



Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms

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Abstract

The iron isotope compositions of Shergotty–Nakhla–Chassigny (SNC) meteorites thought to come from Mars, eucrites and diogenites assumed to sample asteroid 4 Vesta, and rocks from the Moon and Earth have been measured using high precision plasma source mass spectrometry. The means of eight samples from Mars and nine samples from Vesta are within error identical despite a range of rock types. They are lighter by $\sim 0.1\text{‰}$ in $\delta^{57}\text{Fe}/^{54}\text{Fe}$ compared to the average of 13 terrestrial mantle-derived rocks. The latter value is identical within uncertainty with a previously published mean of 46 igneous rocks from the Earth. The average for 14 lunar basalts and highland plutonic rocks covering a broad spectrum of major element composition is heavier by $\sim 0.1\text{‰}$ in $\delta^{57}\text{Fe}/^{54}\text{Fe}$ relative to our estimate for the Earth's mantle, and therefore $\sim 0.2\text{‰}$ heavier than the eucrites, diogenites and SNC meteorites. However, the data scatter somewhat and the Apollo 15 green glass and Apollo 17 orange glass are identical to samples from Mars and Vesta. There is no clear relationship between petrological characteristics and Fe isotope composition despite a wide spectrum of samples. Instead, contrasted planetary isotopic signatures are clearly resolved statistically. After evaluating alternative scenario, it appears that the most plausible explanation for the heavier Fe in the Earth and Moon is that both objects grew via processes that involved partial vaporisation leading to kinetic iron isotope fractionation followed by minor loss. This is consistent with the theory in which the Moon is thought to have originated from a giant impact between the proto-Earth and another planet. Combined with numerical simulations, Fe isotope data can offer the potential to provide constraints on the processes that occurred in planetary accretion.

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1. Introduction

The study of planet formation is difficult because most potential tracers of such early processes have been eradicated by subsequent geological processing.

One therefore has to rely on deductions from estimates of bulk composition inferred from geophysical measurements and experimental petrology, indirect petrological and geochemical evidence provided by primitive meteorites, and theoretical modelling [1]. The best-known planet, the Earth, is also the body that underwent the most active geological history, and therefore its earliest stages are particularly elusive.

An ideal tracer of planetary accretion processes should be sensitive to the mechanisms involved in planet formation, but be little affected by subsequent processing. It has long been known that transition metals do not show large stable isotope fractionations as a result of geological processing [2,3], yet ongoing analytical developments have been making their subtle isotopic variations amenable to study. Iron, in particular, is of great interest, given that it has more than one oxidation state and is the most abundant element in the terrestrial planets after oxygen [4–7].

Thermal ionization mass spectrometry (TIMS) has been used to show that there are exotic mass independent iron isotopic variations found in some refractory inclusions [8]. However, even refined TIMS approaches using the double spike technique have been unable to resolve any planetary differences such as between the Earth and the Moon, for example [9]. The development of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) has improved the analytical precision of Fe isotope ratio measurements by an order of magnitude [10], and this makes it worthwhile to re-examine the issue of whether there are Fe isotopic differences between planetary objects.

Here we report the first detailed MC-ICPMS study of Fe isotope compositions of the main planetary bodies from the solar system for which samples are available for laboratory investigation [11,12]. As expected, the degree of isotopic variation is found to be small. However, there appear to be systematic and resolvable differences in samples from the Moon and to a lesser extent the Earth, relative to Mars and Vesta. These may relate to the mechanisms of planetary accretion.

2. Analytical procedures

Most meteorite and lunar samples analysed in this study come from over 1 g of bulk-rock powders

previously used for Hf-W investigations [13,14], whereas terrestrial samples are either homogeneous international rock standards, or gabbro powders made of several hundred grams of rock (samples PE9101 and OT9102s [15,16]). It is therefore considered that all powders analysed were representative of whole-rocks. The meteorites selected were essentially falls or Antarctica finds, to minimize the potential effect of weathering. Meteorite fusion crusts were also discarded since they display Fe isotope fractionation, as illustrated below. Lunar samples too much affected by meteoritic bombardment, such as soils, were avoided since it is well established they display large stable isotope fractionations [17–19]. Apollo 15 and 17 glass beads were handpicked under a binocular microscope.

Typically 1 to 23 mg of powder (Table 1) was decomposed with concentrated HF–HNO₃–HCl in closed Teflon beakers. Ultramafic rocks containing chromite were dissolved in high-pressure vessels at 135 °C for 3 days. After evaporation, the samples were further dissolved in 6 M HCl and evaporated again. Iron was quantitatively purified with anion exchange resin (Bio-Rad AG1 X4, 200–400 mesh) in an HCl medium [20]. Total procedural blanks were at or below the nanogram level. This is 10⁵ times smaller than the typical sample sizes, which were in excess of 100 µg of Fe.

