

Iron Isotopic Compositions of Geological Reference Materials and Chondrites

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High-precision iron isotopic compositions for Fe-bearing geological reference materials and chondrites with a wide range of matrices (e.g., silicates, oxides, organic-bearing materials) are reported. This comprehensive data set should serve as a reference for iron isotopic studies across a range of geological and biological disciplines for both quality assurance and inter-laboratory calibration. Where comparison is available, the iron isotopic compositions of most geological reference materials measured in this study were in agreement with previously published data within quoted uncertainties. Recommendations for the reporting of future iron isotopic data and associated uncertainties are also presented. Long-term repeat analyses of all samples indicate that highly reproducible iron isotopic measurements are now obtainable ($\pm 0.03\text{‰}$ and $\pm 0.05\text{‰}$ for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, respectively).

Keywords: mass spectrometry, certified reference materials, geological reference materials, iron, isotope ratios, precise determination, calibration.

Les compositions isotopiques du fer de plusieurs matériaux de référence géologiques et chondrites, couvrant une large gamme de matrices (e.g., silicates, oxides, roches riches en matière organique), sont présentées. Les compositions isotopiques mesurées dans cette étude sont identiques, aux incertitudes près, aux valeurs publiées précédemment par d'autres laboratoires. Cette base de données pourra servir de point de comparaison dans les calibrations inter-laboratoires afin d'évaluer la qualité des mesures. Des recommandations pour exprimer les variations isotopiques du fer et calculer leurs incertitudes sont également présentées. Des mesures repliquées sur un large intervalle de temps montrent que les compositions isotopiques mesurées sont très reproductibles ($\pm 0.03\text{‰}$ et $\pm 0.05\text{‰}$ pour $\delta^{56}\text{Fe}$ et $\delta^{57}\text{Fe}$, respectivement).

Mots-clés : spectrométrie de masse, matériaux de référence certifiés, matériaux de référence géologiques, fer, rapports isotopiques, déterminations précises, calibration.

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Fractionation of the stable isotopes of iron has received considerable attention in the Earth Sciences over the past decade. Initial interest was spurred by the fact that iron, as an essential micronutrient, might be isotopically fractionated by a wide range of metabolic processes, and so measurable variations in iron isotopic compositions in the environment might be used as discriminate biosignatures (Beard *et al.* 1999). Indeed, experimental research has demonstrated significant iron isotope fractionation ($> 1\text{‰}$ for $^{56}\text{Fe}/^{54}\text{Fe}$ ratios) during biologically mediated iron cycling, in particular oxidation-reduction (redox) between ferric and ferrous-iron through dissimilatory Fe(III) reduction (DIR) (Beard *et al.* 1999, 2003a, Icopini *et al.* 2004, Johnson *et al.* 2005, Crosby *et al.* 2007) and anaerobic photosyn-

thetic Fe(II) oxidation (Croal *et al.* 2004, Balci *et al.* 2006). It is now recognised that iron isotopes are comparably fractionated by a wide range of abiotic processes at both low and high temperature, for example by aqueous precipitation of iron as iron-oxide (Bullen *et al.* 2001, Skulan *et al.* 2002), carbonate (Wiesli *et al.* 2004) and sulfide (Butler *et al.* 2005), alteration and weathering of oceanic and continental crust (Rouxel *et al.* 2003, Fantle and DePaolo 2004, Dauphas *et al.* 2010), high-temperature evaporation/condensation (Wang *et al.* 1994, Dauphas *et al.* 2004), thermal and chemical diffusion of iron among solid metal, silicate minerals and melts (Roskosz *et al.* 2006, Dauphas 2007, Richter *et al.* 2009a, b) and high-temperature equilibrium fractionation among melts and minerals

(Schuessler *et al.* 2007, Shahar *et al.* 2008). While the range of known processes that fractionate the isotopes of iron complicates efforts to decipher the origin of iron isotopic signatures, the data clearly attest to the potential for iron isotopes to trace both biological and geochemical cycling of iron in modern and ancient environments (see reviews by Beard and Johnson 2004, Dauphas and Rouxel 2006).

An important, but often secondary, aspect of geochemical research – in particular for non-traditional stable isotope geochemistry – is the determination and certification of isotopic compositions of geological reference materials. Such materials are essential in analytical research for (a) sample calibration and normalisation, (b) quality assurance, (c) estimations of analytical uncertainties and long-term data reproducibility, and (d) inter-laboratory data comparison. For most non-traditional stable isotope systems (e.g., Fe, Mg, Ca, Mo, Cu, Zn), extensive databases of well-characterised isotopic geological reference materials with a range of composition/matrix appropriate for geochemical and biological studies are lacking. Given the widespread interest in iron isotopes as tracers of biological and geological processes, a database of consensus iron isotopic values in a comprehensive suite of geological reference materials is warranted. While recent reviews (e.g., Dauphas and Rouxel 2006) have compiled iron isotopic compositions for several well-characterised geological reference materials, existing compilations are not inclusive of a wide range of matrices appropriate for all geological and biological studies. In this study, high-precision iron isotope compositions are reported for a wide range of reference materials available from national laboratories (National Institute of Standards and Technology, NIST; US Geological Survey, USGS; Institute for Reference Materials and Measurements, IRMM; Service d'Analyse des Roches et des Minéraux, SARM; Institute of Geophysical and Geochemical Exploration, IGGE) including meteorites, silicates, shales, Fe oxides, carbonates and organic-rich materials. These data are critically compared against those reported by other laboratories. The analytical precision and long-term reproducibility of iron isotopic compositions obtained in this study are significantly improved relative to previous studies, which provides a better baseline for quality assurance and inter-laboratory comparison.

