The iron isotope composition of enstatite meteorites: Implications for their origin and the metal/sulfide Fe isotopic fractionation factor

Kun Wang\textsuperscript{a,b,*}, Paul S. Savage\textsuperscript{a,c,d}, Frédéric Moynier\textsuperscript{a,d}

\textsuperscript{a}Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St Louis, One Brookings Drive, St. Louis, MO 63130, USA
\textsuperscript{b}Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA
\textsuperscript{c}Department of Earth Sciences, Durham University, Science Labs, Durham DH1 3LE, United Kingdom
\textsuperscript{d}Institut de Physique du Globe de Paris, Institut Universitaire de France, Université Paris Diderot, Sorbonne Paris Cité, 1 rue Jussieu, 75238 Paris Cedex 05, France

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Abstract

Despite their unusual chemical composition, it is often proposed that the enstatite chondrites represent a significant component of Earth’s building materials, based on their terrestrial similarity for numerous isotope systems. In order to investigate a possible genetic relationship between the Fe isotope composition of enstatite chondrites and the Earth, we have analyzed 22 samples from different subgroups of the enstatite meteorites, including EH and EL chondrites, aubrites (main group and Shallowater) and the Happy Canyon impact melt. We have also analyzed the Fe isotopic compositions of separated (magnetic and non-magnetic) phases from both enstatite chondrites and achondrites.

On average, EH3–5 chondrites (Δ\textsuperscript{56}Fe = 0.003 ± 0.042\% 2 standard deviation; \(n = 9\); including previous literature data) as well as EL3 chondrites (Δ\textsuperscript{56}Fe = 0.030 ± 0.038\% 2 SD; \(n = 2\)) have identical and homogeneous Fe isotopic compositions, indistinguishable from those of the carbonaceous chondrites and average terrestrial peridotite. In contrast, EL6 chondrites display a larger range of isotopic compositions (–0.180\% < Δ\textsuperscript{56}Fe < 0.181\%; \(n = 11\)), a result of mixing between isotopically distinct mineral phases (metal, sulfide and silicate). The large Fe isotopic heterogeneity of EL6 is best explained by chemical/mineralogical fragmentation and brecciation during the complex impact history of the EL parent body.

Enstatite achondrites (aubrites) also exhibit a relatively large range of Fe isotope compositions: all main group aubrites are enriched in the light Fe isotopes (Δ\textsuperscript{56}Fe = −0.170 ± 0.189\% 2 SD; \(n = 6\)), while Shallowater is, isotopically, relatively heavy (Δ\textsuperscript{56}Fe = 0.045 ± 0.101\% 2 SD; \(n = 4\); number of chips). We take this variation to suggest that the main group aubrite parent body formed a discreet heavy Fe isotope-enriched core, whilst the Shallowater meteorite is most likely from a different parent body where core and silicate material remixed. This could be due to intensive impact-induced shearing stress, or the ultimate destruction of the Shallowater parent body.

Analysis of separated enstatite meteorite mineral phases show that the magnetic phase (Fe metal) is systematically enriched in the heavier Fe isotopes when compared to non-magnetic phases (Fe hosted in troilite), which agrees with previous experimental observations and theoretical calculations. The difference between magnetic and non-magnetic phases from enstatite achondrites provides an equilibrium metal-sulfide Fe isotopic fractionation factor of Δ\textsuperscript{56}Fe\textsubscript{metal–troilite} = Δ\textsuperscript{56}Fe\textsubscript{metal} − Δ\textsuperscript{56}Fe\textsubscript{troilite} of 0.129 ± 0.060\% (2 SE) at 1060 ± 80 K, which confirms the predictions of previous theoretical calculations.
1. INTRODUCTION

Enstatite chondrites have received much attention due to their remarkable resemblance to the Earth with respect to various isotope systems, notably O, but also N, Ti, Cr, Ni, Sr, Mo, Ru, and Os (Javoy and Pineau, 1983; Clayton et al., 1984; Dauphas et al., 2004; Trinquier et al., 2007, 2009; Regelous et al., 2008; Chen et al., 2010; Moynier et al., 2012; Steele et al., 2012). This has led some authors to propose that enstatite chondrites comprised a substantial component of the “building blocks” of the proto-Earth, or that enstatite chondrites and Earth have the same precursor materials (Javoy, 1995; Javoy et al., 2010; Kaminski and Javoy, 2013). However, it is difficult to reconcile the refractory lithophile element (e.g., Al, Si, Mg) budget of enstatite chondrites with the current composition of the terrestrial mantle (Larimer and Anders, 1970; Baedecker and Wasson, 1975). In addition, significant Si isotopic differences exist between the terrestrial mantle and enstatite chondrites, which would require an unrealistic amount of Si in the Earth’s core if the Si isotopic fractionation was mainly due to metal/silicate differentiation, or other alternative scenarios (i.e., an isotopically light lower mantle or preferential light Si isotope loss during impacts; Fitoussi and Bourdon, 2012; Savage and Moynier, 2013; Zambardi et al., 2013).

After O, Fe is the most abundant element on Earth. Given this, understanding the relationship between the Fe isotopic compositions of enstatite chondrites and Earth may be important for testing the enstatite chondritic Earth model. The enstatite meteorites include both the enstatite chondrites and the differentiated enstatite achondrites, also known as aubrites. Enstatite chondrites can be further divided into two subgroups: the Fe-rich EH and the Fe-poor EL. Each of these groups is composed of several petrographic types according to their degree of thermal metamorphism: EH3–6 and EL3–6 (Huss et al., 2006), with 3 being the least altered. The genetic relationship between EL and EH is still debated. Based on the relationship of moderately volatile element abundances with petrographic type between EH and EL groups, Kong et al. (1997) proposed that both meteorite families originated from a single parent body, while Keil (1989) considered that they were derived from two separate parent bodies based on the absence of EL clasts in EH chondrites (and vice versa). In addition, Savage and Moynier (2013) shows that the two groups also have different Si isotope compositions. Happy Canyon is an impact-melt breccia, probably of enstatite chondritic parentage, but the precise origin of the precursor is debated; it seems that material of EL3-chondrite composition is the most likely possibility (McCoy et al., 1995; Moynier et al., 2011).

Enstatite achondrites (aubrites) are FeO-poor enstatite orthopyroxenites, which formed under very reducing conditions (Keil, 1989), comparable to those of the enstatite chondrites. All the aubrites (except Shallowater) are brecciated and appear to have formed on the same parent body (Keil, 1989). In contrast, the Shallowater aubrite is the only unbrecciated aubrite and probably comes from a distinct parent body (Keil, 1989; Moynier et al., 2011). A comprehensive study of the Fe isotopic compositions of enstatite meteorites could provide some insights on the genetic relationships between these subgroups. To date, such an investigation has not been performed.

Even though the few existing Fe isotope data for enstatite chondrites appears, on average, similar to that of carbonaceous chondrites (e.g., Craddock and Dauphas, 2011), some samples have shown large and intriguing variations. For example, the EL6 meteorite Blithfield shows a depletion by of 0.140‰ in $^{56}$Fe (Dauphas et al., 2009; $^{56}$Fe/$^{54}$Fe ratio expressed as parts per 1000 deviations relative to the standard IRMM-014), whereas another EL6, Daniel’s Kuit, is enriched by 0.121‰ in $^{56}$Fe (Craddock and Dauphas, 2011). Due to the limited amount of Fe isotopic data available, no compositions of EL3 (unmetamorphosed EL6 precursors) have been reported; hence, the interpretation of the enrichment in both light and heavy isotopes is difficult. In this study, we focus on the entire enstatite meteorite group, derived from at least four distinct parent bodies (EH, EL, aubrite-main group and aubrite-Shallowater), to systematically investigate their Fe isotopic variations using Multi-Collector Inductively-Coupled-Plasma Mass Spectrometry (MC-ICPMS). In addition to bulk samples, we have also studied phase separates (magnetic and non-magnetic phases) to assess to what extent igneous processes such as metal/silicate/sulfide separation have affected the Fe isotopic compositions of the enstatite meteorites. The main goal of this study is to investigate the Fe isotopic composition of the enstatite meteorites, in terms of variations within this meteorite class, as well as in comparison to other meteorite groups and the terrestrial mantle.