Iron isotope analyses were performed using a multiple collector inductively coupled plasma mass spectrometer (Nu Instruments, Wrexham, UK), in conjunction with a modified MCN 6000 microconcentric desolvating nebuliser (Cetac, Omaha, USA) to minimise interferences on the iron masses due to argon oxides and hydroxides. No nitrogen flux was used in order to avoid argon nitrides. The four isotopes 54, 56, 57 and 58 of iron were measured and the contributions of Cr and Ni were monitored using masses 53 and 60, respectively. These appeared to be below detection level for all samples following separation of the iron. Each analysis consisted of 20 measurements of two 5 s cycles, totaling approximately 10 min including the background measurement time, wash-up and sample transfer time. These two cycles were required in order to use an external Faraday cup (L5) fitted with a 10¹⁰ Ω resistor, thus permitting the measurement of ⁵⁶Fe with a signal of up to 10^{–9} A for improved signal/background ratio without sacrificing other instrument applications. The sample-standard bracketing ap-

Table 1
Iron isotope results from planetary samples of the inner solar system

Sample	Petrology (location)	[Fe] (wt.%)	Sample mass ^a (mg)	$\delta^{57}\text{Fe}/^{54}\text{Fe}$ (‰)	Uncertainty ^b (2S.E.)	$\delta^{57}\text{Fe}/^{56}\text{Fe}$ (‰)	Uncertainty ^b (2S.E.)	Number of analyses ^c
<i>Vesta</i>								
Bouvante	Polymict noncumulate eucrite	15.3	752.5	0.050	0.077	−0.020	0.052	5
Serra de Magé	Unbrecciated cumulate eucrite	9.60	1.91	0.069	0.073	−0.023	0.036	6
Juvinas	Monomict noncumulate eucrite	13.9	9.96	−0.035	0.042	0.026	0.179	3
Béréba	Monomict noncumulate eucrite	14.8	11.4	0.033	0.042	0.021	0.054	6
Sioux County	Monomict noncumulate eucrite	14.1	2.90	0.045	0.063	0.012	0.090	4
Pasamonte	Polymict noncumulate eucrite	14.4	5.75	0.066	0.093	0.018	0.237	3
ALHA78132	Polymict noncumulate eucrite	14.3	7.86	0.000	0.068	−0.046	0.072	5
Tatahouine	Diogenite	12.6	4.88	−0.008	0.013	0.042	0.055	3
Johnstown	Diogenite	12.4	5.13	0.053	0.084	−0.043	0.038	3
Mean eucrites and diogenites				0.031	0.028	−0.001	0.025	9
<i>Mars</i>								
Nakhla	Olivine clinopyroxenite	16.0	5.28	−0.003	0.043	−0.092	0.055	6
Nakhla fc.	Fusion crust	20.7	1.23	−0.201	0.070	−0.097	0.115	6
Chassigny	Dunite	21.2	2.02	−0.002	0.046	0.037	0.054	6
ALH84001	Orthopyroxenite	13.6	2.69	−0.027	0.051	−0.028	0.034	6
ALHA77005	Lherzolite	15.5	2.31	0.035	0.047	0.022	0.057	6
Y793605	Lherzolite	14.7	4.47	−0.021	0.043	0.026	0.064	6
Shergotty	Basalt	15.1	2.36	0.016	0.056	0.017	0.125	3
EETA79001A	Basalt	14.2	5.38	0.033	0.047	−0.004	0.232	3
QUE94201	Basalt	15.4	4.19	−0.006	0.105	−0.011	0.136	3
Mean SNC^d				0.003	0.018	−0.004	0.032	8
<i>Moon</i>								
15555.115	Olivine normative basalt	17.1	7.59/3.46	0.208	0.058	0.103	0.039	9
15058	Quartz normative basalt	15.4	5.27	0.255	0.089	0.072	0.089	3
15475.31	Quartz normative basalt	15.5	9.35	0.111	0.083	0.032	0.161	3
12045.13	Picritic basalt	16.0	5.59	0.138	0.078	−0.008	0.141	3
12045.13 ol	Olivine separate	20.0	1.72	−0.117	0.099	0.059	0.088	3
12045.13 px	Pyroxene separate	16.0	0.50	0.106	0.050	0.042	0.120	3
70035	High-Ti basalt	14.3	8.39	0.274	0.021	0.048	0.076	6
71566.19	High-Ti basalt	14.4	6.42	0.267	0.034	0.007	0.153	4
71596.6	High-Ti basalt	14.6	5.01	0.204	0.037	−0.026	0.254	3
77516.25	High-Ti basalt	15.7	5.41/6.30	0.238	0.058	0.096	0.055	12
75075.158	High-Ti basalt	14.6	2.51	0.229	0.054	0.139	0.119	3
77215	Norite	7.77	6.04/7.44	0.128	0.024	−0.005	0.061	5
15386	KREEP basalt	8.08	1.87	0.230	0.033	0.008	0.179	3
65315.30	Fe-anorthosite	0.241	14.9	0.196	0.066	0.094	0.133	3
60025	Fe-anorthosite	0.504	26.9	0.225	0.063	0.004	0.051	3
62255.134	Fe-anorthosite	0.365	22.6	0.176	0.062	0.105	0.134	3
15426.163	Green volcanic glass	12.0	1.33	−0.027	0.050	−0.029	0.047	3
74220	Orange volcanic glass	16.3	2.45	0.013	0.031	−0.014	0.186	3
Mean Moon^c				0.206	0.029	0.048	0.031	14
<i>Earth</i>								
PCC-1	Peridotite (Cazadero, CA, USA)	5.83	9.55	0.034	0.038	0.001	0.048	6
DTS-1	Dunite (Twin Sisters, WA, USA)	6.07	18.6	0.159	0.044	0.009	0.049	3

(continued on next page)

Table 1 (continued)