Analytical procedure

Sample digestion and chemical purification of iron

The procedure for routine sample digestion and chemical purification of iron in geological materials in our labo-

ratory has been described in recent publications (Dauphas *et al.* 2004, 2009b). For this study, powdered test portions (typically ~ 10 mg, but up to 40 mg for materials containing Fe < 1% m/m) were weighed into 6 ml Savillex PFA vials (Savillex Corp., Minnetonka, MN, USA) and subjected to hot-plate acid dissolution with mixtures of concentrated HF-HNO₃-HClO₄ and HCl-HNO₃-HClO₄ (Table 1). Biological samples analysed in this study were ashed prior to acid dissolution in order to remove organic carbon. Ashing was achieved by heating the samples in a capped quartz crucible for 24 hr in a furnace at 500 °C. Biological samples were subsequently dissolved using the hot-plate acid treatment described above for other sample matrices.

Alternative procedures for digestion of refractory geological materials were used in order to demonstrate that the sample dissolution procedures adopted by our laboratory yield accurate and reproducible bulk iron isotopic data for a range of geological materials with different matrices and iron concentrations. It has been shown that refractory minerals, such as spinels, have a range of iron isotopic compositions different to the bulk rock (e.g., Williams *et al.* 2005) and so complete digestion of all minerals is necessary to ensure reproducible and accurate iron isotopic measurements.

High-pressure Parr Bombs were used for digestion of a selection of geological reference materials and samples, specifically meteorites and ultramafic rocks that can host refractory spinels. Dissolution of samples in high-pressure Parr Bombs used a protocol following Pourmand and Dauphas (2010). Between 10 and 50 mg of powdered material was weighed into a 6 ml Savillex PFA vial and 1 ml of concentrated HF + 0.5 ml of concentrated HNO₃ was added to this vial. The vial was closed and then heated inside a 45 ml PTFE Parr Bomb at ~ 170 °C for 5 d. The dissolved mixture was evaporated and then fumed with ~ 100 µl of concentrated HClO₄ to convert insoluble fluorides to soluble complexes. The residue was then dissolved in ~ 3 ml of concentrated HNO₃ by re-heating in Parr Bombs at ~ 170 °C for up to 5 d. The dissolved sample was evaporated once more and the final residue taken back into solution with ~ 500 µl of 6 mol l⁻¹ HCl.

Powders of meteorites and several geological reference materials were also digested by high-temperature flux fusion using lithium metaborate flux (Pourmand and Dauphas 2010). Purified LiBO₂ flux (Spex CertiPrep, Metuchen, NJ, USA) and powdered sample material were weighed into ultra-pure 8 ml graphite crucibles (minimum ratio of flux/sample = 6:1). To this ~ 150 mg of ultra-pure LiBr non-wetting agent (Spex CertiPrep) was also added. The

Table 1.
Sample digestion and iron column purification protocols (see also Dauphas *et al.* 2009b, Tang *et al.* 2009)

Routine sample dissolution protocol

1. Addition of 1 ml of concentrated HF + 0.5 ml of concentrated HNO₃ + drops of concentrated HClO₄
2. Heated in closed beakers overnight at ~ 150 °C on hot-plate
3. Evaporation and addition of 0.75 ml of concentrated HCl + 0.25 ml of concentrated HNO₃ + drops of concentrated HClO₄
4. Heated overnight and evaporation on hot-plate
5. Addition of 1 ml of concentrated HCl + 0.5 ml of concentrated HNO₃ (+ drops of concentrated HClO₄)
6. Heated overnight and evaporation on hot-plate. Dissolution of residue in 0.5 ml of 6 mol l⁻¹ HCl

Short-column purification

1. Disposable Bio-Rad Poly-Prep polyethylene columns filled with 1 ml of AG1-X8 200–400 mesh Cl-form anion exchange resin
2. Resin conditioning: 10 ml of MilliQ H₂O, 5 ml of 1 mol l⁻¹ HNO₃, 10 ml of MilliQ H₂O, 9 ml of 0.4 mol l⁻¹ HCl, 5 ml of MilliQ H₂O and 2 ml of 6 mol l⁻¹ HCl
3. Sample loaded onto column in 0.5 ml of 6 mol l⁻¹ HCl (typically ~ 25% of sample is loaded and the remaining sample retained for other uses)
4. Matrix eluted by addition of 8 ml of 6 mol l⁻¹ HCl (0.5 ml + 0.5 ml + 1 ml + 2 ml + 4 ml increments)
5. Iron recovered into Teflon beakers by addition of 9 ml of 0.4 mol l⁻¹ HCl (0.5 ml + 0.5 ml + 1 ml + 3 ml + 4 ml increments)
6. Purified solution was evaporated to dryness and taken up in 0.25 ml of 6 mol l⁻¹ HCl.
7. Sample purification was repeated a second time with new resin following the procedure in 1–6.
8. Purified solution was evaporated to dryness and finally dissolved in 10 ml of 0.3 mol l⁻¹ HNO₃ for analysis.