In addition, utilizing mineral separate data of enstatite achondrites (equilibrated high-temperature igneous rocks in contrast to unequilibrated/partially-equilibrated enstatite chondrites), we aim to provide an empirical estimate of the equilibrium Fe isotope fractionation factor between metal and sulfide. This metal/sulfide fractionation factor has been evaluated by theoretical calculations based on experimental Mössbauer spectroscopy or nuclear resonant inelastic X-ray scattering (NRIXS) data (Polyakov and Soultanov, 2011; Polyakov et al., 2007), or by ab initio calculation (Blanchard et al., 2012), however, there is still disagreement on these theoretically calculated fractionation factors by different research groups (Blanchard et al., 2012; Polyakov and Soultanov, 2012). Previously, enstatite achondrites have been demonstrated as ideal materials to obtain the Si isotope equilibrium fractionation factors between metal and silicate (Ziegler et al., 2010) and Fe isotope equilibrium fractionation factors between metal and silicate (Jordan and Young, 2014). Here we acquire a metal/sulfide Fe isotope fractionation factor through measurements of the metal and sulfide phases in enstatite achondrites, which can be used in more general applications.

2. SAMPLES AND METHODS

2.1. Sample description

We have studied twenty-two bulk meteorite samples, likely representative of four (EH, EL, aubrite-main group
and aubrite- Shallowater) enstatite meteorite parent bodies. Fifteen enstatite chondrites include two EH3 (Kota- Kota and Qingzhen), two EH4 (Abee and Indarch), two EL3 (MAC 88184 and PCA 91020), eight EL6 (Atlanta, Blithfield, Eagle, Hvittis, Khaipur, LON 94100, North West Forrest, and Yilmia) and the Happy Canyon impact melt. Six aubrite samples were analyzed from the aubrite main group (ALH 84007, Aubres, Bustee, Cumberland Falls, Khor Temiiki, and Norton County) and one from Shallowater. All the main group aubrites are brecciated: Bustee and Khor Temiiki are regolith breccias, Cumberland Falls is a polymict breccia and the remaining main group aubrites are monomict fragmental breccias (Kell, 1989, 2010; Rubin, 2010). Shallowater is the only unbrecciated sample.

To test the degree of Fe isotopic heterogeneity within bulk enstatite meteorite samples, different chips of the same meteorites (Norton County-3 chips; Shallowater-3 chips; and Blithfield-2 chips) were analyzed separately.

Finally, in order to test the accuracy of our measurements we analyzed the Fe isotopic composition of two previously well-characterized USGS geostandards: USGS GSP-1, a granoidite from the Silver Plume Quarry, Colorado and USGS AGV-1, an andesite from Guano Valley, Oregon.

2.2. Analytical methods

Meteorite chips of ~500–1000 mg were crushed into a fine powder in an agate pestle and mortar. For enstatite chondrites, ~10 mg were dissolved under pressure in Parr bombs in concentrated HNO3/HF for several days; the rest of the samples were dissolved in concentrated HNO3/HF in closed Teflon beakers.

In addition to whole-rock dissolution, selected aubrites and enstatite chondrites were subjected to phase separation, whereby magnetic and non-magnetic phases were separated with a hand magnet. The magnetic phase (metal) was dissolved in aqua regia. The non-magnetic fraction (silicate and non-magnetic sulfide) was dissolved in concentrated HNO3/HF. Fine silicates often adhere to the metal particles separated by hand-magnet (Torigoye and Shima, 1993). The isotopic compositions measured here for the different phases will therefore represent the minimum isotopic variations between the pure phases.

Iron was purified by anion-exchange chromatography using the same procedure employed in our previous studies (Wang et al., 2011, 2012a, b, 2013). The samples were dissolved in 6 N HCl, centrifuged and loaded on 1 ml AG-1X8 (200–400 mesh) chromatographic columns; Fe was extracted in 0.4 N HCl. This process was repeated to further purify Fe. Iron isotope ratios were measured on either a Thermo Scientific Neptune or Neptune Plus MC-ICPMS at the University of Chicago or Washington University in St. Louis (respectively). Isotopic ratios are expressed as parts per 1000 deviations (‰) relative to the standard IRMM-014 in Eq. (1):

\[
\delta^{56}\text{Fe} = \left( \frac{\langle \text{Fe}^{56}/\text{Fe}^{54}\rangle_{\text{sample}}}{\langle \text{Fe}^{56}/\text{Fe}^{54}\rangle_{\text{IRMM-014}}} - 1 \right) \times 1000 \tag{1}
\]

where \( x = 56 \) or 57. Every sample was measured 8 or 9 times. The analytical uncertainties are reported as 2 standard error (2SE), calculated as the standard deviation (2SD) divided by the square root of the total number of analyses and multiplied by the Student’s t-value for the relevant degree of freedom at the 95% confidence level. The 2SE values are typically better than \( \delta^{56}\text{Fe} = 0.030\% \) for most of the samples (see Tables 1 and 2).

3. RESULTS

Iron isotopic compositions are reported in Table 1 for bulk enstatite meteorites and geostandards, and in Table 2 for separated mineral phases from enstatite meteorites. The terrestrial standard GSP-1 \( (\delta^{56}\text{Fe} = 0.143 \pm 0.027\% ) \) and 3 different dissolutions of AGV-1 \( (\delta^{56}\text{Fe} = 0.101 \pm 0.027\% , 0.115 \pm 0.028\% , \text{and } 0.097 \pm 0.021\% ) \) are all in excellent agreement with previously published values for GSP-2 and AGV-2 which although different samples, are taken from the same outcrops (see Table 1).

Literature data for enstatite chondrites (Zhu et al., 2001; Poittrasson et al., 2005; Schoenberg and von Blankenburg, 2006; Craddock and Dauphas, 2011) are also included in Table 1 for comparison and are used in the group averages reported below. As expected for mass-dependent isotopic fractionation, all the data fall on a straight line of slope ~1.5 on a three-isotope \( \delta^{56}\text{Fe} \) vs. \( \delta^{56}\text{Fe} \) plot (Fig. 1).

3.1. Iron isotope compositions of bulk enstatite meteorites

As shown in Fig. 2, the Fe isotope data for EH chondrites ranges from \( \delta^{56}\text{Fe} = -0.016 \pm 0.057\% \) to \( 0.009 \pm 0.023\% \). The EL3 are similar to EH chondrites with a range of \( 0.016 \pm 0.018-0.043 \pm 0.029\% \). The EL6 show more variability, viz. \( \delta^{56}\text{Fe} \) from \( -0.180 \pm 0.027\% \) to \( 0.181 \pm 0.021\% \) and the impact melt Happy Canyon is enriched in the heavier isotopes with a \( \delta^{56}\text{Fe} \) of 0.143 \pm 0.041\% .

The absence of Fe isotopic fractionation in EH chondrites confirms previous observations, based on scant data (Zhu et al., 2001; Poittrasson et al., 2005; Schoenberg and von Blankenburg, 2006; Craddock and Dauphas, 2011). However, our data for the EL6 and impact melt enstatite chondrites (which are possibly of EL parentage, see later) do not always agree with previous data (see Table 1). For example, one of our two chips of Blithfield \( \delta^{56}\text{Fe} = -0.122 \pm 0.018\% \) is in fairly good agreement with data reported by Dauphas et al. (2009) \( \delta^{56}\text{Fe} = -0.140 \pm 0.030\% \) whereas the second chip \( \delta^{56}\text{Fe} = 0.030 \pm 0.031\% \) is markedly different. We attribute these disagreements to isotopic heterogeneity of EL6, and we will explore it in detail in Section 4.