Sample	Petrology (location)	[Fe] (wt.%)	Sample mass ^a (mg)	$\delta^{57}\text{Fe}/^{54}\text{Fe}$ (‰)	Uncertainty ^b (2S.E.)	$\delta^{57}\text{Fe}/^{56}\text{Fe}$ (‰)	Uncertainty ^b (2S.E.)	Number of analyses ^c
<i>Earth</i>								
JP-1	Peridotite (Horoman, Hokkaido, Japan)	5.85	2.98/5.79	0.006	0.034	−0.042	0.015	8
WITS-1	Komatiite (Barbeton, South Africa)	8.34	3.07	0.057	0.024	0.086	0.091	5
BIR-1	Tholeiitic olivine basalt (Iceland)	7.90	1 to 20	0.102	0.015	0.039	0.018	46
BCR-1	Basalt (Columbia River, WA, USA)	9.37	2.97	0.109	0.055	−0.011	0.084	6
BHVO-1	Basalt (Hawaii, USA)	8.55	18.6	0.164	0.032	0.098	0.093	5
OU-2	Dolerite (Belford, Northumberland, UK)	9.30	6.68	0.132	0.071	−0.035	0.148	3
DRN	Diorite (Neuntelsein, Vosges, France)	6.78	3.79	0.054	0.053	−0.014	0.124	3
PE9101	Gabbro (Fozzano, Corsica, France)	7.47	18.3	0.126	0.017	−0.008	0.091	3
PMS	Microgabbro (Pitscurrie, Scotland, UK)	7.06	5.34	0.168	0.044	0.073	0.052	9
OT9102s	Gabbro (Ota, Corsica, France)	7.78	3.67	0.072	0.072	0.033	0.048	6
AGV-1	Andesite (Lake County, OR, USA)	4.73	8.85	0.139	0.064	0.004	0.140	3
Mean mafic Earth				0.102	0.032	0.018	0.027	13
<i>Chondrite</i>								
Orgueil	Carbonaceous type I	16.2	5.40	−0.043	0.066	−0.029	0.067	5

^a Several masses indicate means including more than one sample dissolution.

^b The iron isotope composition and two standard error uncertainties quoted are calculated from the number of analyses indicated and using the Student's *t*-correcting factors.

^c Or number of samples for the planetary means.

^d Excluding Nakhla fusion crust.

^e Excluding mineral separates and volcanic glasses.

proach was used to correct for mass discrimination as it was known to give excellent accuracy and reproducibility for Fe isotope measurements [10]. It has the advantage of implying no specific mass discrimination law, nor prior knowledge of the accurate isotopic composition of the standard used as long as it is universally adopted. It also means that any bias induced by residual argide molecular interference can be cancelled out when sample and standard Fe concentrations are within $\pm 20\%$, which is typically 10 ± 2 ppm for this study.

The $^{57}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{56}\text{Fe}$ ratios are expressed in a conventional delta notation:

$$\delta^{57}\text{Fe}/^{54}\text{Fe} = \left(\frac{^{57}\text{Fe}/^{54}\text{Fe}_{\text{sample}}}{^{57}\text{Fe}/^{54}\text{Fe}_{\text{IRMM14}}} - 1 \right) \times 10^3$$

where $^{57}\text{Fe}/^{54}\text{Fe}_{\text{sample}}$ is the measured sample $^{57}\text{Fe}/^{54}\text{Fe}$ ratio and $^{57}\text{Fe}/^{54}\text{Fe}_{\text{IRMM14}}$ is the average of the measured $^{57}\text{Fe}/^{54}\text{Fe}$ ratios of the IRMM-14 standards placed before and after the sample in the analytical sequence. Each $\delta^{57}\text{Fe}/^{54}\text{Fe}$ and $\delta^{57}\text{Fe}/^{56}\text{Fe}$ value in Table 1 represents the mean of typically around 3 to 6 replicate analyses spread across different analytical sessions separated by weeks to months. The uncertainties of these analyses are around 0.1‰ for $\delta^{57}\text{Fe}/^{56}\text{Fe}$ and 0.07‰ for $\delta^{57}\text{Fe}/^{54}\text{Fe}$ (Table 1). The slightly worse figures for $^{57}\text{Fe}/^{56}\text{Fe}$, despite only one atomic mass unit (amu) difference for this ratio, may result from the narrower peak flat tops in the cycle measuring this ratio. This comes from the contraction of the ion beam, using the Nu Plasma zoom optics, to have 0.25 amu between each collector instead of normally 0.333, in order to measure ^{56}Fe

using the external L5 cup. Finally, it should be mentioned that our long-term reproducibility based on repeated analyses of BIR-1 also includes the sample decomposition and purification procedure with various sample sizes since the 46 analyses were made on six different aliquots with varying sample sizes (from 1 to 20 mg; Table 1). Additional total replicates of lunar and terrestrial samples did not show significant variations (Table 1). The means of all the measurements of the replicates are therefore reported in Table 1. It can also be seen that $\delta^{57}\text{Fe}/^{54}\text{Fe}$ and $\delta^{57}\text{Fe}/^{56}\text{Fe}$ are in agreement within uncertainty given the difference of masses, and therefore only the more reproducible $\delta^{57}\text{Fe}/^{54}\text{Fe}$ values, especially on a per amu basis, are used in the discussion [21].

The sample-standard bracketing approach does not take into account possible systematic mass bias effects introduced from the sample matrix relative to the pure IRMM-14 Fe isotopic European reference material used as a standard. To minimize these problems it is essential to achieve an excellent chemical purification of iron prior to analysis. Semi-quantitative quadrupole ICP-MS analyses for several samples revealed that the iron fractions are devoid of impurities after the chemical procedure described above. Potential matrix effects were further checked by admixing our in-house hematite iron standard (from Milhas, France) into the matrix of sample 75075, a high-Ti lunar basalt, after its own iron had been extracted, and then performing a new chromatographic separation. After this treatment, the hematite standard gave an iron isotope composition that was within error of the normal value. Matrix effects do not appear to be an issue with the low resolution Nu Plasma instrument after our chemical purification method for the sample analyzed. This is confirmed by (1) the similarity of Fe isotopic compositions among lunar samples, despite varied matrixes, ranging from high-Ti basalt to Fe-anorthosites; and (2) the fact that the main differences in isotopic composition are found between samples of broadly similar major element composition but different planetary objects (see below).