Long-column purification

1. Reusable Savillex PFA columns (10.5 cm column length, 0.62 cm column diameter) filled with ~ 3 ml of AG1-X8 200–400 mesh Cl-form anion exchange resin
 2. Resin conditioning: 10 ml of MilliQ H₂O, 10 ml of 0.4 mol l⁻¹ HCl, 5 ml of MilliQ H₂O, 10 ml of 0.4 mol l⁻¹ HCl and 4 ml of 10 mol l⁻¹ HCl
 3. Sample loaded onto column in 0.5 ml of 6 mol l⁻¹ HCl (typically ~ 25% of sample is loaded and the remaining sample retained for other uses)
 4. Matrix eluted in two stages by addition of 5 ml of 10 mol l⁻¹ HCl (0.5 ml + 0.5 ml + 1 ml + 3 ml increments) and 22 ml of 4 mol l⁻¹ HCl (0.5 ml + 0.5 ml + 1 ml + 5 ml + 5 ml + 15 ml increments)
 5. Iron recovered into Teflon beakers by addition of 8 ml of 0.4 mol l⁻¹ HCl (0.5 ml + 0.5 ml + 1 ml + 2 ml + 4 ml increments)
 6. Purified solution was evaporated to dryness and taken up in 0.25 ml of 10 mol l⁻¹ HCl.
 7. Sample purification was repeated a second time (a third time for matrices with low Fe concentrations < 0.5% m/m) with new resin following the procedure in 1–6.
 8. Purified solution was evaporated to dryness and finally dissolved in 10 ml of 0.3 mol l⁻¹ HNO₃ for analysis.
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crucibles were capped with a second graphite crucible to minimise sample loss and contamination and the powdered mixture was fused at > 1000 °C for 12 min. The resulting melt was transferred directly to a 30 ml Savillex PFA vial containing ~ 15 ml of 3 mol l⁻¹ HNO₃. The use of a non-wetting agent ensured that the fused melt could be transferred easily and quantitatively to the Savillex vial

as a single molten mass without loss to the crucible (Pourmand and Dauphas 2010). After addition of the melt to 15 ml of 3 mol l⁻¹ HNO₃, the volume of acid was brought up to ~ 25 ml. Dissolution of the fused sample was achieved by rapid agitation and stirring on top of a vibrating plate, followed by ultrasonic treatment (Pourmand and Dauphas 2010). Aliquots of samples digested by flux fusion were taken and evaporated to dryness, and the residue taken back into solution with ~ 500 µl of 6 mol l⁻¹ HCl.

Iron was routinely separated from matrix elements by anion exchange chromatography (Bio-Rad, Hercules, CA, USA; AG1-X8, chloride form, 1 ml volume, ‘short-column method’; Table 1) in a HCl medium (Strelow 1980, Dauphas *et al.* 2009b). The digested sample was loaded in 6 mol l⁻¹ HCl in which iron was quantitatively retained on the resin and matrix elements were eluted. Iron was subsequently eluted from the resin in 0.4 mol l⁻¹ HCl. The chromatographic separation of iron was performed twice using newly conditioned resin. The purified iron solution was evaporated to dryness, taken up in ~ 100 µl of concentrated HNO₃ and evaporated to dryness again to eliminate chloride complexes. The iron residue was then dissolved in a 10 ml stock solution of 0.3 mol l⁻¹ HNO₃ in preparation for isotopic determination. The isotopic reference material (IRMM-014) and blanks used for calibrator bracketing and on-peak zero correction, respectively, were prepared from the same batch of 0.3 mol l⁻¹ HNO₃ to ensure perfect matching of the dilution medium.

A method for the improved separation of iron from other transition metal elements (e.g., Cu) has also been developed (Tang *et al.* 2009) and was used for purification of iron in a subset for geological reference materials and meteorite samples. This method utilised a long (10.5 cm height, 0.62 cm diameter) Savillex PFA column filled with 3 ml of AG1-X8, chloride-form resin (‘long-column method’; Table 1). Iron was fixed on the column in concentrated acid (> 10 mol l⁻¹ HCl) and matrix elements eluted by the addition of 5 ml of concentrated HCl, followed by 22 ml of 4 mol l⁻¹ HCl. Iron was eluted from the column in 8 ml of 0.4 mol l⁻¹ HCl. The column purification was repeated twice using new resin. The purified iron solution was evaporated to dryness and taken up in 10 ml of 0.3 mol l⁻¹ HNO₃ for subsequent isotopic determination by MC-ICP-MS.

