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On the iron isotope composition of Mars and volatile depletion in the terrestrial planets

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ABSTRACT

Iron is the most abundant multivalent element in planetary reservoirs, meaning its isotope composition (expressed as $\delta^{57}$Fe) may record signatures of processes that occurred during the formation and subsequent differentiation of the terrestrial planets. Chondritic meteorites, putative constituents of the planets and remnants of undifferentiated inner solar system bodies, have $\delta^{57}$Fe $\approx 0\%$; an isotopic signature shared with the Martian Shergottite–Nakhlité–Chassignite (SNC) suite of meteorites. The silicate Earth and Moon, as represented by basaltic rocks, are distinctly heavier, $\delta^{57}$Fe $\approx +1\%$. However, some authors have recently argued, on the basis of iron isotope measurements of abyssal peridotites, that the composition of the Earth’s mantle is $\delta^{57}$Fe $= +0.04 \pm 0.04\%$, indistinguishable from the mean Martian value. To provide a more robust estimate for Mars, we present new high-precision iron isotope data on 17 SNC meteorites and 5 mineral separates. We find that the iron isotope compositions of Martian meteorites reflect igneous processes, with nakhlites and evolved shergottites displaying heavier $\delta^{57}$Fe ($+0.05 \pm 0.03\%$), whereas MgO-rich rocks are lighter ($\delta^{57}$Fe $\approx −0.01 \pm 0.02\%$). These systems are controlled by the fractionation of olivine and pyroxene, attested to by the lighter isotope composition of pyroxenes compared to whole rock nakhlites. Extrapolation of the $\delta^{57}$Fe SNC liquid line of descent to a putative Martian mantle yields a $\delta^{57}$Fe value lighter than its terrestrial counterpart, but indistinguishable from chondrites. Iron isotopes in planetary basaltic of the inner solar system correlate positively with Fe/Mn and silicon isotopes. While Mars and IV-Vesta are undepleted in iron and accordingly have chondritic $\delta^{57}$Fe, the Earth experienced volatile depletion at low (1300 K) temperatures, likely at an early stage in the solar nebula, whereas additional post-nebular Fe loss is possible for the Moon and angrites.

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1. Introduction

How planets in the inner solar system accreted and differentiated is a question fundamental to understanding the chemical differences that exist between them today. Iron offers a unique opportunity to address this question. Not only is it abundant in each of the major planetary reservoirs, the crust, mantle and core, it exists in three different oxidation states – Fe$^{3+}$, Fe$^{2+}$ and Fe$^{0}$ – the relative proportions of which are constrained by local redox conditions. These redox states confer different properties to the element, making it capable of tracing a variety of processes.

Despite the range of iron oxidation states, its isotopes are remarkably constant in chondritic meteorites, identical to the IRMM-014 reference material (Schoenberg and von Blanckenburg, 2006; C A Codd and Dauphas, 2011; Needham et al., 2009; Theis et al., 2008; Wang et al., 2013); i.e., \( ((57\text{Fe}/54\text{Fe})_{\text{chondrite}}/\) \( 57\text{Fe}/54\text{Fe})_{\text{IRMM-014}} - 1 \) ×1000 $= \delta^{57}$Fe $= 0\%$. This constancy is independent of chondrite class, thus, if planets accreted from chondritic material, deviations from 0\% should reflect post-nebular processes. Mass-dependent fractionation laws dictate that, in general, Fe$^{3+}$-bearing phases are heavier than Fe$^{2+}$-bearing phases, i.e., $\delta^{57}$Fe$^{3+} - \delta^{57}$Fe$^{2+} = \Delta^{57}$Fe$^{3+−2+} > 0\%$ (Polyakov and Mineev, 2000; Shahar et al., 2008), although no apparent isotopic fractionation exists between Fe$^{2+}$ and Fe$^{0}$ under terrestrial core-forming conditions (Hin et al., 2012; Poitrasson et al., 2009; Roskosz et al., 2006).

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Using this behaviour as a guide, causes for isotopic differences in basaltic rocks from different planetary bodies can be evaluated. Initial studies considered that \( \delta^{57}\text{Fe} \) in the BSE \( \approx 0.1\% \), owing to the overlap of ultramafic to intermediate magmatic rocks, (Beard and Johnson, 2004; Poitrasson et al., 2004). This signature is also observed in the lunar low-Ti basalts (Liu et al., 2010; Poitrasson et al., 2004; Weyer et al., 2005), whereas the lunar high-Ti basalts are systematically enriched in \( \delta^{57}\text{Fe} \) (\( \approx 0.2\% \)). Iron isotope signatures for the Earth–Moon system, based on basaltic rocks, are resolvably heavier than estimates for SNC meteorites (Anand et al., 2006; Poitrasson et al., 2004; Wang et al., 2012; Weyer et al., 2005) and the Howardite–Eucrite–Diogenite rocks from asteroid IV-Vesta (Poitrasson et al., 2004; Schoonenberg and von Blanckenburg, 2006; Wang et al., 2012; Weyer et al., 2005), both of which give chondritic values. Further, the recognition of basaltic achondrites extending to even heavier values than those of the Earth–Moon system (i.e., angrites, \( \approx 0.2\% \)) suggests heavy isotope enrichment is a consequence of planetary differentiation. Possible explanations include vaporisation and loss of isotopically-light Fe during planetary collisions (Poitrasson et al., 2004), isotope fractionation during mantle partial melting (Dauphas et al., 2009; Weyer and Ionov, 2007) and fractionalization by high-pressure phases in the lower mantle during core formation (Polyakov, 2009; Williams et al., 2012).