When combined with previous data, the different groups of enstatite meteorites give the following average values: EH3–5 \( \delta^{56}\text{Fe} = 0.003 \pm 0.042\% \); 2 standard deviation; \( n = 9 \); number of individual meteorites; EL3 \( \delta^{56}\text{Fe} = 0.030 \pm 0.038\% \); 2 SD; \( n = 2 \); EL6 \( \delta^{56}\text{Fe} = 0.016 \pm 0.195\% \); 2 SD; \( n = 11 \); impact melt enstatite chondrites \( \delta^{56}\text{Fe} = 0.094 \pm 0.015\% \); 2 SD; \( n = 2 \); aubrite main group \( \delta^{56}\text{Fe} = -0.170 \pm 0.189\% \); 2 SD; \( n = 6 \); and the
Table 1
Iron isotope compositions of enstatite meteorites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Fall/find</th>
<th>Shock stage</th>
<th>Mass (mg)</th>
<th>Fe (wt.%)</th>
<th>$\delta^{56}$Fe ($^{16}$O) ± 2 SE</th>
<th>$\delta^{57}$Fe ($^{16}$O) ± 2 SE</th>
<th>n</th>
<th>Museum code</th>
</tr>
</thead>
<tbody>
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<td>Kota-Kota</td>
<td>EH3</td>
<td>Find</td>
<td>S3</td>
<td>15.0</td>
<td>-0.016 ± 0.057</td>
<td>-0.027 ± 0.086</td>
<td>5</td>
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<td>Qingzhen</td>
<td>EH3</td>
<td>Fall</td>
<td>S3</td>
<td>27.4</td>
<td>0.009 ± 0.023</td>
<td>0.031 ± 0.075</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sahara 97072</td>
<td>EH3</td>
<td>Find</td>
<td>S2</td>
<td>28.8</td>
<td>-0.002 ± 0.053</td>
<td>-0.015 ± 0.071</td>
<td>9</td>
<td></td>
<td></td>
</tr>
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<td>Abee</td>
<td>EH4</td>
<td>Fall</td>
<td>S2–S4</td>
<td>36.5</td>
<td>0.002 ± 0.027</td>
<td>-0.030 ± 0.050</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhi Kot</td>
<td>EH4</td>
<td>Find</td>
<td>S3</td>
<td>29.5</td>
<td>0.017 ± 0.053</td>
<td>0.022 ± 0.071</td>
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<td>AMNH 3993</td>
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<td>0.027 ± 0.051</td>
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<td>EH4</td>
<td>Fall</td>
<td>S3</td>
<td>28.3</td>
<td>0.010 ± 0.032</td>
<td>0.033 ± 0.048</td>
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<td>0.005 ± 0.091</td>
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<td>Indarch</td>
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<td>0.110 ± 0.060</td>
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<td>St. Mark’s</td>
<td>EH5</td>
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<td>29.8</td>
<td>0.047 ± 0.054</td>
<td>0.058 ± 0.072</td>
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<td>29.1</td>
<td>-0.035 ± 0.033</td>
<td>-0.022 ± 0.067</td>
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<td>MAC 88184</td>
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<td>Find</td>
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<td>0.043 ± 0.029</td>
<td>0.059 ± 0.047</td>
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<td>0.055 ± 0.036</td>
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<td>EL6</td>
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<td>S2</td>
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<td>Find</td>
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<td>23.7</td>
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<td>0.037 ± 0.045</td>
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<td>EL6</td>
<td>Find</td>
<td>S4</td>
<td>18.9</td>
<td>0.064 ± 0.036</td>
<td>0.100 ± 0.046</td>
<td>9</td>
<td>FM 2740</td>
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</tr>
<tr>
<td>Happy Canyon</td>
<td>Impact melt</td>
<td>Find</td>
<td>S2</td>
<td>8.7</td>
<td>0.143 ± 0.041</td>
<td>0.233 ± 0.076</td>
<td>8</td>
<td>ASU 1058f</td>
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<tr>
<td>Happy Canyon</td>
<td>Impact melt</td>
<td>Find</td>
<td>S2</td>
<td>16.3</td>
<td>0.056 ± 0.035</td>
<td>0.099 ± 0.040</td>
<td>9</td>
<td>FM 2760</td>
<td></td>
</tr>
<tr>
<td>Ilafegh 009</td>
<td>Impact melt</td>
<td>Find</td>
<td>S4</td>
<td>23.2</td>
<td>0.089 ± 0.033</td>
<td>0.143 ± 0.046</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Description</td>
<td>Find</td>
<td>Mass (g)</td>
<td>Error (g)</td>
<td>146Sm (ppm)</td>
<td>Error (ppm)</td>
<td>147Sm (ppm)</td>
<td>Error (ppm)</td>
<td>Museum Code</td>
<td></td>
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<tr>
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<tr>
<td>ALH 84007 Aubrite (main group) Fall</td>
<td>S4</td>
<td>12.0</td>
<td>0.3</td>
<td>−0.205 ± 0.016</td>
<td>−0.293 ± 0.046</td>
<td>9 JSC</td>
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<td>Aubres Aubrite (main group) Fall</td>
<td></td>
<td>4.2</td>
<td>0.6</td>
<td>−0.182 ± 0.024</td>
<td>−0.240 ± 0.037</td>
<td>9 NHM 63552</td>
<td></td>
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<tr>
<td>Bustee Aubrite (main group) Fall</td>
<td></td>
<td>3.6</td>
<td>0.3</td>
<td>−0.008 ± 0.031</td>
<td>0.012 ± 0.048</td>
<td>9 NHM 32100</td>
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<tr>
<td>Khor Temiki Aubrite (main group) Fall</td>
<td></td>
<td>4.4</td>
<td>0.9</td>
<td>−0.160 ± 0.014</td>
<td>−0.274 ± 0.058</td>
<td>9 NHM 1934,781</td>
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<tr>
<td>Norton County chip 1 Aubrite (main group) Fall</td>
<td></td>
<td>0.7</td>
<td></td>
<td>−0.156 ± 0.021</td>
<td>−0.234 ± 0.035</td>
<td>9 UNM</td>
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<tr>
<td>Norton County chip 2 Aubrite (main group) Fall</td>
<td></td>
<td>9.4</td>
<td>0.8</td>
<td>−0.157 ± 0.030</td>
<td>−0.227 ± 0.035</td>
<td>9 UNM</td>
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<tr>
<td>Norton County chip 3 Aubrite (main group) Fall</td>
<td></td>
<td>10.9</td>
<td>0.4</td>
<td>−0.167 ± 0.039</td>
<td>−0.258 ± 0.055</td>
<td>9 UNM</td>
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<tr>
<td>Shallowater chip 1 Aubrite (Shallowater) Find</td>
<td>S2</td>
<td>14.0</td>
<td></td>
<td>−0.029 ± 0.028</td>
<td>−0.019 ± 0.038</td>
<td>9 USNM 1206</td>
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<td>Shallowater chip 2 Aubrite (Shallowater) Find</td>
<td>S2</td>
<td>7.4</td>
<td>7.0</td>
<td>0.067 ± 0.029</td>
<td>0.077 ± 0.068</td>
<td>9 USNM 1206</td>
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<tr>
<td>Shallowater chip 2 (replicates) Aubrite (Shallowater) Find</td>
<td>S2</td>
<td>7.0</td>
<td></td>
<td>0.084 ± 0.021</td>
<td>0.071 ± 0.120</td>
<td>9 USNM 1206</td>
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<tr>
<td>Shallowater chip 3 Aubrite (Shallowater) Find</td>
<td>S2</td>
<td>5.3</td>
<td>18.2</td>
<td>0.058 ± 0.030</td>
<td>0.093 ± 0.043</td>
<td>9 ASU 318.9</td>
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</tbody>
</table>

AGV1 Geostandard
AGV1 Geostandard
AGV1 Geostandard
AGV2 Geostandard
GSP1 Geostandard
GSP2 Geostandard

---

- Shock stage values are from Rubin et al. (1997, 2009), Rubin (2010), Izawa et al. (2011) and Grossman (1998). Values for Sahara 97072 and MAC 88184 are from those of their paired meteorites Sahara 97096 and MAC 88136, respectively.
- The analytical uncertainties are 2 standard errors (2 SE = standard deviation divided by the square root of the total number of analyses and multiplied by Student’s t-value for the relevant degree of freedom at the 95% confidence level) for data from this study or reported uncertainties for data from literatures.
- Number of measurements.
- Data from Craddock and Dauphas (2011).
- Data from Schoenberg and von Blanckenburg (2006).
- Data from Poitrasson et al. (2005).
- Data from Zhu et al. (2001).
- Data from Zhang et al. (1995).
Shallowater aubrite ($\delta^{56}\text{Fe} = 0.045 \pm 0.101\%_{\text{oo}}$; $n = 4$; number of chips). More importantly, EL6 chondrites ($-0.180\%_{\text{oo}} < \delta^{56}\text{Fe} < 0.181\%_{\text{oo}}$) and aubrites ($-0.302\%_{\text{oo}} < \delta^{56}\text{Fe} < 0.084\%_{\text{oo}}$) display a large range of isotopic compositions. The ranges of $\delta^{56}\text{Fe}$ variations in different groups are shown in both Figs. 1 and 2. Except for the aubrite and impact melt enstatite chondrites, all enstatite meteorite groups have the same average Fe isotopic composition as carbonaceous chondrites ($\delta^{56}\text{Fe} = 0.02 \pm 0.04\%_{\text{oo}}$; $2\text{ SE}$; Wang et al., 2013) and abyssal peridotites ($\delta^{56}\text{Fe} = 0.010 \pm 0.007\%_{\text{oo}}$; 95% confidence interval; Craddock et al., 2013).

