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Iron isotope fractionation during sulfide-rich felsic partial melting in early planetesimals

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ABSTRACT

New Fe isotope data of feldspar-rich meteorites Graves Nunataks 06128 and 06129 (GRA 06128/9) reveal that they are the only known examples of crustal materials with isotopically light Fe isotope compositions (δ^{56}Fe $= -0.08 \pm 0.06$‰; δ^{56}Fe is defined as the *per mille* deviation of a sample's ^{56}Fe/^{54}Fe ratio from the IRMM-014 standard) in the Solar System. In contrast, associated brachinites, as well as brachinite-like achondrites, have Fe isotope compositions (δ^{56}Fe $= +0.01 \pm 0.02$‰) that are isotopically similar to carbonaceous chondrites and the bulk terrestrial mantle. In order to understand the cause of Fe isotope variations in the GRA 06128/9 and brachinite parent body, we also report the Fe isotope compositions of metal, silicate and sulfide fractions from three ordinary chondrites (Semarkona, Kernouve, Saint-Séverin). Metals from ordinary chondrites are enriched in the heavier isotopes of Fe (average δ^{56}Fe $= 0.15$‰), sulfide fractions are enriched in the lighter isotopes of Fe (average δ^{56}Fe $= -0.14$‰), and the δ^{56}Fe values of the silicates are coincident with that of the bulk rock (average δ^{56}Fe $= 0.03$‰).

The enrichment of light isotopes of Fe isotopes in GRA 06128/9 is consistent with preferential melting of sulfides in precursor chondritic source materials leading to the formation of Fe–S-rich felsic melts. Conceptual models show that melt generation to form a GRA 06128/9 parental melt occurred prior to the onset of higher-temperature basaltic melting ($<1200\,°$C) in a volatile-rich precursor and led to the generation of buoyant felsic melt with a strong Fe–S signature. These models not only reveal the origin of enrichment in light isotopes of Fe for GRA 06128/9, but are also consistent with petrological and geochemical observations, experimental studies for the origin of Fe–S-rich felsic melts, and for the cessation of early melting on some asteroidal parent bodies because of the effective removal of the major radioactive heat-source, ^{26}Al. The mode of origin for GRA 06128/9 contrasts strongly with crust formation on Earth, the Moon, Mars and other asteroids, where mantle differentiation and/or oxygen activity are the major controls on crustal Fe isotope compositions.

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1. Introduction

Planet formation studies rely on a robust understanding of how the outermost solid crust of a planet is formed. Most planetary bodies are currently only studied remotely, or from meteorites that originate from the crust of the body, and thus most of the chemical and physical information obtained on the planets formation, differentiation and cooling history is obtained from its crust. Direct study of terrestrial crust has shown a funda-mental dichotomy of dense basaltic crust in the ocean basins formed at mid-ocean ridges through adiabatic decompression, and evolved more buoyant feldspar-rich (felsic) continental crust. Unlike oceanic crust, felsic continental crust cannot be formed by single-stage melting of peridotite. Many processes have been proposed for continental crust formation, all of which require complex multi-stage melting of primary or recycled materials since at least 3 Ga ago (*e.g.*, Rudnick and Gao, 2003; Rudnick, 1995; Taylor and McLennan, 1985).

By contrast, although it has been proposed that felsic melts may have formed early on some planetesimals (Cohen et al., 2004; Keil, 2010), the preponderance of crust formed in the early Solar System appears to have been basaltic (Taylor and McLennan, 2009).

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For example, angrite and howardite–eucrite–diogenite (HED) meteorites represent crustal materials formed within 3 to 8 Ma of calcium–aluminum-rich inclusions (CAIs); the first solid materials condensed from the solar nebula (Amelin, 2008; Blichert-Toft et al., 2002; Trinquier et al., 2008). These two meteorite groups are broadly basaltic in composition and probably formed early during global-scale differentiation (magma ocean) events and subsequent to core formation on their parent bodies (Riches et al., 2012; Day et al., 2012b). The identification of the paired achondrite meteorites GRA 06128/9 as evolved felsic crustal materials (Day et al., 2009a, 2012a; Shearer et al., 2010) has challenged the canonical view that the earliest planetary crusts were dominantly basaltic in composition. As rocks containing >70 modal percent sodic plagioclase, GRA 06128/9 represent a primordial felsic crust formed early in Solar System history – no later than 4517 ± 60 Ma (^{207}Pb–^{206}Pb age; Day et al., 2009a) – and before metallic core formation within their parent body. The bulk chemistry of GRA 06128/9 reflects broadly andesitic compositions, similar to the composition of bulk terrestrial continental crust (Day et al., 2009a, 2009b).

Geochemical and petrological evidence indicates that GRA 06128/9 represent the crustal differentiation complements to olivine-dominated brachinite achondrites that represent melt-depleted mantle restites within a planetesimal (Day et al., 2012a). These similarities include overlap in oxygen isotope compositions, complementary petrology and trace-element geochemistry, similar oxidation conditions, and crystallization model ages of 2–3 Ma after the first Solar System solids (Arai et al., 2008; Day et al., 2009a, 2012a; Shearer et al., 2010; Zeigler et al., 2008). Brachinite-like achondrites, which have more magnesian compositions than brachinites, appear to be related by similar melt-depletion processes to brachinites, but are unlikely to derive from the same parent body, but point to similar processes acting on more than one asteroid (Day et al., 2012a).

Despite detailed petrological, geochemical and experimental studies on GRA 06128/9 (*e.g.*, Day et al., 2009a, 2012a; Gardner-Vandy et al., 2013; Shearer et al., 2010), uncertainties remain in the formation mechanisms for GRA 06128/9, brachinites and brachinite-like achondrites. In particular, inter-element fractionations of highly siderophile elements in GRA 06128/9 and brachinites indicate complex melting processes and, possibly, more than a single-stage process in their formation. Elucidating the mode of formation of asteroidal felsic crust is important not only for comparison with continental crust formation on Earth, but because early formation of felsic asteroidal crust offers a potential mechanism for the loss of radioactively generated heat within planetary bodies early in their history (Day et al., 2012a). This process would occur through the direct loss of ^{26}Al, a short-lived radioisotope (half life of 7.17×10^5 yrs) and which is considered to be a major heat source during the initial stages of planetary melting (Mittlefehldt, 2007).