However, and while not widely agreed upon (see, e.g., Zhao et al., 2012; Poitrasson et al., 2013) some recent studies on the composition of mantle peridotites (Craddock et al., 2013; Weyer and Ionov, 2007) suggest a BSE value that is lighter (\( \delta^{57}\text{Fe} \approx 0.04 \pm 0.04\% \)) than mean values for terrestrial and lunar basalts, as represented by Mid-Ocean Ridge Basalt, MORB (\( \delta^{57}\text{Fe} \approx 0.1\% \); Teng et al., 2013) and the low-Ti suite, respectively. Importantly, this value is similar to chondrites, Mars and IV-Vesta, removing the need to appeal to fractionation mechanisms between Earth and these bodies. In order to shed light on the isotopic characteristics of Mars, we have analysed 17 whole-rock SNC meteorites and 5 mineral separates using high-precision techniques (Poitrasson and Freydlter, 2005; Sossi et al., 2015). Through identification of the primary and parental magma compositions of SNCs, and applying corrections for the effects of magmatic differentiation, the iron isotopic composition of Martian primary magmas is calculated and shown to be lighter than that of primary MORB, meaning the Martian and terrestrial mantles are isotopically distinct. A comparison of planetary basalts shows a systematic dependence on Fe/Mn ratios, implying a common process leading to iron isotope fractionation. Mass balance constrains the transfer of material to be significant on the planetary-scale, namely by volatile depletion or core-formation. We interpret these results in the context of the accretion and differentiation histories of the terrestrial planets.

2. Samples and methods

2.1. Samples and dissolution

Samples Shergott, Zagami, Los Angeles, SaU 005, NWA 1183, Nakhl, Governor Valdares, Lafayette and Chassigny were provided by the Natural History Museum, London. Samples Y 980459 and Y 000953 were obtained from the National Institute for Polar Research, Japan. The Australian National University samples DaG 476 and Zagami were purchased from a meteorite dealer, whereas samples ALHA 77005, EETA 79001A, LAR 06319, RBT 4262 and MIL 03346 were provided by the Meteorite Working Group (MWWC), NASA, in the form of 1 g rock chips, free of fusion crusts. Exactly 500 mg of these chips was hand-crushed in a boron carbide mortar and pestle to create a fine powder. Of this batch, 100 mg was dissolved in duplicate for the stable isotope analyses, first by a mixture of concentrated HCl–HF–HNO\(_3\) in the ratio 1:0.5:0.2 in a 3 mL Savillex Teflon beaker on a table-top hotplate set to \( \approx 130^\circ \text{C} \).

After drying down in nitrate form, 15 M HNO\(_3\) with a few drops of HF were added to the samples and then placed, still in their 3 mL Teflon beaker, inside 20 mL FEP Teflon vessels with 2–3 mL of MQ H\(_2\)O to create a vapour pressure, and inserted into steel bombs. These were left to dissolve in an oven set to \( \approx 210^\circ \text{C} \) for 7 days. Subsequent evaporation with addition of concentrated HNO\(_3\) confirmed that the samples had been dissolved in their entirety.

2.2. Column chromatography and mass spectrometry

Samples were analysed in two batches – those marked ‘Poitrasson’ were processed at Geosciences Environment Toulouse (GET) CNRS laboratory, following the procedure detailed in Poitrasson and Freydlter (2005). Owing to the reproducibility of data acquired during multiple sessions over the period, standard-sample bracketing (SSB) results were used rather than the combined SSB and Ni-doped regression method of Poitrasson and Freydlter (2005). Samples labelled ‘Sossi’ were analysed at the Australian National University, following the procedure described in Sossi et al. (2015). Three well-characterised standard materials, Allende, BHVO-2 and Milhas Hematite were run throughout to ensure total procedural accuracy and precision were maintained (Table 1) in agreement with published values (Sossi et al., 2015).

3. Results

Iron isotope measurements for the SNC meteorites are summarised in Table 1. Whole-rock major- and trace-element data and literature iron isotope data are listed in Appendix A.

The iron isotope compositions of whole rocks show a restricted range, \( -0.07 \pm 0.01 < \delta^{57}\text{Fe}(\% \text{r}) < +0.10 \pm 0.03 \), overlapping with those of both chondrites and mantle peridotites. Measured \( \delta^{57}\text{Fe} \) values are inversely correlated with whole-rock MgO contents (Fig. 1a), mimicking trends observed in terrestrial mafic rocks (Sossi et al., 2012; Teng et al., 2008). Within the shergottites, a similar correlation is found with iron isotopes and CaO (Fig. 1b), with the nakhlites displaced towards higher CaO values as a result of clinopyroxene accumulation. Similar systematics are observed when compared with other indices of magmatic differentiation, such as Ni, Sc and modal olivine content (Fig. 1c). Individual analyses compare favourably with other recent measurements (shown in grey, Fig. 1), and most notably with recent high precision measurements (Wang et al., 2012). For meteorites analysed in both studies \((n = 7)\), a correlation coefficient of 0.6 is observed, respectable considering the limited isotopic range (0.15\%) compared to analytical uncertainty (0.03–0.05\%). This argues against any significant sample heterogeneity or bias in analytical methods, such that values reported herein can be interpreted with confidence.

Although based on a smaller dataset \((n = 5)\), pyroxene (from nakhlites) and olivine (from Chassigny) separates define an even narrower spread than the whole rocks, extending from \( \delta^{57}\text{Fe} \approx -0.04 \pm 0.05\% \text{r} \) to \( +0.05 \pm 0.06\% \text{r} \). Calculated pyroxene–whole rock fractionation factors are resolvable in the Y 000593 and Lafayette nakhlites, where \( \Delta^{57}\text{Fe}_{\text{pyrox-nak}} = -0.08 \pm 0.01\% \text{r} \) and \( -0.07 \pm 0.05\% \text{r} \), respectively (Fig. 1d). Pyroxene– nakhlite pairs from Nakhl and MIL 03346 show no resolvable difference, a result mirrored by the olivine–chassigny pair (Fig. 1d).

4. Discussion

4.1. Petrogenesis of Martian SNCs

In attempting to link the geochemistry and iron isotope compositions of SNC meteorites to that of the Martian mantle and terrestrial rocks, estimates of parental magma compositions are required. On the basis of geochemical criteria, Martian basalts are derived...
from disparate sources: ‘depleted’, ‘intermediate’ and ‘enriched’ (Blickert-Toft et al., 1999; Borg and Draper, 2003; Herd et al., 2002; Jones, 1989). As a result, a single parental magma for the SNC meteorites is untenable. Rather, the degree to which each whole-rock composition is representative of a liquid can be estimated through mineral–liquid equilibria. Of these, the best-constrained is the $K_{\text{D}}^{\text{OL-Melt}}$ (Filiberto and Dasgupta, 2011; Roeder and Emslie, 1970; Toplis, 2005), and, as olivine is present in both the mantle, and as the liquidus phase in basaltic melts, it is also the most useful mineral for this purpose.