Iron isotopic determinations

Iron isotopic determinations were carried out using a Thermo Scientific Neptune MC-ICP-MS (Dauphas *et al.* 2009b). Sample solutions were introduced as wet aerosols

through a Scott-type cyclonic spray chamber (Stable Sample Introduction System, Elemental Scientific Inc., Omaha, NE, USA). Measurements were performed in either medium or high mass resolution mode whereby Fe^+ peaks were resolved from interfering ArO^+ , ArOH^+ and ArN^+ isobars as flat-topped plateaus on the low mass shoulder of argide peaks (Weyer and Schwieters 2003). Potential isobaric interferences from Cr and Ni were monitored at masses $^{53}\text{Cr}^+$ and $^{64}\text{Ni}^+$ and subtracted from Fe signals as necessary. On-peak zero was determined by measurement of a clean $0.3 \text{ mol l}^{-1} \text{ HNO}_3$ blank solution at the beginning of each analytical session and is subtracted from all calibrator and sample data. Instrumental mass fractionation (β), which is inherent to MC-ICP-MS, is described by the exponential law, $r = R(1 + \Delta M/M)^\beta$ (Russell *et al.* 1978, Maréchal *et al.* 1999) that relates the measured isotopic ratio (r) to the true ratio (R) as a function of the relative mass difference of the isotopes ($\Delta M/M$). Instrumental mass fractionation was corrected using calibrator-sample bracketing (e.g., Belshaw *et al.* 2000), from which β was calculated from repeat measurements of the calibrator that bracketed the sample and the average of these two values was then applied to the sample. Iron isotopic compositions were measured for twenty-five cycles, each cycle being integrated for 8.389 s. Each sample was typically measured nine times non-sequentially during an analytical session and 95% confidence error bars of the average calculated accordingly. As discussed by Dauphas *et al.* (2009b), the uncertainty associated with instrumental instability alone does not account for all sources of analytical error (see below).

Reporting of iron isotopic data

Nomenclature for reporting of iron isotopic ratios

We apply conventional the δ -notation for reporting iron isotopic ratios,

$$\delta^i\text{Fe}(\text{‰}) = [(^i\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^i\text{Fe}/^{54}\text{Fe})_{\text{calibrator}} - 1] \times 10^3 \quad (1)$$

where ^iFe is isotope 56, 57 or 58, sample refers to the ratio of the measured sample and calibrator refers to the interpolated ratio of bracketing calibrator measurements. The iron isotopic reference material IRMM-014 (Taylor *et al.* 1992) was used for normalisation. Seven independent replicate measurements of the reference material IRMM-524a carried out in this study yielded identical iron isotopic values, with an average composition relative to IRMM-014 of $\delta^{56}\text{Fe} = -0.001 \pm 0.013\text{‰}$ and $\delta^{57}\text{Fe} = +0.003 \pm$

0.019‰ . Therefore, either IRMM-014 or IRMM-524a (from which IRMM-014 is prepared) can in practice be used as iron isotopic reference materials because these materials have an iron isotopic composition that is identical within analytical uncertainty.

While most laboratories report iron isotopic compositions normalised to the iron metal reference material IRMM-014, some laboratories report iron isotopic ratios normalised to that of terrestrial igneous rocks (e.g., Beard and Johnson 1999, Beard *et al.* 2003a, Fantle and DePaolo 2004, Heimann *et al.* 2008). The first studies of iron isotope variations reported similar isotopic compositions in a range of igneous rocks (e.g., continental and oceanic peridotite, basalt, gabbro). These data suggested that 'igneous Fe', 'bulk-Earth' or 'Earth-Moon' had uniform iron isotopic compositions within analytical uncertainty ($\pm 0.10\text{‰}$, 2s) and therefore provided an unparalleled baseline from which to determine iron isotopic fractionation in the terrestrial environment (Beard and Johnson 1999, Beard *et al.* 2003a). On the igneous Fe scale, the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ composition of IRMM-014 is -0.09‰ and -0.11‰ , respectively (Beard *et al.* 2003a). Note that these original igneous Fe values adopted by Beard *et al.* (2003a) do not follow expected mass-dependent fractionation (i.e., $\delta^{57}\text{Fe} \approx 3/2 \times \delta^{56}\text{Fe}$) leading to erroneous reporting of iron isotopic data between normalising scales. As suggested in a number of previous publications and recommended here, normalisation to IRMM-014 should be universally adopted and the use of 'igneous Fe' should be discontinued to ensure consistency in future studies. There are several important reasons to justify this recommendation. First, recent studies employing high-precision iron isotopic determination have demonstrated that the iron isotopic compositions of different igneous rocks are not uniform at precisions now obtainable (± 0.03 , 2s) (Poitrasson and Freydier 2005, Weyer *et al.* 2005, Williams *et al.* 2005, 2009, Schoenberg and von Blanckenburg 2006, Weyer and Ionov 2007, Heimann *et al.* 2008, Teng *et al.* 2008, Dauphas *et al.* 2009a, Schuessler *et al.* 2009), contesting the idea that igneous Fe is a homogeneous isotopic baseline. As shown recently, this is also true for subduction-related basalts (Dauphas *et al.* 2009a). Accordingly, it is uncertain to the extent that the range of iron isotopic compositions measured in continental and oceanic lithospheric rocks faithfully record that of the bulk-Earth or bulk solar system. Second, the iron isotopic composition of IRMM-014 is indistinguishable from that of primitive solar system materials (i.e., chondrites) (Dauphas *et al.* 2009a) suggesting that IRMM-014 is a more appropriate reference material from which iron isotope fractionations among terrestrial and extraterrestrial geological reservoirs (e.g., the Earth, Moon and Mars) can be identi-