Iron isotopes have the potential to allow discrimination between models for asteroidal crust formation because of their potential to be fractionated during various magmatic differentiation processes, such as partial melting, mineral fractionation and fluid exsolution (Dauphas et al., 2009; Heimann et al., 2008; Liu et al., 2010; Poitrasson and Freydier, 2005; Schoenberg and von Blanckenburg, 2006; Schuessler et al., 2009; Sossi et al., 2012; Telus et al., 2012; Teng et al., 2008; Wang et al., 2012a; Weyer et al., 2005). In particular, iron isotopes can provide useful constraints on the origins of melts and melt residues from chondritic precursor materials because of the distinct Fe isotope fractionations observed between sulfide and metal phases (Needham et al., 2009). Here we show that Fe isotopes are powerful tracers of planetesimal differentiation processes during partial melting and provide constraints on the petrogenetic processes responsible for GRA 06128/9, brachinites and brachinite-like achondrites.

2. Samples and methods

2.1. Sample description

Iron isotope compositions for ungrouped achondrite stones GRA 06128, GRA 06129, six brachinites, three brachinite-like achondrites, and phase separates (metal, silicate and sulfide) from three ordinary chondrites (Tables 1 and 2) were analyzed in this study. Two geostandards, AGV-2 and BCR-2, were prepared and measured during the same analytical sessions with the meteorite samples and are also reported.

Ungrouped achondrites GRA 06128/9 are paired feldspathic stony meteorites. They are relatively coarse-grained stones with granoblastic textures and are dominated by sodic plagioclase (oligoclase; ~80 vol%), orthopyroxene and clinopyroxene (~10 vol%), Fe-rich olivine (~10 vol%), and minor amounts of Ca-phosphate (apatite and merrilite), sulfide (troilite and pentlandite) and FeNi metal (Arai et al., 2008; Day et al., 2009a, 2012a; Shearer et al., 2010; Zeigler et al., 2008). Their oxygen isotope and major/minor element bulk compositions show complementarity with brachinites, and are distinct from other extra-terrestrial plagioclase-rich rocks, such as lunar anorthosites (Day et al., 2009a; Shearer et al., 2010; Zeigler et al., 2008). GRA 06128/9 was formed early in Solar System history, with a metamorphic age of 4517 ± 60 Ma (Day et al., 2009a), which is consistent with the 4565.9 ± 0.3 Ma age inferred from ^{26}Al–^{26}Mg chronology (Shearer et al., 2008). The oxygen fugacity ($f O_2$) is estimated to be between iron-wüstite buffer (IW) -0.1 and IW $+1.1$ (Shearer et al., 2010). GRA 06128/9 is hypothesized to have formed by low-to-moderate-degree (13–30%) Fe–S bearing partial melting of a primitive, volatile-rich source region from an asteroid that had not fully differentiated a metallic core (Day et al., 2009a; Shearer et al., 2010).

Six brachinites were studied here: Brachina, Elephant Moraine (EET) 99402, Northwest Africa (NWA) 1500, NWA 3151, NWA 4872 and NWA 4882. Brachinites are dunitic wehrlites and they contain a majority of olivine (usually >80 vol%), with variable amounts of augite, chromite, Fe-sulfide, phosphate, and Fe–Ni metal (Day et al., 2012a; Mittlefehldt et al., 1998). Like GRA 06128/9, brachinites are ancient, with a ^{53}Mn–^{53}Cr age of 4563.7 ± 0.9 Ma for Brachina (Wadhwa et al., 1998). It has previously been suggested that brachinites represent igneous cumulates (Mittlefehldt, 2007), but recent work indicates that they are partial melt residues (Day et al., 2012a).

Three ungrouped meteorites NWA 5400, NWA 6077 and Zag (b) (referred to as brachinite-like achondrites; Table 1) were also analyzed for their bulk Fe isotope compositions. They are all olivine dominated ultramafic achondrites, with similar mineralogy and geochemical composition to brachinites (Day et al., 2012a). NWA 5400 and NWA 6077 are possibly paired and they have an oxygen isotope composition close to the terrestrial fractionation line and are clearly distinct from brachinites (Day et al., 2012a). These differences in the oxygen isotope composition, as well as differences in the absolute and relative highly siderophile element abundances compared with brachinites, indicate that they were probably formed on different parent-bodies, but formed by similar partial melting processes (Day et al., 2012a).

Phase separations (metal, sulfide, silicate) were done on three extensively studied ordinary chondrite falls of various chemical class and petrologic type. Semarkona (LL3.0) is recognized as one of the least metamorphosed ordinary chondrites (Huss et al., 1981; Sears et al., 1980). Kernouve (H6) and Saint-Séverin (LL6) are two equilibrated ordinary chondrites.

Table 1
Iron isotope compositions of GRA 06128/9, brachinites and brachinite-like achondrites.