### 3.2. Iron isotopic compositions of separated mineral phases

The magnetic phases (Fe from Fe-metal) from enstatite meteorites are all (with the exception of the impact melts) systematically enriched in heavy Fe isotopes when compared to the non-magnetic phases (Fe from non-magnetic sulfide, dominated by troilite; see Section 4.5 for discussion.}

#### Table 2: Iron isotope compositions of mineral fractions of aubrites and enstatite chondrites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral Type</th>
<th>Fall/find</th>
<th>Fe (wt.%)</th>
<th>$\delta^{56}\text{Fe}$ ($<em>{%</em>{\text{oo}}}$) ± 2 SE</th>
<th>$\delta^{57}\text{Fe}$ ($<em>{%</em>{\text{oo}}}$) ± 2 SE</th>
<th>n</th>
<th>Museum code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallowater chip 1</td>
<td>Metal Aubrite Find 1</td>
<td>30.1</td>
<td>0.075 ± 0.059</td>
<td>0.114 ± 0.097</td>
<td>8 USNM 1206</td>
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</tr>
<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>1.5</td>
<td>0.021 ± 0.042</td>
<td>0.037 ± 0.082</td>
<td>6 USNM 1206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shallowater chip 2</td>
<td>Metal Aubrite Find 2</td>
<td>46.4</td>
<td>0.039 ± 0.044</td>
<td>0.054 ± 0.047</td>
<td>8 USNM 1206</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>5.8</td>
<td>-0.090 ± 0.041</td>
<td>-0.108 ± 0.062</td>
<td>6 USNM 1206</td>
<td></td>
<td></td>
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<tr>
<td>Qingzhen</td>
<td>Metal EH3 Fall 3</td>
<td>43.0</td>
<td>0.077 ± 0.024</td>
<td>0.115 ± 0.038</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>8.6</td>
<td>-0.185 ± 0.031</td>
<td>-0.288 ± 0.053</td>
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<td>Abee</td>
<td>Metal EH4 Fall 4</td>
<td>47.4</td>
<td>0.055 ± 0.037</td>
<td>0.110 ± 0.010</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>14.3</td>
<td>-0.072 ± 0.048</td>
<td>-0.101 ± 0.037</td>
<td>4</td>
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<tr>
<td>Indarch</td>
<td>Metal EH4 Fall 5</td>
<td>41.5</td>
<td>0.106 ± 0.038</td>
<td>0.167 ± 0.100</td>
<td>7 FM 1404</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>12.2</td>
<td>-0.184 ± 0.033</td>
<td>-0.263 ± 0.018</td>
<td>5 FM 1404</td>
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<tr>
<td>St. Mark’s</td>
<td>Metal EH5 Fall 6</td>
<td>50.9</td>
<td>0.155 ± 0.050</td>
<td>0.238 ± 0.059</td>
<td>7 USNM 3027</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>5.8</td>
<td>-0.338 ± 0.043</td>
<td>-0.509 ± 0.086</td>
<td>5 USNM 3027</td>
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<tr>
<td>MAC 88184</td>
<td>Metal EL3 Find 7</td>
<td>48.8</td>
<td>0.151 ± 0.051</td>
<td>0.215 ± 0.067</td>
<td>8 JSC</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>17.2</td>
<td>-0.067 ± 0.054</td>
<td>-0.111 ± 0.072</td>
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<tr>
<td>Blithfield</td>
<td>Metal EL6 Find 8</td>
<td>29.5</td>
<td>0.110 ± 0.070</td>
<td>0.199 ± 0.158</td>
<td>4 FM 1979</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>10.9</td>
<td>-0.170 ± 0.084</td>
<td>-0.204 ± 0.124</td>
<td>4 FM 1979</td>
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<tr>
<td>Eagle</td>
<td>Metal EL6 Fall 9</td>
<td>33.3</td>
<td>0.100 ± 0.049</td>
<td>0.154 ± 0.067</td>
<td>4 USNM 6411</td>
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<td></td>
<td>Silicate + sulfide</td>
<td>6.6</td>
<td>-0.071 ± 0.059</td>
<td>-0.098 ± 0.080</td>
<td>4 USNM 6411</td>
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<tr>
<td>Happy Canyon</td>
<td>Metal Impact melt 10</td>
<td>33.5</td>
<td>0.114 ± 0.046</td>
<td>0.171 ± 0.084</td>
<td>6 ASU 1058f</td>
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<tr>
<td></td>
<td>Silicate + sulfide</td>
<td>11.8</td>
<td>0.204 ± 0.071</td>
<td>0.296 ± 0.089</td>
<td>6 ASU 1058f</td>
<td></td>
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</tr>
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</table>

* Standard errors (2 SE = standard deviation divided by the square root of the total number of analyses and multiplied by Student’s t-value for the relevant degree of freedom at the 95% confidence level).

* Number of measurements.