3. Iron isotope results

A total of 46 terrestrial and extra-terrestrial bulk rock samples representing much of the igneous pet-

rological variability of the mafic Earth, Moon, and meteorites thought to come from Mars and asteroid 4 Vesta have been analysed (Table 1). Data are also reported for olivine and pyroxene separates of a lunar picritic basalt, for a fusion crust from the meteorite Nakhla and for a bulk sample of the CI carbonaceous chondrite Orgueil. The reproducibility obtained for $\delta^{57}\text{Fe}/^{54}\text{Fe}$ is similar to that obtained by other laboratories that also use ion chromatography and MC-ICPMS [10,22,23]. This is about one order of magnitude better than the best TIMS data obtained with the double spike technique published so far [9,23]. It thus offers the opportunity to re-evaluate the degree of homogeneity of the Earth and Moon inferred from TIMS measurements [9].

Our analyses show that eight Shergotty–Nakhla–Chassigny (SNC) meteorites, likely to come from Mars, seven cumulate and non-cumulate eucrites as well as two diogenites, probably from asteroid 4 Vesta, located at 2.36 astronomic units (AU) in the asteroid belt, between Mars and Jupiter, all give indistinguishable $\delta^{57}\text{Fe}/^{54}\text{Fe}$ values (Table 1 and Fig. 1).

In contrast, most of the 14 bulk lunar samples analysed yield Fe isotopic compositions that are distinctly heavy relative to the SNC meteorites, eucrites and diogenites (Table 1 and Fig. 1). Only two volcanic (orange and green) glasses give $\delta^{57}\text{Fe}/^{54}\text{Fe}$ indistinguishable from that of the meteorites. Mineral separates from picritic basalt 12045 also show distinct Fe isotope composition, with $\delta^{57}\text{Fe}/^{54}\text{Fe}$ heavier by 0.2‰ for the pyroxene (55% modal content [24]) compared to the olivine (10% modal content [24]). This difference is similar to that found for the same minerals in terrestrial mantle xenoliths by Zhu et al. [22]. Despite these isotopic variations at the mineral-scale, the bulk sample 12045 displays a $\delta^{57}\text{Fe}/^{54}\text{Fe}$ ratio indistinguishable from those of the majority of the lunar samples analysed. Wiesli et al. [19] report very similar values for other Apollo 12 basalts. There is no straightforward interpretation of the heavier Fe isotope composition observed in most bulk lunar samples in terms of crystal fractionation or variable modal mineral content given that the lunar lithologies analysed are extremely variable and representative of cumulates as well as magmatic liquids. They include anorthosite, norite, KREEP basalt, and low- and high-titanium basalts (Table 1). Furthermore,