fied. A wide range of chondrites (CM, CV, CO, H, L, LL, EH, EL classes) for which iron isotopic data have been published previously, in particular those chondrite that have experienced little or no metamorphism or aqueous alteration, have remarkably uniform iron isotopic compositions with an average $\delta^{56}\text{Fe} = -0.005 \pm 0.006\text{‰}$ (95% c.i.) and $\delta^{57}\text{Fe} = 0.004 \pm 0.010\text{‰}$ (95% c.i.) relative to IRMM-014 (Dauphas *et al.* 2009a). The EL6 chondrite Blithfield measured by Dauphas *et al.* (2009a) has a very different iron isotopic composition ($\delta^{56}\text{Fe} = -0.140 \pm 0.030\text{‰}$) relative to other chondrites and is excluded from this average. This meteorite shows evidence for high-temperature metamorphism and extensive iron remobilisation (Rubin 1984). Third, the use of a single, isotopically homogenous reference material is critical to allow inter-laboratory comparison among reported iron isotope data, particularly as increasingly precise iron isotopic measurements enable smaller isotopic fractionations to be discriminated.

A plot of $\delta^{57}\text{Fe}$ vs. $\delta^{56}\text{Fe}$ (Figure 1) yielded the mass fractionation curve in three-isotope space that, for the samples analysed in this study, was characterised by a slope of 1.475 ± 0.022 and was identical within uncertainty to the mass-dependent fractionation line of 1.466 ± 0.015 obtained by Malinovsky *et al.* (2003). δ values for $^{57}\text{Fe}/^{56}\text{Fe}$ isotope ratios have been used less commonly in the literature (e.g., Poitrasson *et al.* 2005) and can be transposed into standard $\delta^{56}\text{Fe}$ notation following $\delta^{56/54}\text{Fe} = \delta^{57/54}\text{Fe} - \delta^{57/56}\text{Fe}$. Typically, $\delta^{58}\text{Fe}$ is not reported, reflecting the difficulties of measuring accurately and precisely abundance variations of this low abundance isotope (0.282%). However, iron 58 can be useful in studies of primitive solar system materials for examining non-mass dependent nucleosynthetic processes (Völkening and Papanastassiou 1989, Dauphas *et al.* 2004, 2008).

Estimation of analytical uncertainties

It is common for different laboratories to report analytical uncertainties calculated by several methods, such as 1s internal precision based on a single sample analysis (in-run statistics) and 2 standard deviation based on the reproducibility of several *n* replicate analyses during a