on mass-balance calculation). The average values of magnetic (metal) and non-magnetic (sulfide) are $0.101 \pm 0.076$ (2 SD; $n = 8$), and $-0.140 \pm 0.200$ respectively (Fig. 3). The difference between magnetic and non-magnetic phases in different meteorites ranges from $-0.003 \pm 0.195$ (2 SD; $n = 11$), indistinguishable with the EH and EL3 averages. As shown in Fig. 4, EH, EL3 and the average value of EL6 share the same Fe isotopic composition (within error) with previously published carbonaceous, ordinary chondrites, HED and martian meteorites, and terrestrial abyssal peridotite samples, where $\delta^{56}\text{Fe} = 0.003 \pm 0.042$ (2 SD; $n = 9$). The two EL3 appear isotopically identical within error ($\delta^{56}\text{Fe} = 0.030 \pm 0.038$ (2 SD; $n = 2$) and have the same isotopic composition as EH. Even though the highly metamorphosed EL6 chondrites are relatively heterogeneous ($-0.180_\text{in} < \delta^{56}\text{Fe} < 0.181_\text{in}$) (see Section 4.2), the average composition of EL6 is $0.016 \pm 0.195$ (2 SD; $n = 11$), indistinguishable with the EH and EL3 averages. As shown in Fig. 4, EH, EL3 and the average value of EL6 share the same Fe isotopic composition (within error) with previously published carbonaceous, ordinary chondrites, HED and martian meteorites, and terrestrial abyssal peridotite samples, where $\delta^{56}\text{Fe} \sim 0.00$ (e.g., Poitrasson et al., 2004; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006; Dauphas et al., 2009; Craddock and Dauphas, 2011; Wang et al., 2012a, 2013). All enstatite chondrites (except EL6 and impact melts) provide an extremely homogeneous Fe isotopic composition of $0.008 \pm 0.045$ (2 SD; $n = 8$), which we propose as the best estimate of the initial Fe isotopic composition of the bulk enstatite meteorite
parent bodies. With respect to the enstatite chondrite Earth model (e.g., Javoy et al., 2010), in terms of Fe isotopes we cannot rule out enstatite chondrites as building blocks of the proto-Earth, assuming no Fe isotope fractionation during core formation (Poitrasson et al., 2009; Hin et al., 2012; Huang et al., 2011; Hibbert et al., 2012; Craddock et al., 2013), and are significantly different from the $\delta^{56}\text{Fe}$ value of terrestrial basalts (Beard and Johnson, 1999; Beard et al., 2003; Poitrasson et al., 2004; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006; Dauphas et al., 2009; Teng et al., 2013). This $0.10^{\%}\text{ref}$ difference between enstatite meteorite $\delta^{56}\text{Fe}$ and the terrestrial basalt value can be explained by (1) non-enstatite chondritic precursor of the Earth; (2) isotopic fractionation between metal and perovskite at high-pressure core-mantle boundary (Polyakov, 2009; Rustad and Yin, 2009; Williams et al., 2012); (3) preferential evaporation of light Fe isotopes during the Moon-forming giant impact (Poitrasson et al., 2004); and/or (4) fractionation during partial melting of their mantle sources at oxidized environments (Weyer and Ionov, 2007; Dauphas et al., 2009; Williams et al., 2009; Wang et al., 2012a). The important and still unsettled question lies in whether the Fe isotopic composition of the peridotites (highly scattered $\delta^{56}\text{Fe}$ with an average $\sim 0.00^{\%}\text{ref}$) or basalts (clustered at $\delta^{56}\text{Fe} \sim 0.10^{\%}\text{ref}$) represent the current bulk silicate Earth composition. One argument is that peridotites represent the upper mantle lithosphere and their Fe isotopes have been highly altered by local metasomatism, while basalts have sampled a deeper source of mantle which is well mixed via mantle convection (Poitrasson et al., 2013). The other argument is that since the peridotite average is identical with carbonaceous, ordinary and enstatite chondrites (again confirmed by this study), it more likely to represent the bulk Earth value. This implies that the heavy Fe isotope enrichment in basalts is...
processing (rather than nebular processes). The origin of the isotopic variation observed in EL6 is therefore best explained by mixing between three isotopically distinct mineral phases (metal, sulfide and silicate), as suggested before for ordinary chondrites (Mouyner et al., 2007). Theoretical calculations (Polyakov and Mineev, 2000; Schauble et al., 2001; Polyakov et al., 2007) suggest that, at equilibrium, metal should be enriched in the heavier isotopes of Fe compared to coexisting sulfide and silicate phases. This is exactly what is observed in the mineral separate data (see Fig. 3). The average values of magnetic (metal) and non-magnetic separates (silicate and sulfide) are $0.101 \pm 0.076\%_{\text{iso}}$ (2 SD; $n=8$), and $-0.140 \pm 0.200\%_{\text{iso}}$ (2 SD; $n=8$). This $\delta^{56}\text{Fe}$ difference is in the same range as theoretical calculations made from 600 to 1200 K (Polyakov and Mineev, 2000; Polyakov and Soulitanov, 2011); this large temperature range covers that proposed for enstatite chondrites and aubrites formation and equilibration (Wasson et al., 1994; Zhang et al., 1995). Heavy Fe isotope enrichments in the metallic phase compared to the silicate and sulfide phases have previously been observed in pallasites (Zhu et al., 2002; Poitrasson et al., 2005; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006); ordinary chondrites (Theis et al., 2006). In contrast to other enstatite chondrites (EH3–5 and EL3), the EL6 chondrites show a large range of Fe isotope compositions ($-0.180_{\text{iso}} < \delta^{56}\text{Fe} < 0.181_{\text{iso}}$). The highly metamorphosed EL6 ([Fe] = 21.3–21.9%; Kong et al., 1997) are depleted in Fe when compared to EL3 ([Fe] = 26.2–26.6%; Kong et al., 1997), whereas among the different EH chondrite groups, there is no trend of Fe depletion with degree of metamorphism (EH3: [Fe] = 26.7–30.7%; EH4: [Fe] = 27.7–31.3%; EH5: [Fe] = 28.7–31.2%; Kong et al., 1997). This suggests that increasing thermal metamorphism did not modify the chemical abundance and, as such, the isotopic composition of Fe on the EH parent body. Similarly, the unequilibrated EL3 share the same Fe isotopic composition as EH. In contrast, the highly metamorphosed EL6 have lost some of their initial Fe and are isotopically fractionated compared to EL3; therefore the more variable Fe isotopic compositions of EL6 are more likely a result of parent-body processes (rather than nebular processes).

To understand the mechanism(s) for the origin of the bulk-level Fe isotope variations observed in EL6, we will first discuss the possible evaporation-driven kinetic Fe isotopic fractionation. The EL6 chondrites have experienced thermal metamorphism and also impact melting and/or brecciation (Rubin et al., 2009). Rubin and Wasson (2011) suggest that $\sim 60\%$ of EL6 meteorites were formed by impact melting. Kinetic isotopic fractionation during vaporization would enrich EL6 samples in the heavier isotopes. Enstatite chondrite impact melts Happy Canyon and Ilafegh 009 are such examples (see Section 4.3). However, we consider evaporation-driven Fe isotopic fractionation for EL6 less likely for the following reasons. Firstly, both the Cd and Zn isotope compositions of all EL6 samples so far analyzed are heavy compared to other enstatite chondrites, as would be expected if EL6 are residues of evaporation (Wombacher et al., 2003, 2008; Mouyner et al., 2011). In contrast, the Fe isotope compositions of EL6 chondrites scatter toward both light and heavy $\delta^{56}\text{Fe}$ values ($-0.180_{\text{iso}} < \delta^{56}\text{Fe} < 0.181_{\text{iso}}$). Also, Fe is a major mineral-forming element in enstatite chondrites and it is not as volatile as Zn and Cd (half-mass condensation temperatures: 1328 K vs. 723 and 650 K; Lodders, 2003). There is also no correlation between impact shock level and $\delta^{56}\text{Fe}$. Finally, there is no correlation between Fe concentrations and isotopic compositions (see Fig. 5). This contrasts with the expected correlation for Fe isotopic fractionation due to vaporization as shown in laboratory experiments (Wang et al., 1994). In summary, evaporation-driven kinetic Fe isotopic fractionation is unlikely to be the main contributor to the large $\delta^{56}\text{Fe}$ variations observed for EL6 meteorites.

4.2. Iron isotopic fractionation in EL6 chondrites

In contrast to other enstatite chondrites (EH3–5 and EL3), the EL6 chondrites show a large range of Fe isotope compositions ($-0.180_{\text{iso}} < \delta^{56}\text{Fe} < 0.181_{\text{iso}}$). The highly metamorphosed EL6 ([Fe] = 21.3–21.9%; Kong et al., 1997) are depleted in Fe when compared to EL3 ([Fe] = 26.2–26.6%; Kong et al., 1997), whereas among the different EH chondrite groups, there is no trend of Fe depletion with degree of metamorphism (EH3: [Fe] = 26.7–30.7%; EH4: [Fe] = 27.7–31.3%; EH5: [Fe] = 28.7–31.2%; Kong et al., 1997). This suggests that increasing thermal metamorphism did not modify the chemical abundance and, as such, the isotopic composition of Fe on the EH parent body. Similarly, the unequilibrated EL3 share the same Fe isotopic composition as EH. In contrast, the highly metamorphosed EL6 have lost some of their initial Fe and are isotopically fractionated compared to EL3; therefore the more variable Fe isotopic compositions of EL6 are more likely a result of parent-body processing (rather than nebular processes).