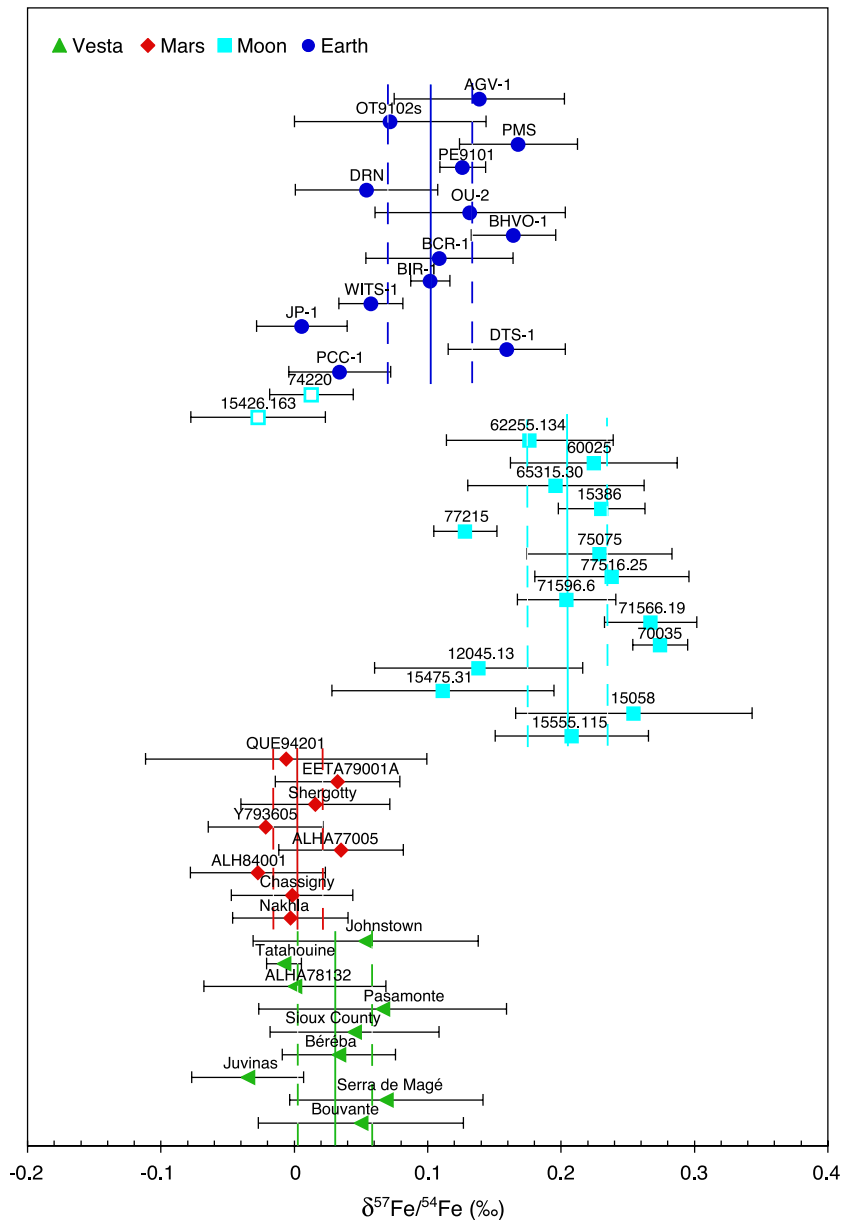


Fig. 1. Iron isotope composition of eucrites and diogenites (Vesta), SNC meteorites (Mars), lunar and terrestrial bulk-rocks. Individual sample uncertainties are 2 standard errors. Student *t*-tests (Table 2) indicate with a confidence level higher than 99% that the Moon is isotopically heavier than the Earth, which is itself heavier than Mars and Vesta. The two lunar glasses (open squares) are not included in these calculations. See text for discussion. Data from Table 1.

an iron-rich mineral like ilmenite, that is known to play a noticeable role in lunar magmatism, is also one of the rock-forming minerals inducing the smallest Fe isotope fractionation according to the theoretical esti-

mates currently available [25]. Hence, the variable petrology may just be responsible for the isotopic scatter observed between lunar samples (Fig. 1). The two lunar glasses are the only samples to yield precise

and well-defined values that are similar to Mars and Vesta. These two glasses are, with the mineral separates, the only lunar samples analysed in this study that are not powdered bulk rocks. As discussed in more detail below, their relatively light isotope composition might be related to their eruptive style on the Moon surface. Alternatively they may sample an isotopically distinct, deeper portion of the Moon [26–28]. They will thus be considered separately. Setting aside these two lunar glasses, the average $\delta^{57}\text{Fe}/^{54}\text{Fe}$ for the remaining 14 bulk lunar samples is $0.206 \pm 0.029\text{‰}$. Student's *t*-tests confirm what is apparent from Fig. 1, that this mean value is distinctly different from the averages for martian meteorites and eucrites–diogenites at the >99% confidence level (Table 2).

Thirteen mantle-derived rocks from the Earth, ranging from peridotite to andesite give a mean $\delta^{57}\text{Fe}/^{54}\text{Fe}$ of $0.102 \pm 0.032\text{‰}$ (Table 1). This intermediate value is indistinguishable within uncertainty from the mean of 46 terrestrial igneous rocks recently reported [23]. Of the geostandards also analysed by the University of Wisconsin group (PCC-1, AGV-1 and BCR-1) our $\delta^{57}\text{Fe}/^{54}\text{Fe}$ relative to IRMM-14 agree at the 0.01‰ level, illustrating the good agreement between the two laboratories, despite the different MC-ICPMS instrument used. Student *t*-tests show that this terrestrial mean is different from that derived for either the martian meteorites, the eucrite–diogenites or lunar samples at >99% confidence level (Table 2).

The fact that the IRMM-14 standard is isotopically lighter than the mean of terrestrial mantle-derived rocks may result from isotopic fractionation that occurred during ore formation, since iron minerals from Fe ores can show large mass-dependent isotopic variations [29]. Alternatively it might be related to subsequent metallurgical processing during production of the IRMM-14 reference material [30].

The *t*-tests compare the means of several rock samples from different planetary objects and this procedure averages out the small variations between individual rock samples. Lower temperature geological processes generate the largest Fe isotope fractionation [23,25]. Therefore, it is likely that hydrothermal or metasomatic fluid–rock interactions enhance the Fe isotope spread observed between igneous bulk-rock samples from the Earth [31]. The terrestrial samples showing the lightest Fe isotope composition, PCC-1 and JP-1, have both been subjected to fluid–rock interaction [32,33]. Therefore, the scatter observed between individual samples on the Earth and the Moon most likely reflects reduced-scale (mineral to geological formation) features, but is not representative of large-scale planetary reservoirs.

There may be a sampling scale issue when comparing our data with those of Zhu et al. [29]. The data reported here are averages of multiple analyses of either ultramafic rocks or the product of basaltic melting of relatively well-mixed silicate mantles. Even though our sample aliquots are small, they are taken from large (gram sized) powders, prepared for other purposes, that serve to minimise the effects of within-sample heterogeneity, illustrated here with olivine and pyroxene separates of lunar basalt 12045 (Table 1). This may explain, for example, why a previously reported composition for Nakhla [29] deviates slightly from our highly reproducible values for all eight Martian meteorites. Our analysis of a fusion crust from Nakhla (Table 1) gives a value similar to that reported by these authors. As a final check that the heterogeneity reported previously is not a large-scale feature, we include data for the chondrite with the most extreme composition reported by Zhu et al. [29]. This meteorite alone, Orgueil, the CI primitive chondrite, is responsible for most of the spread observed at the bulk-rock scale for chondrites by these authors. However, our data for this meteorite, based on a powder made from several grams of whole-rock, are indistinguishable from the values we obtain for Mars and Vesta (close to zero per mil, Table 1), as well as from another analysis of this chondrite recently reported [34]. The isotopic spread reported by Zhu et al. [29] for bulk samples may reflect small-scale heterogeneity produced by fractionation in the solar nebula and parent bodies but does not appear to be a large-scale feature.