Sample	Type	Fall/Find	Mass (mg)	Fe (wt%)	δ^{56}Fe		2SE[a]	δ^{57}Fe		2SE[a]	n[b]	Laboratory[c]
GRA 06128 #1	Ungrouped	Find	1.8	3.2	−0.05	±	0.04	−0.08	±	0.09	7	Chicago
GRA 06128 #2	Ungrouped	Find			−0.09	±	0.05	−0.14	±	0.09	9	Chicago
GRA 06129 #1	Ungrouped	Find	13.3	5.6	−0.06	±	0.05	−0.10	±	0.09	9	Chicago
GRA 06129 #2	Ungrouped	Find			−0.09	±	0.05	−0.10	±	0.09	9	Chicago
GRA 06129 #3	Ungrouped	Find	4.0	5.4	−0.09	±	0.05	−0.14	±	0.07	9	Chicago
Average					**−0.08**	**±**	**0.06**	**−0.11**	**±**	**0.05**	**2**	
Range(max-min)					0.04			0.06				
Brachina #1	Brachinite	Find			0.02	±	0.03	0.04	±	0.07	9	Chicago
Brachina #2	Brachinite	Find			0.02	±	0.05	0.02	±	0.09	9	Chicago
Brachina #3	Brachinite	Find	3.7	20.0[d]	0.01	±	0.04	0.03	±	0.03	12	St. Louis
EET 99402 #1	Brachinite	Find	2.1	19.9	0.00	±	0.05	0.04	±	0.07	9	Chicago
EET 99402 #2	Brachinite	Find	4.0	20.8[d]	−0.01	±	0.03	0.00	±	0.04	12	St. Louis
NWA 1500	Brachinite	Find	8.6	23.9[d]	0.01	±	0.02	0.01	±	0.03	11	St. Louis
NWA 3151	Brachinite	Find	4.0	29.2[d]	0.00	±	0.04	0.02	±	0.07	13	St. Louis
NWA 4872	Brachinite	Find	9.5	25.6[d]	0.04	±	0.03	0.09	±	0.04	11	St. Louis
NWA 4882	Brachinite	Find	3.1	23.5[d]	0.01	±	0.04	0.02	±	0.06	14	St. Louis
Average					**0.01**	**±**	**0.02**	**0.03**	**±**	**0.03**	**6**	
Range(max-min)					0.05			0.09				
NWA 5400	Brachinite-like	Find	4.6	19.6[d]	0.00	±	0.02	0.01	±	0.05	10	St. Louis
NWA 6077	Brachinite-like	Find	4.7	20.9[d]	0.04	±	0.04	0.07	±	0.06	12	St. Louis
Zag (b)	Brachinite-like	Find	6.0	20.9[d]	0.07	±	0.04	0.12	±	0.07	13	St. Louis
AGV-2	Andesite	Geostandard	15.3		0.09	±	0.05	0.14	±	0.07	9	Chicago
AGV-2	Andesite	Geostandard	9.9		0.10	±	0.03	0.14	±	0.04	13	St. Louis
BCR-2	Basalt	Geostandard	5.1		0.11	±	0.03	0.14	±	0.04	13	St. Louis

[a] Standard errors (2SE = 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).
[b] The number of analyses or number of individual meteorite samples for the group means.
[c] Chicago = University of Chicago; St. Louis = Washington University in St. Louis.
[d] These samples are from the same digestions of Day et al. (2012a) and the concentrations have been reported therein.

Table 2
Iron isotope compositions of magnetic (metal), non-magnetic (sulfide) and non-magnetic (silicate) fractions of three ordinary chondrites.

Sample	Type	Fall/Find	Mass (mg)	Fe (wt%)	δ^{56}Fe		2SE[a]	δ^{57}Fe		2SE[a]	n[b]	Laboratory[c]
Semarkona												
Magnetic (metal)	LL3.0	Fall	8.1	24.1	0.11	±	0.02	0.19	±	0.10	9	St. Louis
Non-magnetic (silicate)	LL3.0	Fall	16.8	5.6	0.03	±	0.04	0.04	±	0.06	8	St. Louis
Non-magnetic (sulfide)	LL3.0	Fall	6.2	18.0	−0.17	±	0.06	−0.23	±	0.11	8	St. Louis
Kernouve												
Magnetic (metal)	H6	Fall	15.8	35.8	0.10	±	0.04	0.17	±	0.04	6	St. Louis
Non-magnetic (silicate)	H6	Fall	25.6	8.0	0.02	±	0.05	0.02	±	0.06	7	St. Louis
Non-magnetic (sulfide)	H6	Fall	3.6	25.3	−0.21	±	0.05	−0.33	±	0.06	8	St. Louis
Saint-Séverin												
Magnetic (metal)	LL6	Fall	3.4	25.0	0.24	±	0.06	0.36	±	0.09	7	St. Louis
Non-magnetic (silicate)	LL6	Fall	28.4	11.6	0.05	±	0.03	0.10	±	0.04	6	St. Louis
Non-magnetic (sulfide)	LL6	Fall	19.6	27.8	−0.03	±	0.02	−0.05	±	0.05	7	St. Louis
BCR-2	Basalt	Geostandard	10.5	7.6	0.08	±	0.03	0.11	±	0.06	10	St. Louis

[a] Standard errors (2SE = 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).
[b] Number of analyses.
[c] St. Louis = Washington University in St. Louis.

2.2. Experimental and analytical method

Chemical purifications were undertaken in the clean laboratories at Washington University in St. Louis, or at the University of Chicago. The Fe isotope compositions were measured using a *Thermo Scientific* Neptune (in Chicago), or using a *Thermo Scientific* Neptune Plus (in St. Louis) multi-collector inductively-coupled-plasma mass-spectrometer (MC-ICP-MS; Tables 1 and 2). Data acquired for the same samples in both laboratories have identical values within the analytical uncertainties.

All samples were first ground to a fine powder with an agate pestle and mortar. The powders of GRA 06128/9, the brachinites,

the brachinite-like meteorites, and the geostandards were then directly digested with a concentrated 4:1 acid mixture of HF and HNO$_3$ for three days at 180 °C. For the three ordinary chondrites, the metals were first separated from the bulk powder with a hand magnet and then were digested with aqua regia. The non-magnetic fractions (mainly composed of silicates and sulfide) were first treated with cold 3N HCl for 6 hours to ensure dissolution of sulfides with a minimum dissolution of silicates (we cannot exclude the possibility that a minor fraction of the silicates were dissolved at this stage). This is a procedure adapted from Luck et al. (2005) and that was used in Moynier et al. (2011) to separate metal, sulfide and silicate from enstatite chondrites. The sulfide-

Table 3
The modal bulk Fe isotope compositions of ordinary chondrites.