To understand the mechanism(s) for the origin of the bulk-level Fe isotope variations observed in EL6, we will first discuss the possible evaporation-driven kinetic Fe isotopic fractionation. The EL6 chondrites have experienced thermal metamorphism and also impact melting and/or brecciation (Rubin et al., 2009). Rubin and Wasson (2011) suggest that $\sim 60\%$ of EL6 meteorites were formed by impact melting. Kinetic isotopic fractionation during vaporization would enrich EL6 samples in the heavier isotopes. Enstatite chondrite impact melts Happy Canyon and Ilafegh 009 are such examples (see Section 4.3). However, we consider evaporation-driven Fe isotopic fractionation for EL6 less likely for the following reasons. Firstly, both the Cd and Zn isotope compositions of all EL6 samples so far analyzed are heavy compared to other enstatite chondrites, as would be expected if EL6 are residues of evaporation (Wombacher et al., 2003, 2008; Mouyner et al., 2011). In contrast, the Fe isotope compositions of EL6 chondrites scatter toward both light and heavy $\delta^{56}\text{Fe}$ values ($-0.180_{\text{iso}} < \delta^{56}\text{Fe} < 0.181_{\text{iso}}$). Also, Fe is a major mineral-forming element in enstatite chondrites and it is not as volatile as Zn and Cd (half-mass condensation temperatures: 1328 K vs. 723 and 650 K; Lodders, 2003). There is also no correlation between impact shock level and $\delta^{56}\text{Fe}$. Finally, there is no correlation between Fe concentrations and isotopic compositions (see Fig. 5). This contrasts with the expected correlation for Fe isotopic fractionation due to vaporization as shown in laboratory experiments (Wang et al., 1994). In summary, evaporation-driven kinetic Fe isotopic fractionation is unlikely to be the main contributor to the large $\delta^{56}\text{Fe}$ variations observed for EL6 meteorites.

The origin of the isotopic variation observed in EL6 is therefore best explained by mixing between three isotopically distinct mineral phases (metal, sulfide and silicate), as suggested before for ordinary chondrites (Mouyner et al., 2007). Theoretical calculations (Polyakov and Mineev, 2000; Schauble et al., 2001; Polyakov et al., 2007) suggest that, at equilibrium, metal should be enriched in the heavier isotopes of Fe compared to coexisting sulfide and silicate phases. This is exactly what is observed in the mineral separate data (see Fig. 3). The average values of magnetic (metal) and non-magnetic separates (silicate and sulfide) are $0.101 \pm 0.076\%_{\text{iso}}$ (2 SD; $n=8$), and $-0.140 \pm 0.200\%_{\text{iso}}$ (2 SD; $n=8$). This $\delta^{56}\text{Fe}$ difference is in the same range as theoretical calculations made from 600 to 1200 K (Polyakov and Mineev, 2000; Polyakov and Soulitanov, 2011); this large temperature range covers that proposed for enstatite chondrites and aubrites formation and equilibration (Wasson et al., 1994; Zhang et al., 1995). Heavy Fe isotope enrichments in the metallic phase compared to the silicate and sulfide phases have previously been observed in pallasites (Zhu et al., 2002; Poitrasson et al., 2005; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006); ordinary chondrites (Theis et al., 2006).
The variable mixing of metallic (isotopically heavy), sulfide (isotopically light) and silicate (isotopically light) phases is a viable explanation for the considerable Fe isotopic variations observed among EL6 (see Fig. 5). A subsequent question is why then is it only EL6 chondrites that are heterogeneous with respect to Fe isotopes while EH and EL3 are homogeneous? We propose that the Fe isotopic heterogeneity of EL6 chondrites is closely associated with observed chemical/mineralogical fragmentation and brecciation due to their complex impact history (Rubin, 1983a,b, 1984; Rubin and Wasson, 2011; Rubin et al., 1997, 2009). For example, Hvittis consists of centimeter-sized impact-melt clast (Rubin, 1983a); Blithfield contains centimeter-sized metal-poor-sulfide-rich clasts and metal nodules in metal-rich matrix (Rubin, 1984); and Atlanta comprises centimeter-sized sulfide-rich clasts and kamacite veins (Rubin, 1983b; Rubin et al., 1997). Keil and Bischoff (2008) suggested that small amounts of troilite and metal could be mobilized and dispersed during impact events. We hence propose that the considerable Fe isotopic variations observed among EL6 are due to a chemical/mineralogical heterogeneity that is unique for EL6. It reflects the intensive impact history suffered by the EL6 chondrites (as compared to EL3 and the EH chondrites) and it is consistent with the conclusions drawn from petrographic evidence (e.g., Rubin et al., 1997), fractionated refractory lithophile elements patterns (Kallemeyn and Wasson, 1986; Rubin et al., 2009; Barrat et al., 2014) and enrichment in heavy Zn isotopes (Moynier et al., 2011).

4.3. Iron isotopic fractionation in enstatite chondrite impact melts

The impact melts (Happy Canyon and Ilafegh 009) are the only enstatite meteorite group that have an average heavy Fe isotope composition compared to carbonaceous and chondrites and terrestrial material (Ilafegh 009 was measured by Craddock and Dauphas, 2011). Happy Canyon contains up to 70 vol.% impact-melt material, which is intermixed with unmelted target clastic material (up to 30 vol.%). The different Fe isotopic compositions of two different Happy Canyon samples (0.143$_{\text{iso}}$ vs. 0.056$_{\text{iso}}$) are likely caused by the mixing of different proportions of melted and unmelted materials. Ilafegh 009 crystallized from a total impact melt with no identified unmelted target clastic material (McCoy et al., 1995). The Fe isotopic compositions of Happy Canyon and Ilafegh 009 are both significantly heavier than those of the EH and EL3 and are within the upper range of the EL6. On a $\delta^{56}$Fe vs. 1/Fe plot, the $\delta^{56}$Fe of impact melts show a slight positive trend with 1/Fe (see Fig. 5). This correlation of $\delta^{56}$Fe and 1/Fe in impact melts suggests that the enriched Fe isotopic compositions were caused by partial loss of Fe during impact vaporization. In addition, the enstatite chondrite impact melts are the only group with both magnetic (metal) and non-magnetic (sulfide + silicate) portions enriched in heavy Fe isotopes (see Fig. 3). More significantly, the non-magnetic phase has a heavier Fe isotopic composition than the magnetic phase. Since sulfides are more volatile than metal (Lodders, 2003), preferential evaporation of sulfides would lead to enrichment of the heavy isotopes. This conclusion agrees with a previous study which showed that enstatite chondrite impact melts are also enriched in the heavy isotopes of Zn (a more volatile element than Fe) compared to EH and EL3 chondrites, again interpreted as a consequence of impact vaporization (Moynier et al., 2011).

Evaporation-driven kinetic isotopic fractionation during impact has been proposed as one important mechanism of Fe isotopic fractionation and it has been used to explain the enriched heavy Fe isotopic compositions in lunar rocks (Poirrasson et al., 2004) and regolith (Wiesli et al., 2003; Wang et al., 2012b). In the case of the enstatite chondrite impact melts, their enriched heavy Fe isotopic compositions are most likely caused by kinetic evaporation during impacts and provide additional evidence for an impact origin.

Free evaporation experiments in a vacuum show that Fe isotopes fractionate during evaporation following the Rayleigh distillation equation (Wang et al., 1994). Poirrasson et al. (2004) has calculated that $\sim$0.1$_{\text{iso}}$ Fe isotopic fractionation can be produced by losing $\sim$1% Fe during Rayleigh evaporation. However, enstatite chondrite impact melts have lost significantly more Fe compared to their enstatite chondrite parents, and the corresponding Fe isotopic fractionation (tens of per mils) predicted by simple Rayleigh distillation is much larger than that observed in this study (see Fig. 6). Several previous studies have modeled the isotopic fractionation during diffusion-limited evaporation (e.g., Young, 2000; Young et al., 1998; Ozawa and...
Nagahara, 2001; Moynier et al., 2009). At high $\beta$ (Péclet number; ratio evaporation rate over diffusion rate) cases, evaporation is faster than elemental diffusion toward the evaporation site, and magnitudes of isotopic fractionations are suppressed. As shown in Fig. 6, the measured Fe isotopic fractionations in the enstatite chondrite impact melts can be best explained by diffusion-limited evaporation with high $\beta$ (>200). The requirement of high Péclet number can be fulfilled in situations like large melt size (>tens of centimeters) and/or high ambient pressure during evaporation (Young, 2000). The former scenario is more likely in the case of enstatite chondrite impact melts based on petrological evidence (e.g., McCoy et al., 1995).