Table 2
Results of statistical *t*-test for comparisons of planetary means

	Degree of freedom	Calculated <i>t</i>	Critical <i>t</i> (<i>P</i> =0.01)
Moon and Vesta	21	8.93	2.84
Moon and Mars	20	10.56	2.85
Moon and Earth	25	5.21	2.80
Earth and Vesta	20	3.50	2.85
Earth and Mars	19	4.97	2.87

4. Why planetary differences?

The four planetary bodies investigated in this study have different physical and chemical characteristics, and it should first be considered whether the different mean iron isotope compositions of the igneous rocks analyzed correlate with any of these parameters. The mineralogy of the samples analyzed and of their source region that may vary between planets does not appear to play a significant role in the isotopic effects. As illustrated by the olivine and pyroxene separates of lunar basalt 12045 (Table 1), the fractionation of Fe isotopic composition by magmatic minerals is limited, and it is unlikely to produce a systematic difference between whole rock samples from different planetary objects. Indeed, a broad spectrum of rock types has been analysed (Table 1), yet the planetary isotopic differences largely transcend this. The lunar samples in particular span a large range in composition, but their Fe isotopic composition varies relatively little. Only the picritic glasses show a clear resolvable isotopic difference. Most lunar samples, including those studied by Wiesli et al. [19] are heavy relative to the mean of the data for samples from Mars and Vesta.

It has recently been suggested that the Fe isotope composition of terrestrial peridotites might be correlated with the ferric iron content of their spinels [35]. However, we find no relationship between the Fe isotope compositions and the previously inferred oxygen fugacity (fO_2) of the planetary interior. For instance, the Moon and Vesta have similar inferred mantle oxygen fugacity [36], but their rocks are 0.2% different in Fe isotopic composition, whereas Mars and Vesta, with different mantle fO_2 , exhibit indistinguishable $\delta^{57}Fe/^{54}Fe$ (Table 1 and Fig. 1). Planetary mantle oxygen fugacity estimates are difficult because the values may vary with pressure [37]. For the Earth there is a general agreement that the upper mantle oxygen fugacity is within $\sim \pm 1$ log units of the Quartz–Fayalite–Magnetite buffer, but some suggest that under the old South African craton, oxygen fugacity decreases with depth [37], whereas others proposed that the lower mantle may have become systematically enriched in ferric iron as a result of subduction [38]. It has also been suggested on the basis of recent experimental work that the bulk oxygen content is the same for both the lower and

the upper mantle [39]. Support for a uniform Fe isotopic composition for the Earth's mantle can be found in the fact that basalts from hot-spots (BHVO-1 and BIR-1, Table 1), potentially sampling the deepest Earth's mantle, do not show a different iron isotope composition compared to other terrestrial samples.

There is no obvious correlation between content of moderately volatile elements of a planet and the Fe isotopic composition of its rocks since the Moon and Vesta, despite contrasting iron isotope compositions, display similar volatile depletion [40–42]. Similarly Vesta and Mars have identical Fe isotope compositions but radically different levels of moderately volatile element depletion.

Differences in core–mantle differentiation cannot easily explain the variable mantle Fe isotope signatures given that the relative core sizes of the Moon, Earth, Mars and Vesta [40] show no relationship with Fe isotopic composition, nor is there an apparent relationship between Fe isotopic composition and estimated Fe content of the mantle of the Earth, Moon, Mars and Vesta.

Finally, there is no obvious correlation between planetary size overall and Fe isotope composition. Nor is there a systematic Fe isotope variation with heliocentric distance.

Hence, we find that none of the currently known present day petrological, geochemical or planetary properties correlate readily with the different iron isotope compositions that are recorded in mantle-derived rocks of different planets. We therefore now explore the possibility that the iron isotopic fractionation may have been produced at an early stage, during planet formation.

5. Origin of the earth and moon

The heavier Fe isotopic composition of the Earth and more especially the Moon compared to other bodies of the solar system may bear on their genesis. It now is generally accepted that the main stages of Earth's growth were a result of collisions between already formed planetesimals. The formation of the Moon is also widely considered to be the result of a giant impact between the proto-Earth and another planet approaching the size of Mars [43]. Neverthe-

less, several physical aspect of this giant impact theory remain obscure [44–46] and geochemical data may be explained by other processes [41,42,47], thus leaving this scenario still hypothetical. If it occurred, such an energetic process might be responsible for the iron isotope fractionation observed between planets. In contrast, Vesta and even Mars may well have originated by runaway growth in which material in the heliocentric feeding zone of the planet is “mopped up”.

Before exploring this hypothesis further it is worth first considering alternative models of lunar origin. Co-accretion of the Earth and Moon would be expected to result in the same Fe isotope composition. In fact, there is no particular mechanism implied in this scenario that would change the composition of either object relative to that of the other planets of the inner solar system. Similarly, an origin of the Moon by fission from a proto-Earth should not result in different Fe isotopic signatures. If the Earth had captured the Moon, one could explain the Earth–Moon difference in Fe isotopes in terms of formation of the two bodies in a different region of the early solar system. However, this finds no support in oxygen [48] and chromium [49] isotope data, which indicate that the Earth and the Moon accreted from material with very similar average provenance. Furthermore, Mars and Vesta, despite being located 0.84 astronomical units apart and characterised by different O isotopic signatures, still display the same Fe isotope composition. Also, the capture hypothesis provides no explanation for how such a difference could be produced in the first place.