Sample	Type	Metal (wt%)	Silicate (wt%)	Sulfide (wt%)	Fe in metal (%)	Fe in silicate (%)	Fe in sulfide (%)	Modal bulk δ^{56}Fe	Literature values
Semarkona	LL3.0	26.1	54.0	19.9	48.8	23.4	27.9	0.01	
Kernouve	H6	35.1	56.9	8.0	65.6	23.8	10.6	0.05	0.02 ± 0.06[a] or -0.14 ± 0.02[b]
Saint-Séverin	LL6	6.6	55.3	38.1	8.9	34.4	56.8	0.02	0.01 ± 0.04[a]

[a] From Dauphas et al. (2009).
[b] From Needham et al. (2009).

bearing solutions were separated from the silicate residue and the residue was rinsed several times with water, dried and digested with concentrated HF/HNO₃. The bulk samples, dry metal and silicate fractions were weighed, and the masses of sulfide fractions were calculated by difference (Table 2). The masses represent the relative abundances of metals, silicates and sulfides in each ordinary chondrite (see Table 3). We note that this phase separation procedure is not perfect. Torigoye and Shima (1993) have examined phases separated by hand-magnet using binocular microscope and observed fine silicate grains attached to metals. Hence, Fe isotope fractionation effects between metal, silicate and sulfide in chondrites are likely to be more extreme than the reported values.

All samples (bulk and mineral separate fractions) were redigested with 6N HCl before being loaded onto chemical separation columns. We followed the same Fe purification and mass-spectrometer procedure used in Wang et al. (2011, 2012a, 2012b; 2013). Iron was separated from matrix elements in 6N HCl with 1 mL AG1-X8 200–400 mesh anion-exchange resin. Fe was then eluted from the resin in 0.4N HCl. This chemical separation procedure was done twice for each sample to maximize removal of matrix elements.

Samples were introduced into the MC-ICP-MS with a 100 µL/min PFA MicroFlow nebulizer and a cyclonic spray chamber. The intensities of ^{54}Fe, ^{56}Fe and ^{57}Fe were measured on the peak shoulders with Faraday cups L2, C, and H1, respectively, to avoid the Ar-based polyatomic interferences. Isobaric interferences from ^{54}Cr were monitored as ^{53}Cr on Faraday cup L3. We used medium mass resolution and the resolving power ($M/\Delta M$) was ~8500. To circumvent the instrumental bias, we used a sample-standard technique with IRMM-014 as the reference standard. Data are reported as δ^{56}Fe and δ^{57}Fe, where $\delta^{56/57}$Fe $= [(^{56/57}$Fe/^{54}Fe)$_{sample}/(^{56/57}$Fe/^{54}Fe)$_{IRMM-014} - 1] \times 1000$ and are reported as *per mille* units (‰). Errors in this study are reported as 2 standard errors, which are calculated as the standard deviation 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. All data fall on the mass dependent fractionation line, within total analytical uncertainties (Fig. 1).

3. Results

3.1. Iron isotope compositions of GRA 06128/9, brachinites and brachinite-like achondrites

The average δ^{56}Fe of brachinites and brachinite-like achondrites is $+0.01 \pm 0.02$‰ (range from -0.01 to 0.04‰), similar to values obtained for bulk chondrites, a variety of planetary achondrites, and terrestrial mantle peridotites (Fig. 2). Brachinite-like achondrites NWA 5400 and NWA 6077 have indistinguishable Fe isotope compositions from brachinites, within analytical errors, whereas Zag (b) is slightly isotopically heavier (δ^{56}Fe $= 0.07 \pm 0.04$‰). GRA 06128/9 are the first crustal samples from any planetary body in
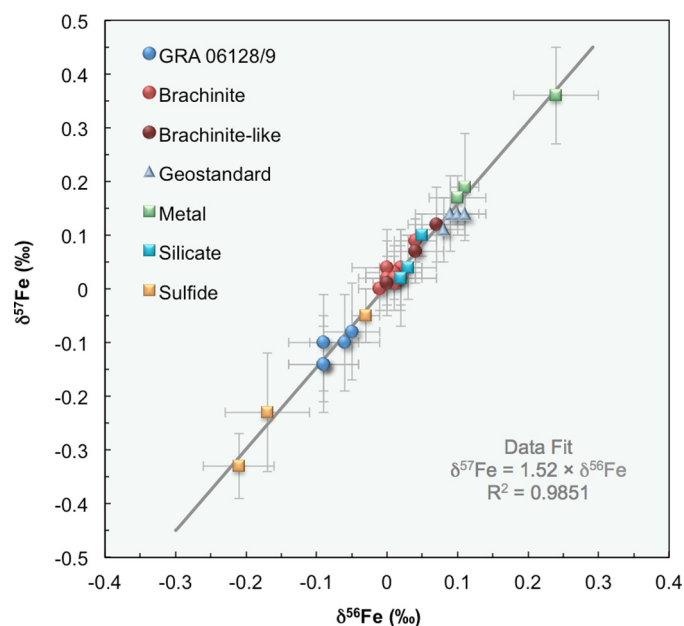
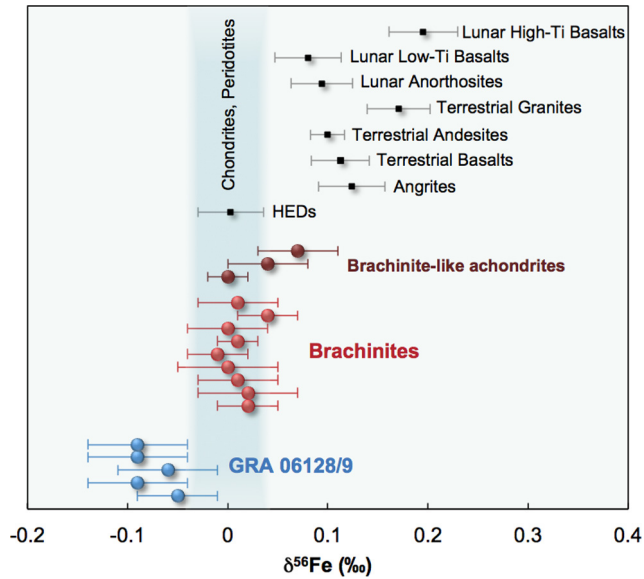**Fig. 1.** Iron isotope compositions (as δ^{56}Fe) of all samples analyzed in this study, shown in 3-isotope (δ^{57}Fe versus δ^{56}Fe) space. All data fall onto the mass-dependent fractionation line of slope ~1.5.