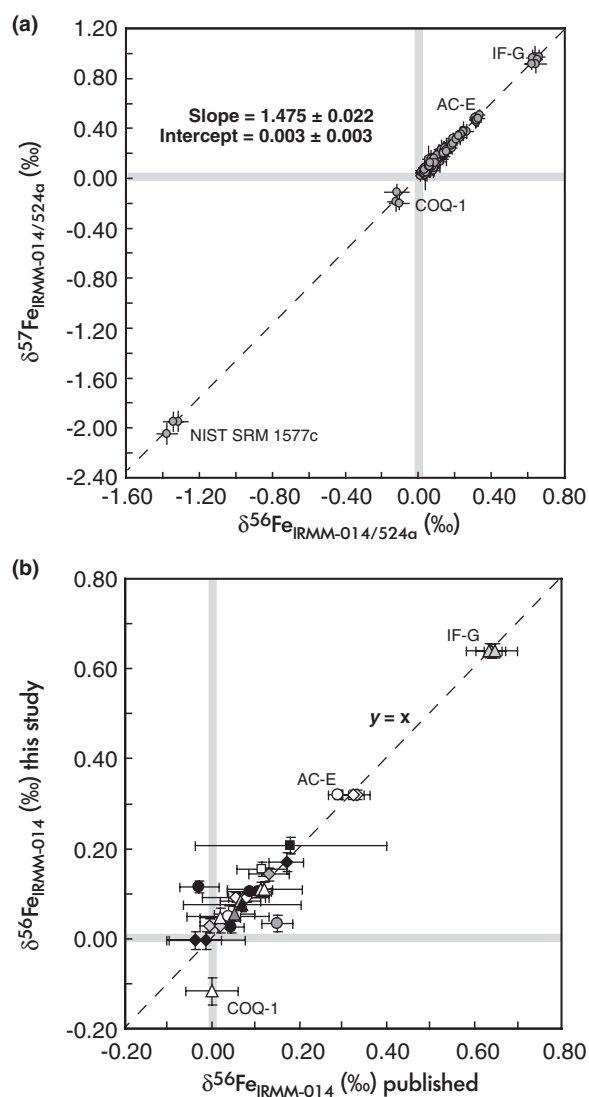


Figure 1. Evaluation of the accuracy of iron isotopic data. (a) Mass fractionation in three-isotope space. The data define a linear trend with a slope of 1.475 ± 0.022 and y-intercept of $+0.003 \pm 0.003$. This relationship is statistically indistinguishable from both theoretical predictions of mass-dependent isotope fractionation (slope equilibrium = 1.475; kinetic = 1.488) and from previously measured isotopic mass-dependent fractionation trends (slope of 1.466 ± 0.015) in natural samples (Malinovsky *et al.* 2003). The data demonstrate that there were no analytical artefacts from unresolved isobaric interferences. (b) Comparison between iron isotope data obtained for geological and other reference materials from this study (y-axis) and from published literature data and compilations (x-axis). See Table 2 for data. Error bars for iron isotopic ratios determined in this study are 95% confidence intervals. The concordance between this and other studies suggests that iron isotopic ratios can be measured accurately at precisions better than $\pm 0.03\text{‰}$. The data obtained in this study represent up to a five times improvement in precision in $\delta^{56}\text{Fe}$ ratios for geological and other reference materials compared to previously published data and compilations.

Table 2.
Iron isotopic compositions of carbonaceous, ordinary and enstatite chondrites

Sample/ Name	Description/ catalogue number	[Fe] (% m/m)*	$\delta^{56}\text{Fe}$ (‰)	95% c.i. [†]	$\delta^{57}\text{Fe}$ (‰)	95% c.i. [†]	Protocol [‡]	Reference
Carbonaceous chondrites								
Allende (CV3)	Smithsonian		-0.004	0.029	0.009	0.044	a, d	
	Reference		-0.005	0.027	0.005	0.037	b, d	
	Powder USNM		-0.017	0.034	-0.008	0.047	b, e	Dauphas <i>et al.</i> (2009a)
	3529		-0.006	0.033	-0.002	0.063	c, e	Dauphas <i>et al.</i> (2009a)
			-0.006	0.030	0.019	0.053	c, e	Dauphas <i>et al.</i> (2009a)
	Allende USNM	23.7	-0.007	0.012	0.003	0.019		
	3529 (recommended)							
	Allende (literature)	23.7	-0.040	0.060	-0.050	0.060		Zhu <i>et al.</i> (2001)
	Allende (literature)	25.6	-0.169	0.040	-0.105	0.066		Poitrasson <i>et al.</i> (2005)
	Allende (literature)		-0.015	0.090	-0.005	0.183		Schoenberg and von Blanckenburg (2006)
	Allende (literature)		-0.010	0.030	-0.010	0.050		Teng <i>et al.</i> (2008)
Grosnaja (CV3)	Field Museum, Chicago, catalogue ME 1732 #21	20.9	-0.025	0.072	-0.024	0.102	c, d	
Viagarano (CV3)	Field Museum, Chicago, catalogue ME 782 #15	19.1	0.026	0.058	0.041	0.092	c, d	
		20.9	-0.058	0.057	-0.056	0.076	a, d	
Ivuna (CI1)	Smithsonian, catalogue USNM 3533	17.7	-0.030	0.053	-0.030	0.071	c, d	
Orgueil (CI1)	Natural History Museum, Paris, catalogue #219 Orgueil (literature)	17.4	-0.015	0.066	-0.017	0.062	c, d	
			0.380	0.060	0.600	0.060		Zhu <i>et al.</i> (2001)
Murchison (CM2)	Natural History Museum, Paris, catalogue #2435	19.4	-0.029	0.029	-0.008	0.044	c, d	
		18.7	-0.007	0.027	0.003	0.042	c, e	
	Murchison (literature)	20.9	0.000	0.060	-0.100	0.060		Zhu <i>et al.</i> (2001)
	Murchison (literature)	20.4	0.034	0.082	-0.037	0.108		Poitrasson <i>et al.</i> (2005)
	Murchison (literature)		-0.062	0.046	0.082	0.073		Schoenberg and von Blanckenburg (2006)
Mighei (CM2)	Field Museum, Chicago, catalogue ME 1456 #43	19.2	0.009	0.054	0.023	0.072	c, d	
Kainsaz (CO3.2)	Field Museum, Chicago, catalogue ME 2755 #6	21.2	0.001	0.034	0.022	0.048	c, d	

Table 2 (continued).