Olivines in Martian shergottites display extensive normal zoning, where Mg# decreases from core to rim (Shearer et al., 2013, 2008), complicating identification of the earliest-crystallised olivine. This uncertainty can be mitigated by assuming that the most magnesian olivine composition, which corresponds to the core of the crystal, is the first to crystallise (provided it is not xenocrystic; Wadhwa et al., 2001). Its forsterite content may be compared with the Mg# of the melt with which it would have been in equilibrium, according to the expressions of Toplis (2005), and Filiberto and Dasgupta (2011). Toplis (2005) showed that the $K_{\text{D}}^{\text{OL-Melt}}$ is sensitive to melt composition, and specifically its SiO2 content. For Martian melt compositions, a blanket value of 0.35 is applicable according to Filiberto and Dasgupta (2011), in agreement with the Toplis (2005) expression, which predicts 0.33 for shergottite–olivine pairs, both of which are higher than canonical $K_{\text{D}}^{\text{OL-Melt}}$. Applying these equilibrium constants, samples that have olivines in equilibrium with the whole-rock, and therefore approximate liquids, are EETA 79001A, Y 98045 and slightly adcumulate LAR 06319 (Fig. 2a). Given the same $K_{\text{D}}^{\text{OL-Melt}}$ for pyroxene–melt (Bédard, 2010; von Seckendorf and O’Neill, 1993), the Shergotty and Los Angeles shergottites are close to (albeit more evolved) melt compositions (Fig. 2b). Assuming the forsterite content is fixed, the vertical departure from the equilibrium lines in Figs. 2a and 2b yields the fraction of mineral accumulation by mass balance:

$$M_{\text{eq}} = \frac{M_{\text{WR}} - M_{\text{Min}} \times f_{\text{Min}}}{(1 - f_{\text{Min}})}$$

(1)

which describes the concentration of an oxide or element, $M$, (here, MgO or FeO) in the melt (Eq) in equilibrium with the most magnesian mineral, Min (either olivine or pyroxene). The subscript WR denotes the whole rock, and $f$ is the fraction, where $0 < f < 1$. $f$ is fixed by the constraint that:

$$\frac{\left(F_{\text{Min}}/M_{\text{Min}}\right)}{\left(F_{\text{Eq}}/M_{\text{Eq}}\right)} = 0.35$$

(2)

As a result, the MgO and FeO contents of the parental melts for each sample are also obtained. A summary of these calculations is presented in Table 2. In general, the amount of accumulation compares well with the observed modal abundances – for example, equation (1) predicts 92% accumulation of Fo88 olivine to create Chassigny, compared with the 91.6% determined petrographically (Prinz et al., 1974).

4.2. Primary melts and the Fe/Mg ratio of the Martian mantle

Correction of a given melt composition along an olivine control line (a vertical trajectory) until it reaches the curve in Fig. 2a gives the composition of the parental liquid. However, the identity of the primary magma, that is, one in equilibrium with its

<table>
<thead>
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<th>Whole rocks</th>
<th>Method</th>
<th>$\delta^{56}\text{Fe}$ (%)</th>
<th>2 SE</th>
<th>$\delta^{56}\text{Fe}$ (%)</th>
<th>2 SE</th>
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Note: SSB: sample and standard backetion mass bias correction and Ni-doping uses natural Ni isotope composition to correct for mass bias. See text, Poitrasson and Freyder, 2005, and Sossi et al., 2015 for analytical details.

n: number of individual MC-ICP-MS measurements.
mantle source, can be determined only by making assumptions as to the Martian mantle composition. For this purpose, we adopt a mantle with \( \approx 30 \text{ wt\% MgO} \) and \( 17\text{–}18 \text{ wt\% FeO} \) (see Taylor, 2013, and Wanke and Dreibus, 1988 for summaries). Together, they suggest \( \text{Mg}^\#_{\text{Mantle-Mars}} = 0.75\text{–}0.77 \), significantly more iron-rich and magnesium-poor than its terrestrial counterpart (\( \text{Mg}^\#_{\text{Mantle-Earth}} = 0.89 \); Palme and O’Neill, 2014). Therefore, applying a \( k^\text{Fe-Mg}_{\text{ol-Melt}} = 0.33 \) to \( 0.35 \), primary Martian melts will have \( \text{Mg}^\# \)s between 0.5 and 0.55, depending on the extent of melting and choice of \( k^\text{Fe-Mg}_{\text{ol-Melt}} \). Whether this condition has been met is illustrated graphically (Fig. 3), showing the melt compositions from Table 2.

The presence of olivines with \( \text{Mg}^\# \geq 0.77 \) in some shergottites (EETA 79001A, 0.81; Liu et al., 2013, Y 980459, 0.84; Usui et al., 2008) highlights a mismatch between their sources and a putative mantle composition. There are several possible explanations for such a discrepancy:

1. The \( \text{Mg}^\# \) of the Martian mantle is higher than 0.77
2. The Martian mantle is heterogeneous, voiding the assumption of a value common to all SNCs
3. The \( \text{Mg}^\# \) of the residual mantle changes substantially with degree of partial melting

The estimated \( \text{Mg}^\# \) varies little between Martian compositional models (option 1), as \( \text{Mg} \), which is lithophile during core formation (O’Neill et al., 1998; Ringwood and Hibberson, 1991), is well-constrained. Iron contents are known less precisely due to uncertainty in the composition of the Martian core (Taylor, 2013; Wanke and Dreibus, 1988). Additionally, the Martian mantle composition may vary with depth (option 2). Crystallisation of a Martian magma ocean would have led to an initially mineralogically-stratified mantle (Borg and Draper, 2003; Elkins-Tanton et al., 2003), where the \( \text{Mg}^\# \) decreased rapidly towards the upper 200 km of the Martian mantle by accumulation.
of olivine and pyroxene at the base. Subsequently, this unstable density configuration might have prompted mantle overturn, acting to re-distribute and homogenise its major element composition, though the lower temperatures than on Earth may have inhibited convection and homogenisation of the mantle such that distinct reservoirs could have survived (Elkins-Tanton et al., 2005). The preservation of characteristic REE and isotopic signatures in SNC groups (Borg and Draper, 2003; Bridges and Warren, 2006; Halliday et al., 2001) point to the diversity of mantle source compositions.