It is important to note that impact-induced Fe isotopic fractionation is not observed in other heavily shocked enstatite chondrite samples. The impact metamorphism level of meteorites can be evaluated from their mineralogy and texture (Stöfler et al., 1991) and enstatite meteorites vary from S2 (very weakly shocked) to S5 (strongly shocked) on this scheme (Rubin et al., 1997). Table 1 lists all available shock levels for individual samples (Rubin et al., 1997; Grossman, 1998; Rubin, 2009, 2010; Izawa et al., 2011). There is no correlation between shock level and Fe isotopic compositions. For example, EL3 chondrite PCA 91020 has been strongly shocked (S5) while EL3 chondrite MAC 88184 (paired with MAC 88136, whose shock stage is reported as S2) has only been very weakly shocked; however they have an identical Fe isotopic composition. The post-annealing shock stages for enstatite chondrite impact melts Happy Canyon and Ilafegh 009 are S2 and S4, respectively, which is also not consistent with their elevated $\delta^{56}$Fe values. In conclusion, shock metamorphism does not play a major role in the Fe isotopic fractionation of enstatite chondrites except in those that have experienced extensive melting during impact, such as Happy Canyon and Ilafegh 009.

4.4. Iron isotopic fractionation in aubrites

All the aubrites (except Shallowater) have negative $\delta^{56}$Fe ($-0.302^\circ_{\text{at}}$ to $-0.008^\circ_{\text{at}}$). If the aubrites started with a Fe isotope composition similar to EH or EL3, the negative $\delta^{56}$Fe of the aubrites implies that a reservoir enriched in heavy isotopes has been segregated from the source of the aubrite meteorites. The aubrite parent body most probably segregated a metallic core (Keil, 1989), however, the metal/silicate segregation was apparently incomplete, leaving nodules of metals in the mantle (Casanova et al., 1993a). As noted in Section 4.2, metallic iron is consistently isotopically heavier than accompanying silicate and/or sulfide phases. We hence suggest that the core of the aubrite parent body, which was enriched in the heavy isotopes of Fe, separated from the silicate (light Fe-enriched) mantle.

The inverse correlation between $\delta^{56}$Fe and the 1/Fe suggests that the isotopic variations among aubrites are due to mixing between isotopically distinct components (see Fig. 5), possibly an incomplete segregation of core and mantle. Aubrites are mainly (~90%) composed of enstatite (MgSiO$_3$), and, although most of their Fe must have segregated into a core (Keil, 1989), some metallic blobs are found in the aubrite matrix (Casanova et al., 1993a,b). Based on the pattern of their siderophile elements, these metal grains are thought to be residual material trapped in the silicate magma during partial melting after incomplete core formation (Casanova et al., 1993a,b).

The minimum Fe isotope fractionation between the core and mantle in aubrite parent-bodies is ~$0.4^\circ_{\text{at}}$ (the observed difference between Fe-rich and Fe-poor samples; see Table 1 and Fig. 5c). Whether there was Fe isotopic fractionation between core and mantle on Earth and other planetary bodies has been a fiercely debated topic. Hin et al. (2012) and Poitrasson et al. (2009) proposed that there is no Fe isotopic fractionation during metal and silicate segregation. However, Shahar et al. (2013) recently observed that the amounts of light elements (especially S) in a metal significantly increases the iron isotope equilibrium fractionation factor between metallic alloy and silicate melt (see Fig. 7). For example, 17 wt.% S in the metal would lift the Fe isotopic fractionation factor between metal and silicate ($A^{56}$Fe) to ~$0.3^\circ_{\text{at}}$.

As shown in Fig. 7, we explore the possibility of this sulfur-controlled Fe isotopic fractionation between metal and silicate. The parent-body(s) of aubrites are unknown, hence so are the core-mantle boundary conditions. However, some estimation can be made through comparison to Vesta 4, the second largest asteroid in the asteroid belt. Righter and Drake (1997) calculated a 1773 K temperature at the bottom of the magma ocean based on the partitioning of moderately siderophile elements. The eutectic temperature of Fe-S melt is 1261 K at 1 atm. At a
core–mantle segregation temperature of 1600 K, the sulfur-controlled Fe isotopic fractionation between metal and silicate model requires >10 wt.% S in the core (Fig. 7). Based on the model, more S partitioning into the core is required if the core–mantle segregation happens at higher temperatures. The relative S-rich core of aubrite parent-body inferred from this model is consistent with the high S-fugacity and low O-fugacity (e.g., containing large amount of exotic sulfide minerals) long known for enstatite meteorites.

This sulfur-controlled Fe isotopic fractionation also plays significant roles in other planetary bodies, especially in those with high sulfur contents partitioning into the cores. For example, magmatic iron meteorites (presumably cores of differentiated asteroids) have been reported to be enriched in heavy Fe isotopes compared to chondrites (Poitrasson et al., 2005; Weyer et al., 2005; Williams et al., 2006; Moynier et al., 2007). Particularly, sulfur-rich IIAB iron meteorites which contain 17 wt.% S in their parental core (Chabot, 2004), have shown relatively higher \( \delta^{56}\text{Fe} \) values than those of other types of iron meteorites (Williams et al., 2006). However, it needs to be noted that this sulfur-controlled Fe isotopic fractionation between metal and silicate is probably not important for the Earth, since estimates of S in Earth’s core is far below that needed to have a significant effect on Fe isotopes (~2 wt.% or less; e.g., Allègre et al., 1995; Dreibus and Palme, 1996; Allègre et al., 2002; McDonough, 2007; Badro et al., 2007, 2014; Rubie et al., 2011). In addition, higher temperatures during core formation on Earth should also suppress the degree of isotopic fractionations (e.g., Schauble, 2004).

Shallowater is an anomalous aubrite and is also the only unbrecciated aubrite. Keil (1989) proposed that Shallowater is derived from a separate parent body to the main group aubrites and other enstatite chondrites. The Shallowater parent body is thought to have experienced a severe impact history whereby the original parent body, which likely consisted of partially or completely molten enstatite covered with a solid carapace, was disrupted by a low-velocity impact with a solid body of enstatite chondrite-like material (Keil, 1989). Such impacts have the potential to fractionate Fe isotopes with loss of light isotopes during vaporization generated by impacts leaving an isotopically heavy residue (see Section 4.3). This could be an explanation for the heavy enrichment in Fe isotopes in the Shallowater samples. In addition, Shallowater is enriched in heavy Zn isotopes compared to other aubrites, also interpreted as a result of impact vaporization (Moynier et al., 2011). However, on a \( \delta^{56}\text{Fe} \) vs. \( 1/[^{56}\text{Fe}] \) plot (Fig. 5), Shallowater plots on the same negative correlation line defined by the other aubrites. Therefore, an alternative explanation could be that Shallowater parent body and main group aubrite parent body have the same Fe isotopic composition and that core formation occurred at similar temperatures. Remixing of core material with silicate portions during the destruction of Shallowater parent body, or core material drawn back into the mantle caused by impact-induced shearing stress (Rushmer et al., 2005; van Acken et al., 2012) should both lead to the enrichment of metal in Shallowater samples and to their enrichment in the heavier isotopes.

4.5. Iron isotopic fractionation between metal and sulfide in enstatite meteorites

It is not possible to precisely determine the abundances of metal, sulfide and silicate phases as well as the Fe concentration of each phase in any given sample by our separation procedure, however, it is possible to estimate the Fe inventory in enstatite meteorites through a mass-balance calculation based on the data compilation of previous studies (Keil, 2010; Javoy et al., 2010). On average, in enstatite chondrites, the metal, sulfide and silicate phases contain 49.53, 49.41 and 1.06 wt.% of all Fe in the sample. Similarly for aubrites, average metal, sulfide and silicate phases carry 49.83, 46.26 and 3.92 wt.% of all Fe in the sample. For both enstatite chondrites and aubrites, metal and sulfides are the major (and almost equally important) carriers of Fe. Therefore in term of Fe budget, the magnetic separates are dominated by Fe-metal, while the non-magnetic portions are dominated by non-magnetic sulfides (i.e., troilite). In addition, theoretical calculations show that \( \Delta^{56}\text{Fe}_{\text{metal-troilite}} \) and \( \Delta^{56}\text{Fe}_{\text{metal-enstatite}} \) are very close at high temperatures (Polyakov and Mineev, 2000; Polyakov et al., 2007), for example, \( \Delta^{56}\text{Fe}_{\text{metal-troilite}} = 0.11\%_\text{oo} \) and \( \Delta^{56}\text{Fe}_{\text{metal-enstatite}} = 0.08\%_\text{oo} \) at 1000 °C. It is hence reasonable to use the \( \delta^{56}\text{Fe} \) difference between magnetic and non-magnetic separates to estimate the metal–sulfide Fe isotopic fractionation factor, even though the quantification of each phase is unknown due to our separation approach.