the Solar System that are depleted in the heavy isotopes of Fe compared to chondrites (δ^{56}Fe $= -0.08 \pm 0.06$‰; range from -0.09 to -0.05). GRA 06128/9 also show a difference in Fe isotope composition with brachinites that is well resolved within analytical uncertainty (see Table 1 and Fig. 2).

3.2. Iron isotope compositions of metal, sulfide and silicate fractions of ordinary chondrites

Phase separations from three ordinary chondrites (LL3.0, L6, and H6) all show the same Fe isotope fractionation behavior: δ^{56}Fe$_{metal} > \delta^{56}$Fe$_{silicate} > \delta^{56}Fe_{sulfide}$ (see Table 2 and Fig. 3) and δ^{56}Fe$_{metal} - \delta^{56}$Fe$_{sulfide} \approx 0.3$‰. The average δ^{56}Fe value of the metals, sulfides and silicates separated from the three ordinary chondrites is 0.15‰ (range from 0.10 to 0.24‰), -0.14‰ (range from -0.21 to -0.03‰) and 0.03‰ (range from 0.02 to 0.05‰), respectively. These average values are consistent with the ranges observed in previous studies of mineral phases in ordinary chondrites (Needham et al., 2009; Okabayashi et al., 2012; Theis et al., 2008). Needham et al. (2009) reported micro-drilling experiments on the Parnallae LL3.6 ordinary chondrite, obtaining more extreme isotopic fractionation between mineral phases than reported in this study (Fig. 3). This difference likely reflects the imperfect nature of the magnetic and leaching separation procedure used in this study. However, the method that we employed has the advantage that it is possible to perform a precise gravimetric mass-balance to understand the total Fe isotope budget of samples (Table 3).

Fig. 2. Iron isotope compositions (as δ^{56}Fe) of GRA 06128/9, brachinites and brachinite-like achondrites. The chondritic and terrestrial mantle value, and its associated uncertainty, is shown in shade and average values for typical terrestrial, lunar rocks, HED and angrite meteorites are also plotted for comparison. All uncertainties in this study are reported as two standard errors, and those in the literature are reported as two sigma standard deviations. Published data are from: carbonaceous chondrites (Wang et al., 2013); terrestrial peridotites (Craddock and Dauphas, 2011; Craddock et al., 2013; Weyer and Ionov, 2007); terrestrial basalts and andesites (Craddock and Dauphas, 2011; Dauphas et al., 2009; Poitrasson et al., 2004; Schoenberg and von Blanckenburg, 2006; Weyer and Ionov, 2007; Weyer et al., 2005); terrestrial granites (Poitrasson and Freydier, 2005; Telus et al., 2012); lunar basalts and anorthosites (Liu et al., 2010; Poitrasson et al., 2004; Weyer et al., 2005); HED and angrite meteorites (Wang et al., 2012a).
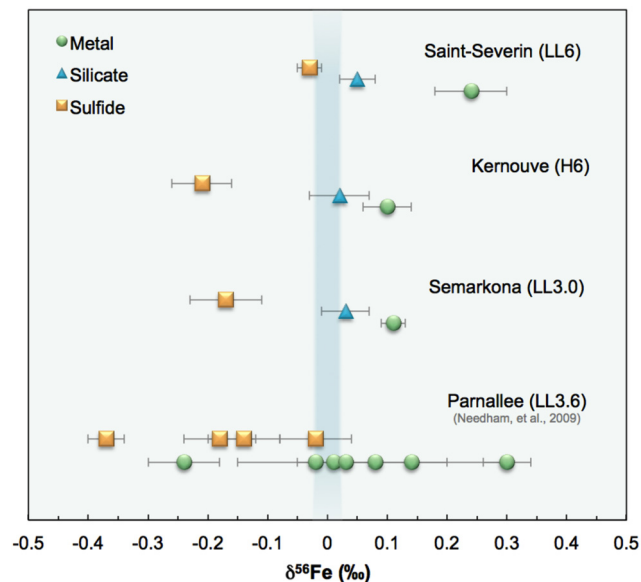
Fig. 3. Iron isotope compositions (as δ^{56}Fe) of magnetic (metal), non-magnetic (sulfide) and non-magnetic (silicate) fractions of three ordinary chondrites measured in this study. Literature data from Needham et al. (2009) are plotted for comparison.