In addition to, and independent of mantle heterogeneity, the increase in Mg# of residual mantle with melt extraction (option 3) is a fundamental result of Fe–Mg partitioning between ferromagnesian minerals and melt. To model the extent of this Mg# change, and to compare the partial melts to those calculated for the primary shergottite magmas (Table 2), the alphaMELTS algorithm (Smith and Asimow, 2005) was used. Equilibrium melting was simulated through incremental isobaric heating of the Dreibus and Wanke (1985) mantle estimate at 1 bar, 0.5, 1, and 2 GPa, at FMQ-2 (Fig. 4). At a given melt fraction (F), higher pressure (P) melts contain both more MgO and FeO. This phenomenon is due to the expansion of the pyroxene stability field at the expense of olivine to higher pressures, such that olivine enters the melt more readily. As these phases have similar Mg#s, that of the melt varies little with $P$, rendering it a powerful indicator of $F$.

The Fe–Mg systematics of primary shergottite melts suggest formation by 10–25% melting at pressures between 0.5 and 1 GPa ($\approx$40–85 km; Fig. 4). These pressures and melt fractions are also in-line with their SiO$_2$ contents of $\approx$50 wt%, whose behaviour is again a function of the proportion of olivine (low SiO$_2$; high $F$, $P$) to pyroxene (high SiO$_2$; low $F$, $P$). For the same source, the more mafic primary melts calculated for EETA79001A and Y 980459 give correspondingly higher melt fractions; 40% and $>$50% respectively. Notably, sample Y 980459 plots at a FeO content too low (or MgO too high) to have been produced from melting of a mantle envisaged by Dreibus and Wanke (1985), even at 1 bar, suggestive of a more magnesian source region (Khan and Connolly, 2008; Musselwhite et al., 2006).

4.3. Iron isotope fractionation during magmatic processes and the effect of oxygen fugacity

Even though the SNCs potentially come from diverse sources (Section 4.2), whether this variation begets a change in iron isotope composition is crucial in understanding the composition of the Martian mantle. On Earth, it has been suggested that frac-
tional crystallisation and perhaps partial melting produce iron isotope fractionation in minerals and melts (Dauphas et al., 2009; Sossi et al., 2012; Teng et al., 2008). The driving force behind this fractionation is the contrasting redox and structural states of iron between the two phases, imparting different vibrational energies on the Fe–O bond by virtue of changing bond stiffness. The stiffer bonds of Fe$^{3+}$, which typically exists in tetrahedral co-ordination, concentrates the heavier isotopes over the larger, octahedrally-co-ordinated Fe$^{2+}$ ion (Schauble, 2004).

However, before these equilibrium systematics can be applied, the extent of kinetic (i.e. disequilibrium) fractionation must be evaluated. Physically, kinetic fractionation can develop in response to crystals attempting to equilibrate with changing melt composition, since isotopes have differential diffusivities. In terrestrial systems, significant iron isotope fractionation occurs during iron diffusion into Mg-rich olivine, manifest as strong negative departures (up to 2‰) from equilibrium values in minerals (Oeser et al., 2015; Sio et al., 2013). However, nakhlites record no kinetic iron isotope fractionation within the analytical uncertainty of ±0.5‰, even in instances were diffusive processes are evidenced by Mg isotopes (Sio et al., 2014), likely reflecting their high Fe contents. Although normal zoning is common in Martian ferromagnesian minerals, zoning caused by fractional crystallisation, where each zone reflects local equilibrium with the coexisting melt, does not produce any additional isotope fractionation. Textural analysis (Richter et al., 2016) suggests that diffusive zoning arose after the bulk of the rock had already crystallised. Thus, diffusive re-equilibration took place in a closed system, affecting only the internal mineral–melt isotope distribution and not the bulk rock. Furthermore, diffusion-produced zones, volumetrically, comprise but a small fraction of the mineral (10–50 µm; Richter et al., 2016), and hence should not contribute significantly to its composition, though Fe–Mg zoning in shergottites can be more extensive. Therefore, more precise in-situ techniques are required to evaluate the extent of diffusive processes. On current evidence, however, mineral pairs should record equilibrium partitioning, a point underlined by the small measured fractionation factors, which are ±0‰ or slightly negative (Fig. 1d). Should these negative values arise from diffusion, they should depend on nakhlite cooling rates, where MIL > Y000593 > Nakhl = GV > Lafayette (fastest to slowest; Day et al., 2006) in which the fastest cooled magmas would have the largest isotope fractionation among minerals, for which there is no evidence. Therefore, the discussion that follows makes the reasonable assumption that equilibrium conditions prevailed during SNC petrogenesis.

Olivine, as the first phase to crystallise upon shallow-level differentiation of mafic and ultramafic melts of both Martian (Musselwhite et al., 2006) and terrestrial (Arndt, 1976) melt compositions, incorporates $^{56}$Fe$^{3+}$ but not Fe$^{2+}$, thereby having lower Fe$^{3+}$/Fe$^{2+}$ than the coexisting liquid. Martian magmas, which crystallise between FMQ-3.5 to FMQ-1, that is IW-0.5 to +2 (Herd, 2003; Herd et al., 2002; Wadhwa, 2008, 2001), have Fe$^{3+}$/ΣFe between 0.02–0.07 (Richter et al., 2013), lower than terrestrial magmas and higher than olivine (≥0). Given the higher oxidation state of terrestrial basalts, where Fe$^{3+}$/ΣFe of MORB = 0.12 (Bézos and Humler, 2005), the Fe isotopic fractionation factor between olivine and melt should be larger (Dauphas et al., 2014; Dauphas et al., 2009; Wang et al., 2012), that is, $\Delta^{57}$Fe$_{	ext{FMQ-3.5}}$ < $\Delta^{57}$Fe$_{	ext{MORB}}$. Enrichment of heavy iron isotopes in the melt by ferromagnesian silicate crystallisation is documented for various localities on Earth (Teng et al., 2008; Sossi et al., 2012; Chen et al., 2014). Taking terrestrial igneous rocks as a whole, heavy $\delta^{57}$Fe only becomes pronounced in granitic compositions (e.g. Poitras and Freydiere, 2005). Although many Martian meteorites are partial cumulates, a first-order constraint on the magnitude of the isotopic fractionation may be attempted by comparing the evolution of $\delta^{57}$Fe with the MgO content of the whole rock as a proxy for the liquid (Fig. 5).