In contrast, vaporisation and sublimation of bodies in space can generate kinetic isotope fractionation, by which the resulting condensed residue becomes enriched in heavier isotopes [50,51]. Here, “kinetic isotope fractionation” is meant in contrast to “equilibrium isotope fractionation”, in which the whole gaseous reservoir remains in equilibrium with the liquid from which it evaporated. Hence, a simple but reasonable interpretation of these results is that the Earth and the Moon underwent partial vaporisation during their formation. This process resulted in kinetic iron isotope fractionation, leading to the escape of the lighter iron isotopes in space, and leaving these two planets with heavier Fe compared to the other bodies of the solar system.

Only accretionary processes like those considered in the giant impact theory, in which a planetary body hits the Earth and yields ejecta that subsequently re-accreted to form the Moon, can readily account for the energy required to partially melt and vaporise at the planetary-scale the Earth and the impactor planet. The calculated temperatures are well in excess of 3000 K [52,53], and locally may have reached 16000 K [54]. In this scenario, the heavier iron isotopic composition of the Moon, therefore, would be consistent with its origin as a high temperature fractionated residue formed from the collision between the proto-Earth and an impactor considered to be as big as Mars. Evidence for a largely molten and gaseous accretion disk leading to the Moon, after the giant impact, is consistent with numerical simulations [55].

Assuming that the largest isotopic effect occurred by Rayleigh isotope fractionation during magma vaporisation, we can compute a first-order estimate of the amount of iron loss required during this process to explain the planetary isotopic differences observed. Taking Mars as a reference planet and the experimentally determined Rayleigh fractionation factor for iron of Wang et al. [56], we calculate that only between 0.8% (Fe evaporation) and 1% (FeO evaporation) loss of the total Fe budget available for evaporation is required to explain the Moon’s estimated heavier isotopic composition. What that total budget was exactly is unknown. Even lower losses of 0.4% and 0.5%, respectively, are calculated from the Earth’s estimated isotopic composition. Such low losses would remain undetectable in estimates of planetary bulk composition given their level of uncertainty, which is worse than 1%.

The iron isotope compositions therefore provide no direct constraint on whether the giant impact involved large degrees of volatile depletion or refractory enrichment for the Moon and the Earth, if only simple Rayleigh isotope fractionation operated. On the other hand, the values may represent minimum estimates if Rayleigh isotope fractionation during evaporation was limited by iron diffusion in molten globules [57] resulting from the giant impact; if evaporation occurred under gas confining pressure [51]; or if gas condensation in space occurred largely close to equilibrium [50,51].

With an impactor approaching the size of Mars (10% of the Earth’s mass) and a proto-Earth close to

its current size [43], 1% Fe loss from the material that made the Moon should translate into an isotope shift that represents less than 0.1% Fe loss for the Earth. This applies if only the impactor was subjected to the vaporisation that led to Fe loss, and that it provided most of the material that made up the Moon. To increase the figure from less than 0.1% to 0.5% Fe loss for the Earth, as computed above, requires either that the impactor/Earth mass ratio was larger than 0.1, as assumed by Cameron [53] (ratio of 0.43), or that part of the proto-Earth was also subjected to vaporisation and Fe loss, as implied above. If in the final stages of accretion, the proto-Earth underwent other large impacts also fractionating Fe isotopes, but not seen by Mars and Vesta given their smaller size, then its present Fe isotopic composition would exert little in the way of constraints on the Moon-forming giant impact.

It also should be stressed that the amount of Fe loss from the Moon and the Earth to explain the observed isotopic shifts may vary by 0.1–0.2%, depending on the species that is evaporating, as illustrated above with Fe and FeO evaporation. Similarly, these iron losses may vary for both the Earth and the Moon by ± 0.2 –0.3% when the uncertainties of the mean Fe isotope composition of planets reported in Table 1 are taken into account. Despite these reservations, it is interesting to note that giant impact simulations envision a loss of matter for the Earth–Moon system of a few percent [43,53], that is of the same order of our loss estimate for iron only.

The premise that lunar-forming material will be preferentially depleted in the lighter isotopes of iron is dependent upon such material escaping from Earth-bound orbit. First order dynamic and petrological calculations (not shown) suggest that light Fe isotope loss is more likely to occur if the melted ejecta have an elliptical trajectory outside lunar accretion disks as envisioned by some after a giant impact [44,45,55]. Furthermore, such a disk may be too gas- and dust-rich to allow efficient Rayleigh isotope fractionation to occur. Loss of a portion of the liquid and gas because of the thermal and dynamic state of matter is consistent with more recent numerical simulations using a larger number of particles. They describe giant impact ejecta as a highly heterogeneous cloud with lobes expanding far beyond twice the Roche limit at their apogees [43,53]. Hence, besides the thermal velocity, part of the escape velocity of the

iron atoms was probably acquired from the ejecta motion due to the impact.