4. Discussion

4.1. Sulfide control on enrichment of light iron isotopes in GRA 06128/9

GRA 06128/9 have the only negative δ^{56}Fe value (-0.08 ± 0.06‰) among all known planetary crust materials (see Fig. 2). In comparison, terrestrial felsic crustal materials (*e.g.*, andesites and granitoids) all have heavy Fe isotope enrichments (δ^{56}Fe $\geqslant 0.1$‰;

e.g., Craddock and Dauphas, 2011; Poitrasson and Freydier, 2005; Telus et al., 2012). Basaltic crustal rocks from Mars and the majority of HED meteorites (excluding the incompatible enriched Stannern-trend eucrites) have Fe isotope compositions identical to carbonaceous chondrites (δ^{56}Fe ~ 0.0‰; *e.g.*, Poitrasson et al., 2004; Wang et al., 2012a, 2013), and basaltic crustal materials from the Moon, the angrite parent body and from terrestrial mid-ocean ridges are enriched in the heavier isotopes of Fe, with δ^{56}Fe values of ~ 0.1‰, or higher (Dauphas et al., 2009; Liu et al., 2010; Poitrasson et al., 2004; Teng et al., 2013; Wang et al., 2012a).

Negative δ^{56}Fe isotope compositions have previously been reported in sulfide phases (troilite and pentlandite) separated from ordinary chondrites (δ^{56}Fe: -0.02 to -0.37‰; Theis et al., 2008; Needham et al., 2009), pallasites (δ^{56}Fe: -0.21‰ to -0.30‰; Weyer et al., 2005) and iron meteorites (δ^{56}Fe: -0.10‰ to -0.45‰; Williams et al., 2006). The new Fe isotope results for ordinary chondrites of various Fe-content and metamorphic grade (LL3.0, L6, and H6) confirm prior observations, with a Fe isotope fractionation pattern of: δ^{56}Fe$_{metal} > \delta^{56}$Fe$_{silicate} > \delta^{56}Fe_{sulfide}$ (Fig. 3), and sulfide compositions ranging from -0.03 to -0.21‰. The new results lie within the extremes of Fe isotope fractionation observed by micro-drilling and hand-separation from crushed samples by Needham et al. (2009). Therefore, different phase separation procedures (*cf.*, this study and Needham et al., 2009) do not induce detectable Fe isotope effects.

To further test the validity of the ordinary chondrite phase separate data, we calculated modal bulk Fe isotope compositions based on the abundances, Fe concentrations and Fe isotope compositions of the metal, silicate and sulfide fractions (Table 3). Two of these three calculated modal compositions are consistent with previous measurements of the bulk samples (Dauphas et al., 2009), however the Kernouve value differs from that reported by Needham et al. (2009). Wang et al. (2013) have observed that individual ordinary chondrites can exhibit large Fe isotopic variations, probably due to the phase distribution effect, where uneven distributions of phases in bulk-rock fragments leads to different apparent Fe isotope ratios.

The new and published data for sulfides (mainly troilites) in chondrites are also consistent with theoretical calculations of Fe isotope fractionation. Equilibrium Fe isotope fractionation factors (*i.e.*, reduced partition function ratios β-factors) can be evaluated from Mössbauer spectroscopy data or synchrotron inelastic nuclear resonant X-ray scattering data (Polyakov et al., 2007; Polyakov and Soultanov, 2011). These theoretical calculations have not only extended the temperature–pressure range, but importantly for our study, have provided significantly more Fe-bearing mineral species over existing limitations of laboratory experiments on natural samples. Such calculations have confirmed that troilite is enriched in the lighter Fe isotopes compared with metal and silicate minerals. These results all indicate the dominant control of Fe from sulfide in GRA 06128/9 in generating an isotopically light Fe isotope composition.

4.2. Formation of sulfide-rich felsic partial-melts in planetesimals

It has been proposed that GRA 06128/9 was formed from Fe–S- and felsic-rich low-to-moderate degree (13–30%) partial melting of a volatile-rich chondritic parent body prior to any core formation event (Day et al., 2009a, 2012a). The light Fe isotope enrichment of GRA 06128/9 is consistent with this mechanism, where sulfide-rich melt (negative δ^{56}Fe signature) formed during partial melting of chondritic precursor materials. In order to examine this process in detail, we have calculated the initial melt reservoir generated from preferential consumption of sulfide minerals from chondritic precursors (Fig. 4; see Supplementary Table S1 for modeling parameters used). Since the separation procedure for metal, sulfide
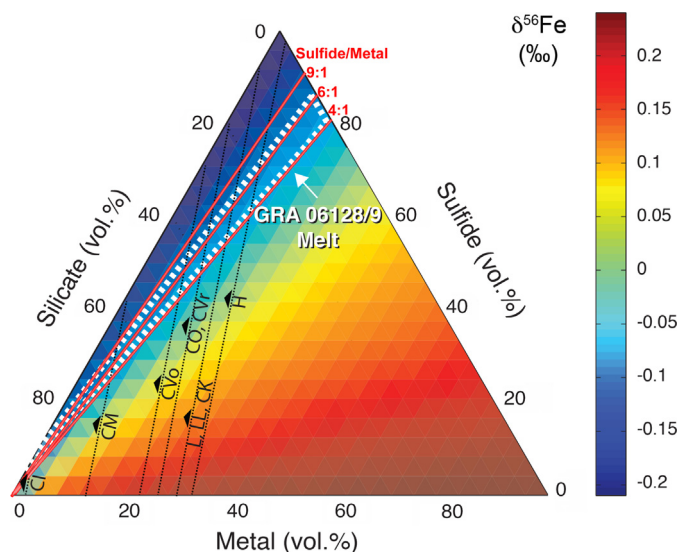
Fig. 4. Ternary diagram showing the Fe isotope compositions of melts composed of varying proportions of silicate, metal and sulfide phases from chondritic precursors. This mass-balance diagram shows the composition of initial melt, and the sulfide/metal ratio. The density considerations are also plotted for different types of ordinary and carbonaceous chondrites. Please refer to main text for details.

and silicate in chondrites is imperfect and the measured fractionation can only represent the minimum value, we use the largest Fe isotope fractionations of metals (δ^{56}Fe $= 0.24$‰) and sulfides (δ^{56}Fe $= -0.21$‰) observed in this study for the calculations.