The differences (\( \Delta^{56}\text{Fe}_{\text{metal-sulfide}} = \delta^{56}\text{Fe}_{\text{metal}} - \delta^{56}\text{Fe}_{\text{sulfide}} \approx \delta^{56}\text{Fe}_{\text{magnetic}} - \delta^{56}\text{Fe}_{\text{non-magnetic}} \)) of metal-dominated magnetic phases and troilite-dominated non-magnetic phases in enstatite chondrites (\( \Delta^{56}\text{Fe}_{\text{metal-sulfide}} = 0.127 - 0.493\%_\text{oo} \) average at 0.263 ± 0.236\%_\text{oo} 2 SD) are significantly
larger than those in Shallowater aubrites (maximum $\Delta^{56}$Fe$_{\text{metal-sulfide}} = 0.129 \pm 0.060\%$; 2 SE). Isotopic fractionation factors are a function of the equilibration temperatures between phases; therefore, do the different $\Delta^{56}$Fe values between aubrites and enstatite chondrites reflect their different equilibration temperatures? The equilibration temperatures of EL chondrites are estimated to be between 1200 and 1400 K, averaging at 1220 ± 80 K (Wasson et al., 1994). Ziegler et al. (2010) calculated final equilibration temperatures for two aubrites at between 1200 and 1130 ± 80 K. Here, we follow Ziegler et al. (2010) and apply the temperature calibration provided by Wasson et al. (1994; using the relationship between mole fraction of Si in the metal and mole fraction of Fe in the enstatite (Wasson and Wai, 1970). This value represents the final equilibration temperature after melting and thermal metamorphism events (Ziegler et al., 2010).

As shown in a $\Delta^{56}$Fe$_{\text{metal-sulfide}}$ vs. temperature plot (Fig. 8), the maximum value measured between Fe-metal and sulfide in Shallowater agrees very well with the fractionation factors predicted by theoretical calculations (Polyakov and Soultanov, 2011; Polyakov et al., 2007), as defined in Eq. (2):

$$
\Delta^{56}\text{Fe}_{\text{metal-troilite}} = \frac{1.774 \times 10^6}{T^2} + \frac{5.6912 \times 10^9}{T^4} + \frac{0.2605 \times 10^{12}}{T^6}
$$

(2)

In contrast, enstatite chondrites exhibit larger $\Delta^{56}$Fe$_{\text{metal-sulfide}}$ fractionations ($\Delta^{56}$Fe$_{\text{metal-sulfide}} = 0.127 \pm 0.493\%$) than those expected in Eq. (2). The origins of metal and sulfide in chondrites have been suggested as direct condensation products from solar nebula or sulfurization of Fe/desulfurization of FeS in later stages (e.g., Campbell et al., 2005; Lehner et al., 2013). This larger $\Delta^{56}$Fe$_{\text{metal-sulfide}}$ than expected during high temperature equilibrium implies that the metal and sulfide are unlikely to be in Fe isotopic equilibrium, or metal and sulfide obtained isotopic equilibrium at a lower temperature reached by later thermal alteration events on parent bodies. Recently, Wang et al. (2014) observed a ~0.3% difference between metal and sulfide phases from three ordinary chondrites, which is similar with the data for enstatite chondrites in this study. Alternatively, we have only considered kamacite as the metal phase and troilite as the major phase of sulfides. Enstatite chondrites contain many additional Fe-bearing phases (e.g., daubreelite, niningerite, and perryite) that would contribute to the Fe isotopic budgets of the different samples. Currently, there are no experimental data or theoretical calculations for these mineral phases.

A previous study by Williams et al. (2006) has reported a large range of $\Delta^{56}$Fe fractionations (0.03 ± 0.03–0.53 ± 0.06%o) between metal and troilite phases separated from magmatic iron meteorites. The Fe isotopic fractionation factor 0.129 ± 0.060%o at 1060 ± 80 K obtained in this study falls in this range. Williams et al. (2006) proposed their maximum $\Delta^{56}$Fe value (0.53 ± 0.06%) as the best estimate of the equilibrium metal–sulfide Fe isotopic fractionation factor for temperature range of 773–1263 K (see Fig 8). At 773 and 1263 K, our measurement as well as theoretical calculations (Polyakov and Soultanov, 2011; Polyakov et al., 2007) predicts a $\Delta^{56}$Fe ~0.31%o and ~0.11%o, respectively, which is a factor two or five smaller than the 0.53 ± 0.06%o observed by Williams et al. (2006). This discrepancy is echoed by disagreements over Fe isotopic fractionation factors acquired by different research groups with different methods (computing from experimental Mössbauer spectroscopy or NRIXS data vs. first-principle calculations; Blanchard et al., 2009, 2012; Polyakov and Soultanov, 2011, 2012). This inconsistency between laboratory measurements and theoretical calculations needs to be further investigated.

5. CONCLUSIONS

We measured the bulk Fe isotopic composition of 22 samples from the different enstatite meteorite groups: EH and EL chondrites, aubrites (main group and Shallowater) and Happy Canyon impact melt as well as in separated phases (magnetic and non-magnetic phases) from these meteorites, by high precision MC-ICPMS.

We find that EH3–5 and EL3 chondrites all have the same homogeneous Fe isotopic composition, 0.008 ± 0.045%o (2 SD; n = 1), which is identical to the averages of ordinary, carbonaceous chondrites, terrestrial mantle rocks, Martian and HED meteorites. Therefore, in terms of the enstatite chondrite Earth model, Fe is another isotopic system that shows a resemblance to terrestrial materials.

The EL6 chondrites have a large range of Fe isotopic compositions (−0.180%o < $\delta^{56}$Fe < 0.181%o). We propose that these Fe isotopic variations are due to the mixing between metallic Fe (isotopically heavy), sulfide (isotopically light) and silicate (isotopically light) components in different proportions. Our mineral separation experiments have shown that, in enstatite meteorites, magnetic (metal; 0.101 ± 0.076%o) and non-magnetic (sulfide; −0.140 ± 0.200%o) phases have distinct Fe isotopic compositions, which agrees with previous experimental observations and theoretical calculations. The extreme heterogeneity of Fe isotopes is unique to EL6 chondrites, and we suggest is likely due to the chemical/mineralogical fragmentation and brecciation as a result of the complex and intense impact history experienced during their formation.

The enstatite chondrite impact melts (Happy Canyon and Ilafegh 009) are the only heavy Fe isotope-enriched group, on average, among all the enstatite chondrites. This enrichment is most likely caused by kinetic fractionation during impact vaporization and is consistent with their impact-melt origin, previously implied by mineralogical, compositional and Zn isotopic studies.

Like the EL6, aubrites exhibit a wide range of Fe isotopic compositions (−0.302%o < $\delta^{56}$Fe < 0.084%o). All the main group aubrites are depleted in heavy Fe isotopes,
while the anomalous aubrite Shallowater is enriched in heavy Fe isotopes. The negative correlation between the Fe isotopic composition and 1/Fe suggests a mixing relation between two isotopically distinct reservoirs of Fe that we suggest are the core and mantle of the aubrite parent body. Our Fe isotopic study of aubrites indicates the separation of a heavy Fe isotope-rich core on the aubrite parent body. If we assume that Shallowater had the same Fe isotope starting composition as main group aubrites, our data suggest that its core material remixed with silicate portions during the destruction of the Shallowater parent body, or alternatively core material draw-back into the mantle occurred due to intensive impact-induced shearing stress.

We have obtained an empirical metal–sulfide Fe isotopic fractionation factor ($\Delta^{56}\text{Fe}_{\text{metal-sulfide}}$) of 0.129 ± 0.060‰ (2 SE) at 1060 ± 80 K from enstatite achondrite samples. This value agrees well with previously calculated theoretical equilibrium fractionation data between Fe-metal and troilite.

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REFERENCES


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