The orange and green volcanic glasses display lower Fe isotope ratios than the other lunar samples. These results are similar to the data for Mars and Vesta (Table 1 and Fig. 1). Two explanations may account for these values. These glasses were erupted on the Moon's surface through fire fountaining volcanism and the magmas may have been subjected to high temperatures in vacuum for at least 10 min [58], leaving ample time for Rayleigh isotope fractionation during vaporisation. These glass beads have surfaces that are the most volatile-enriched of all the materials sampled on the Moon [27]. It is conceivable that they collected the vapours resulting from the fire-fountaining process and that these contained isotopically lighter Fe. This interpretation was provided by Ding et al. [59] upon their finding that orange glass surfaces were indeed enriched in sulfur that was isotopically light compared to the interior of the spheres. For this hypothesis to be correct however, the similarity of the Fe isotope composition of the lunar glasses with Mars and Vesta would be entirely coincidental.

Another possibility is that the lunar glasses sample a very deep portion of the Moon [26–28] that accreted from materials that never underwent large-scale vaporisation. This model is consistent with the finding that these glasses sampled a source having a $^{238}\text{U}/^{204}\text{Pb}$ that was an order of magnitude lower than the sources of the Mare basalts [27]. This less volatile depleted, or less refractory enriched composition is consistent with the view that these lunar glasses are sampling some of the material that was less severely affected by the thermal effects of the giant impact, therefore showing no noticeable Fe isotope difference compared to Mars and Vesta. This would provide evidence that the early lunar magma ocean did not involve the deepest part of the Moon (see also [28]) and was a direct residual thermal consequence of the giant impact.

6. Comparison with K and O isotopes

It remains to be explained why a heavier iron isotopic composition of the Moon resulting from kinetic isotope fractionation during iron volatilisation could not be observed with oxygen [48] and potassium isotopes [50].

The effect observed in $\delta^{57}\text{Fe}/^{54}\text{Fe}$ could in principle also be seen in mass dependent oxygen isotope variations by comparisons between planetary $\delta^{18}\text{O}$ values. Taking into account the reproducibility relative to the expected mass fractionation at lighter masses, if oxygen behaved like Fe during the giant impact, it should also be possible to detect the heavier isotopic composition of the Moon, which is not the case [48]. However, the natural variability in mass dependent oxygen isotope composition in the Earth and Moon that results from magmatic fractionation and alteration is larger for oxygen than for iron [23], rendering it difficult to make such a fine comparison at this stage.

Humayun and Clayton [50] calculated that up to 2% of K evaporation would go unnoticed given their analytical uncertainties. The maximum of 1% of iron loss needed to explain the observed isotopic composition of the Moon is only half that value. Although K is more volatile than Fe, it is feasible that the difference in loss between these elements is less than a factor of two, and therefore less than 2% of the Moon's potassium was lost following the giant impact. Indeed, Wang et al. [56] illustrated that the Fe evaporation flux is more than one order of magnitude larger if it evaporates from liquid Fe compared to liquid iron oxide. In a subsequent study, these authors showed that the iron evaporation flux is even smaller than that determined with FeO if it takes place from a silicate melt [60]. Hence, the different isotopic information given by K and Fe isotopes can be explained if we consider that a significant proportion of the vaporised Fe comes from the cores of the proto-Earth and/or the impactor, whereas K will only occur as oxide in planetary mantles and will therefore evaporate less easily. Direct evaporation of protoplanetary cores is consistent with recent numerical simulations of the giant impact showing that portions of the proto-Earth and impactor cores can be ejected into space after the impact [53]. Part of the molten globules considered here to be responsible for Fe loss could therefore come from these core fractions. All this molten and gaseous matter coming from proto-planetary cores and mantles should be subsequently homogenised prior to and during re-accretion, before Earth and Moon final differentiation, to lead to the rather homogeneous Fe signatures observed at the planetary scale today (Table 1 and Fig. 1).

The maximum of 2% of K evaporation based on Rayleigh fractionation does not take into account any possible additional evaporation effect that would not fractionate isotopes. The large difference in K/U ratios between the Earth and Moon might be due to vaporisation of a large fraction of K into proto-planetary atmospheres blown off during the giant impact for example [61]. In that case isotopic fractionation might not occur.

7. Concluding remarks

The isotopic composition of iron from lunar samples is on average heavy relative to mantle-derived rocks on Earth. These are heavier again than basaltic and ultramafic rocks from Mars and Vesta. This is consistent with the view that whereas Mars and Vesta accreted purely from runaway growth, the accretion of the Earth was characterised by an event energetic enough to partly melt and vaporise iron or its compounds. The heavy iron isotopic composition found in most lunar rocks is consistent with it being dominated by refractory rich residues or condensates from a giant impact.

At the present time this is the most straightforward interpretation of the Fe isotope data. If correct, this provides strong support for the giant impact hypothesis of the origin of the Moon. The exact processes are likely to be more complex than the simple models used in this paper, which are included merely in order to provide quantitative examples. It is possible, for instance, that the isotopic effect was not a pure Rayleigh phenomenon, but was instead partly hindered by vapour pressure. In this case, the figure of 1% of Fe loss computed for the Moon becomes a minimum estimate.

Further high precision work on other stable isotopes not so affected by subsequent magmatic processes should provide further constraints on the exact conditions of the hypothesised vaporisation event and how the proto-Earth and impactor core, mantle and atmosphere were affected. For example, if our model is correct, a siderophile element like Ni, which has a similar volatility to iron, should display the same inter-planetary mass dependent isotope differences. In contrast, silicon or magnesium, which are as volatile as Fe, but are essentially confined to planetary

mantles, should exhibit much smaller variations, if any. These small planetary stable isotope variations, as exemplified in this study for iron, may provide one of the few direct remaining records of the events taking place during planet genesis. In this respect, they can provide invaluable constraints for models of planet formation.

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