To obtain the Fe isotope composition of GRA 06128/9, preferential melting of sulfide relative to metal (sulfide to metal ratio varies from 4:1 to 9:1 in volume) is required (Fig. 4). The minimum amount of FeS in the melt inferred from this model is $\sim$5 vol%; the absolute number could vary based on the end-member values of sulfide/metal/silicate chosen and the mass balance of Fe in the phases. This 5 vol% minimum requirement of FeS in the original melt does not conflict with the sulfide abundance (up to $\sim$2.5 vol%; Day et al., 2012a) observed in polished thin-sections of GRA 06128/9 for two reasons. First, GRA 06128/9 are partially cumulitic (e.g., Shearer et al., 2010) so calculated sulfide abundance is likely to differ from measured abundances depending on the proportion of low-Fe feldspar that has accumulated to form GRA 06128/9 (see below). Second, significant S-loss has been widely reported in partially melting experiments (e.g. Feldstein et al., 2001; Gardner-Vandy et al., 2013; Jurewicz et al., 1993, 1995), and desulfidation is also possible during the generation of asteroidal melts similar to those responsible for GRA 06128/9 (e.g., Keil, 2000).

A sulfide-preferential melting model is in agreement with low-temperature and low-degree partial melting experiments of chondritic materials (e.g., Keil, 2000; McCoy et al., 1997). Experiments on chondrites indicate that progressive partial melting produces a continuum of melt products ranging from Fe–Ni–S melts at relatively low temperatures ($\sim$980 °C), to basaltic melts at higher temperatures ($>$1050–1200 °C; e.g., Jurewicz et al., 1991, 1995; McCoy et al., 1997; Feldstein et al., 2001). The composition of GRA 06128/9 has been interpreted to indicate that felsic melt compositions were produced by partial melting at intermediate temperatures between Fe–Ni–S melting and the main phase of basaltic melting in some asteroids (Day et al., 2009a, 2012a). To generate the felsic composition of GRA 06128/9, a mechanism such as partial melting of volatile and olivine-rich chondritic precursors is required (Morse, 1980; Sessler et al., 1982). Furthermore, the Na-rich composition of precursor material to GRA 06128/9 can act to lower liquidus temperatures by up to 100 °C, shifting melt compositions to feldspar abundances (Tuttle and Bowen, 1958; Kushiro, 1975) that approach oligoclase contents in GRA 06128/9.

The initial volatile contents of chondritic precursor materials in asteroids therefore have a profound effect on temperatures required to generate Fe–Ni–S, felsic and basaltic partial melts, and suggest partial melting occurred at $<$1200 °C and closer to partial melt generation responsible for Fe–Ni–S melts, to generate GRA 06128/9.

Under idealized conditions at $\sim$980 °C, the melts of low-degree partial melting of chondritic precursor materials consist of 85 wt% sulfide and 15 wt% metal. This 85:15 ratio ($\sim$9:1 in volume) of sulfide and metal from experiments agrees well with the predictions from Fe isotopes in the model. In detail, however, there is the requirement of a silicate melt component to account for the bulk felsic composition of the GRA 06128/9. In this scenario, a silicate-rich (up to $\sim$95 vol% silicate) melt can form a Fe isotope composition identical to those of GRA 06128/9 if the sulfide is significantly enriched compared to metal in the melt (Fig. 4). These observations place constraints on the conditions of melt generation ($<$1200 °C) at pressures of asteroidal melting. This is because basaltic partial melts from some asteroids show no isotopically light Fe isotope fractionation (e.g., angrites, eucrites), whereas GRA 06128/9 are generated from lower temperature partial melting that induced buoyant FeS-felsic melts.

Even though our conceptual model emphasizes the importance of the preferential consumption of sulfide minerals over Fe metals from chondritic precursors, it provides no constraint on the absolute proportion of sulfide minerals in the melt, except for a minimum limit ($\sim$5 vol%). Therefore, in order to put a constraint on the maximum percentage of sulfide in the melt, we assessed negative buoyancy effects on the generation of sulfide-rich felsic melts in low gravity environments, such as planetesimals. We have estimated the average density of Fe–S-rich melts with a simplified model (see Supplementary Figure S1). The average densities of common ordinary and carbonaceous chondrites have been plotted as reference lines in Fig. 4 (Consolmagno et al., 2008). Areas on the right of the chondritic reference lines are the forbidden zones according to simple density considerations, while areas on the left are the maximum sulfide/metal allowed with only consideration of density. These simple calculations indicate low maximum proportions of metal and sulfide assuming a carbonaceous or metal-poor R chondrite precursor composition.

The light Fe isotope composition of GRA 06128/9 can be explained as the result of crystallizing and/or plagioclase accumulation from a Fe–S-rich felsic melt with similar composition to the 10–15% degree partial melting of an ordinary or R-type chondrite (Feldstein et al., 2001; Gardner-Vandy et al., 2013). By mixing 60% of the melt composition provided in Feldstein et al. (2001) with 40% plagioclase measured by Day et al. (2012a) or by mixing 40% of the melt composition in Gardner-Vandy et al. (2013) with 60% plagioclase, we can reproduce the major element composition of GRA 06128/9 quite well (Supplementary Table S2). Since plagioclase is nominally Fe free (in reality, very low Fe; see Supplementary Table S2), the Fe isotope composition (negative δ^{56}Fe) of GRA 06128/9 is largely inherited from the Fe–S-rich melt. Our new mixing model is entirely consistent with estimates of partial melting from rare earth elements (13–30%), to form GRA 06128/9 (Day et al., 2012a). Simple mass balance (cf., a preponderance of silicate) means that low-degree partial melting will not significantly change the Fe concentration or isotope composition of the source. Therefore, the residual mantle of the GRA 06128/9 parent-body would not be isotopically fractionated compared to chondrites (δ^{56}Fe $\sim$ 0), as is observed for brachinites (δ^{56}Fe $= 0.01 \pm 0.02$‰).