Two notable features of the $\delta^{57}$Fe–MgO systematics are reversed: 1. The slope of the array is smaller in Martian compositions; 2. Magmas from Earth are displaced towards higher $\delta^{57}$Fe at a given MgO content. The data of Teng et al., 2008 predicts a $\Delta^{57}$Fe$_{\text{Min–Melt}} =$ −0.15‰, as do the magmas of the Red Hill intrusion (Sossi et al., 2012). The greater scatter of the Martian magmas notwithstanding, the trend may be fitted by $\Delta^{57}$Fe$_{\text{Min–Melt}} =$ −0.10‰, an approximation considering that Martian shergottites have experienced varying polythermal cooling histories (Busu Sarbadhikari et al., 2009; Goodrich, 2003) and some of the samples are partially accumulative (see Section 4.1). Generally, however, the degree of fractionation is smaller than on Earth. Lunar basalts, which contain exclusively Fe$^{3+}$, show no dependence of $\delta^{57}$Fe with indices of differentiation (Liu et al., 2010), suggesting that Fe$^{3+}$/Fe$^{2+}$ melt exerts control on the magnitude of iron isotope fractionation. For a given composition, Fe$^{3+}$/ΣFe scales linearly with the mean Fe–O bond strength (quantified by the force constant; Dauphas et al., 2014), hence, for Martian basalts with half as much Fe$^{3+}$ compared to terrestrial tholeiitic basalts, the fractionation factor is commensurately halved, in-line with observations (Fig. 5).

The recognition of the smaller fractionation factor between ferromagnesian minerals and Martian basalts indicates that, should iron isotopic fractionation during melting occur, it would be smaller. Indeed, the magnitude of this effect is limited on Earth ($\delta^{57}$Fe decreases ≤ 1‰ in peridotites that record partial melting; Poitras and Draper, 2003), $\delta^{57}$Fe should be less affected, if at all.

4.4. Iron isotope compositions of primary magmas on Mars

In order to facilitate comparison between planetary basalts, iron isotopes must be corrected for the effects of crystal fractionation (Section 4.3) until the whole rock composition approximates that of a liquid. To perform this correction, we adopt $\Delta^{57}$Fe$_{\text{Ox–Melt}} =$ −0.1‰, as derived in Section 4.3. A change of ±0.05‰ in the fractionation factor makes little difference, particularly at high Mg#s where the whole rocks are already close to liquids (Fig. 5). Furthermore, these more primitive examples, with 0.5 < Mg# < 0.65 are the most suitable for constraining the iron isotope composition of the Martian mantle.

Following correction, Martian liquids define a trend of increasing $\delta^{57}\text{Fe}$ with decreasing Mg# (Fig. 6) similar to that in Fig. 5. Melts with Mg#s near 0.6 have $\delta^{57}\text{Fe} \approx 0.00\%$, whereas the more evolved shergottites and nakhlite liquids (Mg# < 0.5) preserve corrected $\delta^{57}\text{Fe}$ near 0.05%. Extrapolation of this trend to the Mg# of the Martian mantle (0.77) yields a value of $-0.04 \pm 0.03\%$ (1SD). The majority of the uncertainty at Mg# = 0.77 comes from the scatter in the array ($\pm 0.025\%$), with minor effects from the choice of fractionation factor ($\pm 0.005\%$ for a 0.05% change in $\Delta^{57}\text{Fe}_{\text{Mantle-Melt}}$), and the composition of the Martian mantle ($\pm 0.002\%$ per 0.01 change in Mg#). This value is lighter than that of the Earth's mantle based on abyssal peridotites ($\pm 0.04 \pm 0.04\%$; Crockdock et al., 2013), at the 1SD level, though indistinguishable at 2SD, and therefore distinction between them is limited by the precision of the technique. Other estimates for the Earth's mantle are resolvable heavier, however, including those derived from continental xenoliths ($+0.1\%$; Poitrasson et al., 2013) and terrestrial basalts ($+0.10 \pm 0.03\%$; Poitrasson, 2007; Poitrasson et al., 2004).

Owing to the isotopic scatter in terrestrial peridotites, isotopic differences between the Earth and Mars are better resolved by basaltic rocks (Fig. 5). Mid-Ocean Ridge Basalts, the most abundant magmas currently produced on Earth, have $0.57 < \text{Mg#} < 0.68$ (Jennner and O’Neill, 2012), with a mean of $0.62 \pm 0.02$ (1 SD), assuming 12% Fe$^{2+}$ (Bézou and Humler, 2005). At a given Mg#, MORBs are $\approx 0.1\%$ heavier in $\delta^{57}\text{Fe}$ than Martian shergottites, a relationship that holds for Hawaiian basalts and other tholeiitic magmas (Fig. 5). This difference outweighs the effect of increased isotope fractionation during partial melting on Earth, which would account for $\approx 0.03\%$ (Dauphas et al., 2014). Therefore, if the SNC meteorites are a suitable analogue for Martian volcanism, then the Martian mantle is resolvably lighter than that of its terrestrial counterpart.

5. Contrasted accretion of the terrestrial planets

5.1. A comparison of basaltic rocks

To better understand processes operating at the planetary scale, basalts are preferred over a hypothetical mantle, since no unambiguous records of planetary mantles exist. Three caves apply; firstly, fractional crystallisation of Fe–Mg minerals has a small effect on the iron isotope compositions of planetary magmas, depending on the redox state, where $\Delta^{57}\text{Fe}_{\text{Mantle-Melt}} \approx 0.15\% = \text{Earth (FMQ)} > \text{Mars} > \text{Moon (IV-1)} = 0\%$ (Section 4.3). In the same vein, partial melting causes enrichment of heavy iron in partial melts relative to sources, though this effect is smaller compared with fractional crystallisation, owing to the higher temperatures, $\Delta^{57}\text{Fe}_{\text{Mantle-Melt}} \approx 0.05\% = \text{Earth (FMQ)} > \text{Mars} > \text{Moon (IV-1)} = 0\%$ (Section 4.3). Finally, we assume that basalts are representative of the body, which may not be the case (see Section 4.2).