Iron isotopic compositions of carbonaceous, ordinary and enstatite chondrites

Sample/ Name	Description/ catalogue number	[Fe] (% m/m)*	$\delta^{56}\text{Fe}$ (‰)	95% c.i. [†]	$\delta^{57}\text{Fe}$ (‰)	95% c.i. [†]	Protocol [‡]	Reference
Lancé (CO3)	Field Museum, Chicago, catalogue ME 1351 #3 Lancé (literature)	19.5	-0.017	0.039	-0.036	0.065	c, d	Dauphas <i>et al.</i> (2009a)
		23.0	-0.006	0.032	-0.037	0.047	c, e	Dauphas <i>et al.</i> (2009a)
			0.030	0.157	0.191	0.135		Dauphas <i>et al.</i> (2007)
Tagish Lake (C2)	C2 ungrouped	16.1	-0.008	0.035	0.001	0.040	c, d	
		19.6	-0.005	0.066	0.017	0.062	a, d	
Ordinary chondrites								
Bielokrynschie (H4)	Field Museum, Chicago, catalogue ME 1394 #10	25.3	0.007	0.037	-0.037	0.058	c, d	Dauphas <i>et al.</i> (2009a)
		25.5	-0.011	0.030	0.019	0.053	c, e	Dauphas <i>et al.</i> (2009a)
Ochansk (H4)	Field Museum, Chicago, catalogue ME 1443 #13	25.3	0.008	0.055	-0.008	0.090	c, d	Dauphas <i>et al.</i> (2009a)
		18.6	-0.007	0.030	-0.019	0.053	c, e	Dauphas <i>et al.</i> (2009a)
Kesen (H4)	Field Museum, Chicago, catalogue ME 1828 #5	27.8	0.009	0.053	0.012	0.071	c, d	
Kernouvé (H6)	Natural History Museum, Paris, catalogue #602 Kernouvé (literature)	34.4	0.017	0.055	0.038	0.090	c, d	Dauphas <i>et al.</i> (2009a)
		20.8	-0.022	0.032	-0.031	0.047	c, e	Dauphas <i>et al.</i> (2009a)
			-0.140	0.020				Needham <i>et al.</i> (2009)
Bald Mountain (L4)	Field Museum, Chicago, catalogue ME 2392 #11	23.4	-0.006	0.057	0.002	0.076	c, d	
Baratta (L4)	Field Museum, Chicago, catalogue ME 1463 #13	15.7	0.007	0.034	0.018	0.048	c, d	
Dalgety Downs (L4)	Field Museum, Chicago, catalogue ME 2613 #5	17.7	-0.017	0.040	-0.003	0.044	c, d	
Farmington (L5)	Field Museum, Chicago, catalogue ME 347 #10	18.7	-0.043	0.032	-0.047	0.045	c, d	Dauphas <i>et al.</i> (2009a)
		22.4	-0.005	0.030	0.020	0.053	c, e	Dauphas <i>et al.</i> (2009a)
Harleton (L6)	Field Museum, Chicago, catalogue ME 2686 #7	18.4	0.016	0.033	0.017	0.046	c, d	
Kelly (LL4)	Field Museum, Chicago, catalogue ME 2235 #11	22.1	-0.125	0.040	-0.176	0.039	c, d	
		22.1	-0.114	0.034	-0.152	0.048	c, d	
		22.8	-0.108	0.058	-0.142	0.092	a, d	

Table 2 (continued).

Iron isotopic compositions of carbonaceous, ordinary and enstatite chondrites

Sample/ Name	Description/ catalogue number	[Fe] (% m/m)*	$\delta^{56}\text{Fe}$ (‰)	95% c.i. [†]	$\delta^{57}\text{Fe}$ (‰)	95% c.i. [†]	Protocol [‡]	Reference
Soko-Banja (LL4)	Field Museum, Chicago, catalogue ME 1374 #8 Soko-Banja (literature)	17.0	0.014 -0.010	0.035 0.070	0.001	0.040	c, d	 Needham <i>et al.</i> (2009)
Hamlet (LL4)	Field Museum, Chicago, catalogue ME 3296 #5	14.8	-0.003	0.040	-0.007	0.044	c, d	
Paragould (LL5)	Field Museum, Chicago, catalogue ME 2135 #15	13.9 15.1	-0.029 0.042	0.055 0.032	-0.053 0.099	0.090 0.048	c, d c, e	Dauphas <i>et al.</i> (2009a) Dauphas <i>et al.</i> (2009a)
Tuxtuac (LL5)	Field Museum, Chicago, catalogue ME 2850 #7	16.7	0.019	0.054	0.039	0.072	c, d	
Saint-Séverin (LL6)	Natural History Museum, Paris, catalogue #2397	16.7 13.0	0.013 -0.019	0.039 0.030	0.015 0.021	0.065 0.053	c, d c, e	Dauphas <i>et al.</i> (2009a) Dauphas <i>et al.</i> (2009a)
Enstatite chondrites								
Qingzhen (EH3)		28.5	-0.043	0.053	-0.076	0.071	c, d	
Sahara 97072 (EH3)		28.8	-0.002	0.053	-0.015	0.071	c, d	
Indarch (EH4)	Field Museum, Chicago, catalogue ME 1404 #60 Indarch (literature) Indarch (literature)	28.1 23.1 30.4	0.027 0.010 -0.080 0.049	0.029 0.032 0.060 0.050	0.033 0.033 -0.110 0.005	0.047 0.048 0.060 0.091	c, d c, e c, d	Dauphas <i>et al.</i> (2009a) Dauphas <i>et al.</i> (2009a) Zhu <i>et al.</i> (2001) Poitrasson <i>et al.</i> (2005)
Adhi Kot (EH4)	American Museum of Natural History, New York catalogue AMNH 3993	29.5	0.017	0.053	0.022	0.071	c, d	
Saint-Sauveur (EH5)	Field Museum, Chicago, catalogue ME 1456	29.1 33.6	-0.035 0.001	0.033 0.032	-0.022 0.010	0.067 0.048	c, d c, e	Dauphas <i>et al.</i> (2009a) Dauphas <i>et al.</i> (2009a)
St. Marks (EH5)	Smithsonian, catalogue USNM 3027	29.8 29.8	0.047 0.036	0.054 0.103	0.058 0.054	0.072 0.130	c, d c, d	
Daniel's Kuil (EL6)	Field Museum, Chicago, catalogue ME 1500 #6	21.1	0.121	0.034	0.178	0.048	c, d	