As demonstrated by the models above, initial melts from chondritic precursors can be enriched in the light isotopes of Fe due to preferential melting of sulfides. Sulfide minerals, such as troilite and pentlandite, are the main carriers of the highly siderophile elements (HSE: Os, Ir, Ru, Rh, Pt, Pd, Re, Au) in GRA 06128/9

(Day et al., 2012a). The elevated HSE contents of GRA 06128/9, brachinites and brachinite-like achondrites – within factors of approximately one to three of chondritic abundances – are consistent with partial melting processes prior to core formation (Day et al., 2009a, 2012a) and contrast strongly with the low HSE abundances of early-formed felsic and basaltic materials from the Moon and other planetesimal bodies (e.g., Day et al., 2010, 2012b; Riches et al., 2012).

A unique aspect of the HSE abundances for GRA 06128/9 and brachinites is their strongly fractionated patterns, with low Ir, Pt and Pd relative to Ru (Day et al., 2012a). This unusual fractionation cannot be modeled with standard liquid metal–solid metal partitioning in Fe–S systems (e.g., Chabot and Jones, 2003), but requires either: (1) multiple phases in the residue; (2) two-stage melt fractionation; (3) fractional fusion; or (4) a non-chondritic starting composition (Day et al., 2012a). The new iron isotope data has some bearing on this conundrum. The new Fe isotope results do not indicate a non-chondritic starting composition or two-stage melt fractionation. Instead, the new data can most simply be explained by preferential consumption of sulfide and processes more akin to fractional fusion or inefficient melt removal and metal/sulfide retention in the GRA 06128/9 melt source regions. This is because the Fe isotope composition of GRA 06128/9 only requires a single-stage melting process where sulfide-rich felsic melt is inefficiently extracted from the melt region. Similarly, the HSE and REE patterns of both GRA 06128/9 and brachinites indicate inefficient melt extraction and complex liquid metal/sulfide–solid metal/sulfide partitioning behavior.

4.3. Planetary crust comparisons

GRA 06128/9 and brachinites are currently the only extra-terrestrial felsic crust/mantle materials considered to come from the same parent body (Day et al., 2012a). Therefore they represent a key sample suite for inter-planetary comparison to understand early crust formation. Other early asteroidal crusts formed at a comparable time period, such as basaltic angrites or HEDs. However, these samples show completely different Fe isotopic fractionation behavior. Partial melting experiments of carbonaceous chondrites have shown that HED-like melts are formed at low $f\mathrm{O}_2$ while angrite-like melts are formed at high $f\mathrm{O}_2$ (Jurewicz et al., 1991, 1993). Primitive chondritic materials, including carbonaceous, ordinary and enstatite chondrites all have a bulk $\delta^{56}\mathrm{Fe}$ value of $\sim 0\text{‰}$ (Craddock and Dauphas, 2011; Needham et al., 2009; Wang et al., 2013). While HED meteorites (except Stannern-trend eucrites) have a Fe isotope composition indistinguishable from chondrites; angrites are enriched in heavy Fe isotopes, up to $\delta^{56}\mathrm{Fe} \sim +0.12\text{‰}$ (Wang et al., 2012a). These differences of Fe isotope composition between angrite and HEDs basaltic crustal samples are principally controlled by the oxygen fugacities prevailing at the time of formation. Oxidation state is the main parameter, which controls the Fe isotopic fractionation during higher degree 'basaltic' partial melting conditions (Wang et al., 2012a).

In contrast, we show that for low-degree partial melting of chondritic precursors, preferential segregation of isotopically fractionated sulfides controls the Fe isotope composition of the melt and therefore of the accumulated crust. The Fe–S rich melt is characterized not only by a significantly negative $\delta^{56}\mathrm{Fe}$ signature, but also with HSE abundances similar to chondritic abundances, where both features are closely linked with their compatibilities within sulfide minerals. Our results indicate that iron isotopes, in conjunction with other isotopic and elemental tracers (e.g., HSE abundances) have the potential to record mechanisms of early crust formation processes with fidelity.

5. Conclusions

The paired meteorites GRA 06128 and 06129 (GRA 06128/9) are the only example of evolved felsic crust-type materials outside of Earth's continental crust. Remarkably, GRA 06128/9 are also the first example of crust with isotopically light Fe ($\delta^{56}\mathrm{Fe} = -0.08 \pm 0.06\text{‰}$). We also report the Fe isotope compositions of brachinites and brachinite-like achondrite meteorites that are considered to represent mantle residuum after felsic crustal melt extraction to form GRA 06128/9-like melt compositions on asteroidal parent bodies. The new results show that: 1) even though GRA 06128/9 and brachinites have similar oxygen isotope compositions, they have different Fe isotope compositions and 2) GRA 06128/9 is enriched in the lighter isotopes compared to chondrites, while brachinites have $\delta^{56}\mathrm{Fe} = 0.01 \pm 0.02\text{‰}$, similar to chondrites.

New metal, silicate and sulfide phase separations reinforce previous studies and show that sulfide phases are universally enriched in lighter Fe isotopes ($\delta^{56}\mathrm{Fe} = -0.14\text{‰}$) compared with metals ($\delta^{56}\mathrm{Fe} = 0.15\text{‰}$) and silicates ($\delta^{56}\mathrm{Fe} = 0.03\text{‰}$). The unique negative Fe isotope composition of GRA 06128/9 can be best explained as being inherited from preferential melting of sulfide phases from chondritic precursors, forming a Fe–S-rich felsic melt by low-to-moderate degree (13–30%) partial melting of a volatile-rich chondritic precursor (e.g., Day et al., 2009a; 2012a). This conclusion is consistent with previous studies of highly siderophile elements (HSE) in GRA 06128/9 and brachinites and with cessation of melting on some asteroidal parent bodies in response to early melting and segregation of S- and Al-rich melts (cf., GRA 06128/9).

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.02.022.

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