To mitigate bias arising from these uncertainties, primitive (high Mg#) basalts are selected. The ‘Mean Mafic Earch’, $\delta^{57}\text{Fe} = +0.10 \pm 0.03\%$ (Poitrasson et al., 2013) is assumed for the Earth, whereas near-primary shergottites give $\delta^{57}\text{Fe} = -0.01 \pm 0.02\%$, for Mars. For smaller bodies, low-Ti basalts were chosen to better represent the composition of the Moon, as high-Ti basalts have ilmenite in their source regions (caveat 3, e.g. Green et al., 1975). Similarly, the main trend Eucrites (as opposed to Stannern or Nuevo Laredo trend) were selected, owing to their higher Mg#s and lower TiO2 contents (Barrat et al., 2000). The limited number of angrite meteorites constrains an average to be taken from Wang et al. (2012), yielding $+0.19 \pm 0.02\%$. An average of the ureilite analyses of Barrat et al. (2015), $0.08 \pm 0.03\%$, is also represented, even though these are phaneritic, ultramafic partial melting residua.

Iron isotopes in basaltic rocks of inner solar system bodies show a more protracted range than chondrites, extending exclusively to heavier compositions. Only processes that involve a significant mass transfer of Fe, and/or are associated with a large isotope fractionation, can shift its composition on the planetary-scale. These constraints may be satisfied by i) core formation (e.g. Williams et al., 2012) and ii) volatile depletion (e.g., Poitrasson et al., 2004). In discerning between these two commonly invoked modes of fractionation, the Fe/Mn ratio is particularly useful. Manganese behaves like iron geochemically during magma petrogenesis (Davis et al., 2013) such that Fe/Mn remains roughly constant during partial melting and fractional crystallisation (Qin and Humayun, 2008). It does, however, differ in two important ways from Fe under conditions relevant to planet formation: Mn is more volatile and also far less siderophile. The Fe/Mn ratio in planetary basalts shows an excellent positive correlation with their iron isotope compositions (Fig. 7). In the following sections, possible mechanisms giving rise to this trend are explored.

5.2. Core formation

Though planetary bodies possess metallic cores, whether their formation, at disparate $P, T, X$ and $fO_2$ (Rai and van Westrenen, 2013; Righter and Drake, 1996; Rubie and Jacobson, 2015) causes iron isotope fractionation in the complementary mantle is uncertain. Despite this complexity, equilibrium isotope fractionation is subject to a $1/T^2$ dependence, therefore, all else being equal, core formation at lower temperatures should promote greater isotope fractionation. If temperatures of core–mantle equilibration over time reflect that of the peridotite liquids at the interface, then temperature should be directly proportional to pressure (given the positive $dP/dT$ slope of the peridotite liquids; Fiquet et al., 2010). Manganese becomes more siderophile at higher temperatures, with little effect of pressure (Mann et al., 2009). As a result, smaller bodies might be expected to show higher isotope fractionation and lower Fe/Mn ratios. However, the Eucrite parent body (IV-Vesta), despite undergoing core formation at relatively low temperature ($\approx 1900$ K, Righter and Drake, 1996), records no departure in iron isotope composition from that of chondrites. By contrast, the Earth, whose core last equilibrated with the mantle at 2500–3500 K (Wood et al., 2006), does exhibit resolvable fractionation. Furthermore, liquid metal and liquid silicate are isotopically indistinguishable in experiments between
1–7.7 GPa and 1250–2000 °C (Hin et al., 2012; Poitrasson et al., 2009) or light isotope enrichment in the silicate in the presence of $S$ occurs (Shahar et al., 2015), opposite to that observed. Despite this, Barrat et al. (2015) appeal to S-rich metal segregation to explain the heavy composition of ureilites. Nonetheless, Mars’ core is estimated to have $\sim 15$ wt% $S$ (Dreibus and Wanke, 1985), yet its composition is chondritic. The vector of isotope fractionation changes at high pressures, however owing to the incorporation of Fe$^{3+}$ in bridgmanite (Williams et al., 2012), a condition relevant to the Earth. However, mass balance dictates that this mechanism is not sufficient to generate a significant fractionation (Craddock et al., 2013) and in any case would not apply to the much smaller angrite parent body which nevertheless has the most $^{57}$Fe-enriched basalts. Additionally, since Mn does not appreciably partition into the core (log$K_{\text{Mn}} = -1.5$ to $-3$) except under very high temperatures (Mann et al., 2009), core formation would impart a relatively uniform Fe/Mn ratio in planetary mantles, lower than chondrites (Fig. 7). The Earth could be an exception to this, since its core formed at higher temperatures, thereby potentially further depleting Mn relative to other planetary bodies. However, the non-systematic relationship between iron isotope fractionation and modes of core formation, compounded by the lack of fractionation observed experimentally, render core formation an unlikely mechanism of generating the heavy isotope compositions of planetary basalts.

5.3. Volatile depletion

The temperature at which 1/2 of the Mn budget of the nebular gas is condensed, 1158 K, is almost 200 K lower than that of Fe (1334 K, Lodders, 2003). Hence, incomplete condensation or evaporation should increase the Fe/Mn ratio of the solid, processes thought to create Fe/Mn variations in planetary basalts (Drake et al., 1989; Papke et al., 2003). From the hierarchy in Fig. 7, angrites have experienced the greatest volatile depletion, followed by the Moon, Earth, ureilites then Mars and Vesta. These systems are compatible with a scenario in which volatile depletion (manifest as an increase in Fe/Mn) is associated with heavy isotope enrichment in the residue. Volatile loss during a giant impact has been proposed to account for the anomalously heavy Earth–Moon system (Poitrasson et al., 2004). However, identification of other bodies with similar (ureilites) or more extreme (angrites) signatures suggests this may be a common process in the inner solar system.

