystallization modeled by Snyder et al. (1992). A similar figure showing results of Rayleigh fractionation is given in the Supplementary Materials. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

between different lunar samples (e.g., anorthositic rocks, and low-Ti, and high Ti basalts).

Our study does not only provide the first evidence for the hypothesis that the heavy Fe isotopic compositions of various lunar samples (e.g., mare basalts and highland rocks) reflect the removal of the isotopically light olivine through accumulation, the earliest differentiation event of LMO; it would also indicate that Fe equilibrium isotope fractionation between olivine and melts widely exist at magmatic temperatures, in addition to the possible diffusion-driven kinetic fractionation effect. Experimental and theoretical evidence of such fractionation is still lacking. One promising recent attempt shows that the equilibrium isotope fractionation factor between olivine and melts is highly variable depending on the compositions and redox states of the melts (Dauphas et al., 2014). For example, such fractionation is negligible between olivine and basaltic/andesitic melts at oxygen fugacity of IW (Iron-wüstite buffer; similar to the oxidation state of the Moon) in magmatic temperatures; however, the fractionation is relatively large

( $\sim 0.1\text{‰}$ ) between olivine and rhyolitic melts even when there is no  $\text{Fe}^{3+}$  involved (Dauphas et al., 2014). Previously, only redox-controlled fractionation was expected, which caused problems in explaining the observed Fe isotopic fractionation in those environments more reduced (no or low in  $\text{Fe}^{3+}$ ) than Earth, such as the Moon and Angrite Parent Body (Wang et al., 2012a).

Our new results show that the iron isotopic composition of the bulk silicate Moon, after correcting the effect of the light Fe isotopes enrichment in mantle cumulates, can be identical to that of the bulk silicate Earth ( $\sim 0\text{‰}$ ). This supports the magma ocean model for the Moon and is also consistent with isotope compositions of many other elements (e.g., O, Mg, Si, Ti, Cr, and W) that are identical for Earth and Moon. The main exception now is Zn, which is likely fractionated during Giant Impact (Paniello et al., 2012). This isotopic similarity of Earth and Moon is a first order constraint on the origin of Earth and Moon, reflecting either that the impactor forming the Moon had the same isotopic composition with the proto-Earth, or the majority of the mass of the Moon is from the proto-Earth rather than from the impactor, or that the compositions of the proto-Earth and the impactor efficiently re-equilibrated after the Giant Impact.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2015.08.019>.

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