The extent of volatile depletion of an element, $E$, in a body ($B$) can be quantified by normalising it to a lithophile element thought not to be volatile, in this case, Mg. This ratio is then normalised to CI chondrites, whose abundances of moderately volatile elements match that of the solar photosphere, to give the elemental depletion factor, $f_E$:

$$ f_E = \frac{(E/Mg)_B}{(E/Mg)_{CI}}. \quad (3) $$

In Mars and IV-Vesta $f_{\text{Mn}} \approx 1$, implying no loss of Mn during their accretion. Since $T_{\text{Mn}}^{2O2} > T_{\text{Mn}}^{\text{Moon}}$, iron loss from these bodies did not occur, and, accordingly they preserve chondritic $^{57}$Fe ratios. Depletion factors for Mn in the Moon, Earth and angrites are comparable, 0.2–0.3, and are also associated with the heaviest $^{57}$Fe values, suggestive of a causative link between the two parameters. How, mechanistically, such a correlation might arise depends on the timing and locus of volatile depletion. Both Mn/Na (O’Neill and Palme, 2008) and Mn–Cr isotope systematics (Mouyrier et al., 2007) suggest Mn depletion in the Earth is nebular, that is, it occurred contemporaneously with that observed in chondritic meteorites. This, however, poses a problem since chondritic meteorites have uniform iron isotope compositions (Craddock and Dauphas, 2011), despite depletions in Mn. In carbonaceous chondrites (the only class 3 chondrites to show Mn depletion), $f_{\text{Mn}}$ only extends to $\approx 0.5$, and iron loss is minimal (Wasson and Kallemeyn, 1988), with resulting Fe/Mn ratios varying to an extent similar to that in planetary basalts. Therefore, the isotopic homogeneity among chondritic meteorites may be due to less extreme volatile depletion at lower temperatures (causing Mn loss but not appreciable Fe) compared with Earth’s precursors. Conversely, the superchondritic Mn/Na of angrites suggests that they underwent volatile loss at significantly higher oxygen fugacities (O’Neill and Palme, 2008), that is, after dissipation of the solar nebula. Nevertheless, multiple volatile depletion events cannot be excluded, for example, a nebular depletion that affected Fe and Mn, followed by a post-nebular process that resulted in Na loss. Regardless, extensive volatile depletion in angrites with respect to the Earth, as recorded by K/U or Na/Ti ratios (O’Neill and Palme, 2008), is consistent with their heavy Fe isotope composition.

Iron and magnesium share another useful property; the stable gaseous species of both take the form of monatomic metals ($M_{\text{Fe}}$) and $M_{\text{Mg}}$; Fegley, 1993), such that their dependence on the redox state of the gas is comparable. As much is observed in heating experiments, where Fe and Mn evaporate together (Floss et al., 1997). Writing expressions for their volatilisation,

$$ \text{FeO}_{(l,s)} = \text{Fe}_{(g)} + \frac{1}{2} \text{O}_2. \quad (4) $$

$$ \text{MnO}_{(l,s)} = \text{Mn}_{(g)} + \frac{1}{2} \text{O}_2. \quad (5) $$

demonstrates that the effect of oxygen fugacity cancels such that the two reactions can be equated, yielding:

$$ \text{FeO}_{(l,s)} + \text{Fe} = \text{FeO}_{(l,s)} + \text{Mn}_{(g)}. \quad (6) $$

and, at equilibrium, leads to

$$ \ln K = \ln \frac{\alpha_{\text{FeO}_{(l,s)}}}{p_{\text{Fe}_{(g)}}} \frac{p_{\text{Mn}_{(g)}}}{\alpha_{\text{MnO}_{(l,s)}}} = -\frac{(\Delta C_{\text{Mn-MnO}}^0 - \Delta C_{\text{Fe-FeO}}^0)}{RT}. \quad (7) $$

Here, $\Delta G^o$ are the standard state free energies for the reactions of the metal-oxide pair, $R$ the gas constant and $T$ the temperature in Kelvin (note that ideality is assumed). For a finite elemental budget, $M_{(g)}$ is the proportion of the metal in the gas, and therefore $M_{(g)} = (1 - M_{(g)})$. Employing existing thermodynamic data (Chase, 1998), $\Delta G_{Fe-Mn}^{\text{FeO}}$ (kJ/mol) $= -51.7 + 0.09087 - 0.009777T \ln(T)$, such that the relative fraction of Fe to Mn in the gas, assuming a constant pressure, is dependent only on temperature. If volatile depletion occurred at high temperatures (e.g. 3000 K during a giant impact; Melosh, 1990), a similar fraction of Fe and Mn would be lost, implying wholesale iron depletion in terrestrial bodies, which is not recorded. Therefore, volatile depletion must have taken place at significantly lower temperatures, $\approx 1300$ K, as constrained by element abundances in the Earth and Moon for a giant impact scenario (O’Neill, 1991), or upon equilibration condensation of the solar nebula. Since Fe depletion relative to Mn is independent of $f_O$, these two scenarios cannot be distinguished on the basis of Fe/Mn ratios alone, though Mn (and therefore Fe) depletion in the Earth appears to be nebular in origin, as discussed above. Conversely, the Moon’s slightly higher Fe/Mn ratio ($\approx 70$) relative to the Earth permits additional, post-nebular volatile loss, perhaps during the giant impact, though again at 1300 K (O’Neill, 1991). Therefore, adopting temperatures of 1300 K, and an initial Fe/Mn of 35 (Fig. 7), the Fe/Mn ratio in the residual solid as a function of volatile depletion is modelled. Under these conditions, $7 \pm 2$ Fe depletion is required to explain the Fe/Mn ratio of the silicate Earth (60 ± 6), 10 ± 1% for the Moon, and 20 ± 5% for angrites (Fe/Mn = 95 ± 13).

Whether such a process can reproduce the isotopic trend observed in Fig. 7 requires prior knowledge of FeO–Fe$_{(g)}$ isotope fractionation factors, which are, unfortunately, lacking. However, fractionation factors for the equivalent reaction between MgO and Mg$_{(g)}$ have been determined, where $\Delta^{26}MgO-Mg = 2.2 \times 10^{0}/T^{2}$$\%_e$ (Schauble, 2011). Given the ideality of the Fe–Mg solid solution in olivine (Bradley, 1962) and the equality in volatility isotope stoichiometry (eq. (4)) for Fe and Mg, to a good approximation, the iron isotopic fractionation factor can be simply related to that of Mg by the relative isotopic mass difference:

$$\Delta^{57}Fe^{\text{FeO-Fe}} = \left(\frac{57}{26}\right) \times \Delta^{26}MgO-Mg = 1.5 \times 10^{0}/T^{2}$$

At 1300 K, $\Delta^{57}Fe^{\text{FeO-Fe}} = 0.9\%_e$. The isotopic composition of the solid or liquid (FeO) is found assuming a closed-system, Rayleigh distillation process, wherein:

$$\delta^{57}Fe^{\text{FeO}} = \delta^{57}Fe^{\text{bulk}} + \Delta^{57}Fe^{\text{FeO-Fe}} \ln(f_{FeO})$$

$\delta^{57}Fe^{\text{bulk}}$ is assumed to be chondritic (0\%_e for simplicity), and $f_{FeO}$ is given by eq. (7). Together, these calculations very faithfully match the observed iron isotope trends in planetary basaltic systems (Fig. 7). Upon solar nebula condensation, Fe also partitions into metal, particularly in enstatite chondrites. However, since FeO (in olivine or silicate liquid) has an indistinguishable isotope composition to Fe metal at 1523 K (e.g., Hin et al., 2012) and in unequilibrated chondrites (Theis et al., 2008), the net iso3tope fractionation factor (eq. (8)) will be little affected.

5.4. A volatile history of the terrestrial planets

That Fe is controlled by volatility-related processes is also substantiated by Si isotopes (Fig. 8). Despite their vastly different geochemical properties, iron and silicon isotopes in planetary basalts are remarkably well correlated (Fig. 8), suggesting that planetary isotope differences are faithfully captured by basaltic rocks.

The large Si isotope metal–silicate fractionation (Hin et al., 2014; Shahar et al., 2011), is, alone, insufficient in explaining the isotopic discrepancy between chondrites and Earth (Zambardi et al., 2013), and especially angrites, whose parent body would have no Si in its core (Dauphas et al., 2015; Pringle et al., 2014). Furthermore, iron- and silicon isotope metal–silicate fractionation factors are in opposing directions (compare Hin et al., 2014 and Shahar et al., 2015), and therefore a negative correlation would be expected if core formation was the controlling influence. Rather, to explain Si isotope variations, volatile processes have been widely championed, either at a late (Pringle et al., 2014; Zambardi et al., 2013) or early, nebular stage (Dauphas et al., 2015). Silicon, like Fe, is not normally volatile during nebular condensation (e.g. Wasson and Kallemeyn, 1988) or evaporation, except, it appears, in cases where volatile depletion is pronounced, as for the Earth–Moon system and angrite parent body. The fractionation factor between SiO$_2$ (in forsterite) and SiO$_{(g)}$, the stable gas phase, is $\Delta^{30}Si = 4.2 \times 10^{6}/T^{2}$ (Dauphas et al., 2015), $\sim 3 \times$ larger than that for $\Delta^{57}Fe$ (Eq. (8)), predicting a slope of 0.36 in Fig. 8. The observed slope, $\sim 0.5$, indicates larger Fe isotope variation than expected, which could arise from the slightly higher volatility of Fe than Si. Isotopic characterisation of inner solar system bodies for elements that bracket the volatility of Fe, but otherwise behave similarly during igneous processes, namely Zn and Mg, may aid in further elucidating causes of isotope fractionation.

Mars and IV-Vesta preserve their initial Mn budget and are unfractuated from chondritic meteorites in Fe–Si isotope space. In the case of the Earth, volatile depletion is probably nebular, implying that the composition of the Earth is non-chondritic, with respect to both Si and Fe. That the Moon shows a composition indistinguishable (Si) or close to (Fe) that of the Earth lends support to the idea that it was inherited from the Earth’s mantle, as suggested by elemental abundances and isotope systematics (O’Neill, 1991; Ringwood and Kesson, 1977; Zhang et al., 2012). However, the slight differences in Fe/Mn and potentially Fe isotopes (Wang et al., 2015) between the Earth and Moon allow for further lunar volatile depletion, perhaps attending the giant impact. Angrites exhibit the most extreme fractionation in all indices; Fe/Mn, $\delta^{30}Si$ and $\delta^{57}Fe$. Although their non-chondritic Mn/Na suggests post-nebular volatile depletion, Rb–Sr chronology permits the possibility of incomplete nebular condensation, too (Hans et al., 2013). All plane-
tary basalts show differing patterns of moderately-volatile element depletion relative to carbonaceous chondrites. These patterns are the sum of physicochemical parameters such as temperature and oxygen fugacity, and dynamical controls including impact energetics and frequency, and solid-gas mechanics. Therefore, much of the interpretation of the evolution of the terrestrial planets hinges upon the style and timing of volatile depletion, the details of which remain uncertain.

6. Conclusion

Application of the olivine–melt equilibrium Fe–Mg Kp reveals that few Martian shergottites are representative of liquid compositions, with several more falling on olivine control lines that allow for correction to primary magmas. These have Mg#s between 0.5 and 0.65, which can be modelled, using alphaMELTS, to be 10–50% partial melts of a Martian mantle with Mg# = 0.77. The iron isotope compositions of SNC meteorites become heavier for more evolved magmas, defining an array with δ57Fe = −0.1%, smaller than that for terrestrial basalts. This reflects the more reduced redox state of Fe in Martian magmas, resulting in lower δ57Fe. At the same Mg#, Martian basalts are ∼0.1% lighter than terrestrial tholeiitic basalts. Extrapolation of the correlation between δ57Fe and Mg# for SNCs yields a Martian mantle value of −0.04 ± 0.03‰ (1SD), appreciably lighter than that of Earth at the 1SD level, but within uncertainty of chondrites. Owing to the paucity of mantle samples from other planetary bodies, primitive basalts rocks are used to investigate causes of iron isotope fractionation during planetary accretion. Basaltic rocks vary from chondritic values (δ57Fe ≈ 0‰) in Mars and IV-Vesta, +0.1‰ in the Earth and Moon and up to +0.2‰ in angrites, as a positive function of their Fe/Mn ratio and Si isotope composition. Such variation can be explained by progressive volatile depletion giving rise to heavy values in the residuum. For the Earth, iron isotope fractionation likely arises during solar nebula condensation, near 1300 K, requiring ∼7% Fe depletion, however additional, post-nebular volatile loss might have occurred on the Moon and the angrite parent body.

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Appendix A. Supplementary material

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