Table 2 (continued).
Iron isotopic compositions of carbonaceous, ordinary and enstatite chondrites

Sample/ Name	Description/ catalogue number	[Fe] (% m/m)*	$\delta^{56}\text{Fe}$ (‰)	95% c.i.[†]	$\delta^{57}\text{Fe}$ (‰)	95% c.i.[†]	Protocol[‡]	Reference
Hvittis (EL6)	Field Museum, Chicago, catalogue ME 578 #4	24.1 22.2	0.032 -0.013	0.032 0.072	0.037 -0.022	0.045 0.102	c, d c, d	
Blithfield (EL6)	Field Museum, Chicago, catalogue ME 1979 #7	15.5	-0.140	0.030	-0.191	0.045	c, d	Dauphas <i>et al.</i> (2009a)
Pillistfer (EL6)	Field Museum, Chicago, catalogue ME 1647 #3	34.7	0.080	0.036	0.138	0.046	c, d	
Jajh deh Kot Lalu (EL6)	Smithsonian, catalogue USNM 1260	18.8	0.062	0.034	0.092	0.048	c, d	
Yilmia (EL6)	Field Museum, Chicago, catalogue ME 2740 #3	19.8	0.064	0.036	0.100	0.046	c, d	
Eagle (EL6)	Eagle (literature)	14.1	-0.003 0.014	0.040 0.057	-0.027 0.019	0.044 0.084	c, d	Schoenberg and von Blanckenburg (2006)
Khairpur (EL6)	Field Museum, Chicago, catalogue ME 1538 #7	22.4	0.006	0.040	0.036	0.044	c, d	
Happy Canyon (EL6/7)	Field Museum, Chicago, catalogue ME 2760 #3	16.3	0.056	0.035	0.099	0.040	c, d	
Ilafegh 009 (EL7)		24.3	0.089	0.033	0.143	0.046	c, d	

* Iron concentrations (% m/m) were calculated by measuring the concentration of iron in the final stock solution used for isotopic determination (i.e., in 10 ml of 0.3 mol l⁻¹ HNO₃ acid) from which the total iron yield (mg Fe) from chemical purification was determined and was divided by the initial mass of sample digested (mg sample). Uncertainties (2s) were typically 10–15% of the reported iron concentration for each analysis, as estimated from the long-term variability of measured iron concentrations of geological reference materials processed repeatedly in this study.

[†] Reported analytical uncertainties. The uncertainties on iron isotopic measurements performed in this study are 95% confidence intervals. Uncertainties for previously published iron isotopic data are typically 2 standard deviation or 2 standard error.

[‡] Protocols used for sample preparation: **a**, hot-plate digestion; **b**, Parr bomb digestion; **c**, flux fusion; **d**, short-column purification; **e**, long-column purification. Bold text designates our recommended isotopic compositions for future studies.

single session (Beard and Johnson 1999, Beard *et al.* 2003b, Heimann *et al.* 2008), or confidence intervals (95%) calculated from *n* replicate analyses using the appropriate Student's *t* factor (Sharma *et al.* 2001, Poitrasson *et al.* 2004, 2005, Dauphas *et al.* 2009b). Reduced chi-squared (χ^2) tests carried out by Dauphas *et al.* (2009b) have demonstrated that instrumental instability alone does not account for all sources of analytical uncertainty for iron isotopic measurements and that a component of unknown error (e.g., differences in sample

preparation) must be included to properly estimate analytical uncertainties. The analytical uncertainties reported for iron isotope measurements in this study are 95% confidence intervals calculated using the following formula (Dauphas *et al.* 2009b);

$$\sigma_{\text{Data}}^2 = \sigma_{\text{MassSpec}}^2 + \sigma_{\text{Unknown}}^2 \quad (2)$$

where σ_{MassSpec} is the standard deviation associated with instrumental instability and σ_{Unknown} is an additional

Table 3.
Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
Iron metal reference material								
IRMM-524a	Fe metal		0.000	0.032	0.019	0.048		
	reference		0.011	0.032	0.039	0.048		
	material		0.007	0.030	0.020	0.044		
	(IRMM)		-0.003	0.057	0.002	0.077		
			-0.017	0.055	-0.040	0.082		
			0.001	0.030	-0.008	0.044		
			-0.003	0.035	-0.008	0.043		
	IRMM-524A (average)		-0.001	0.013	0.003	0.019		
Ultramafic and mafic rocks								
BCR-2	Basalt, Columbia River, Oregon, USA (USGS)		0.114	0.029	0.163	0.040	a, d	
			0.066	0.031	0.093	0.039	a, d	
			0.102	0.029	0.135	0.043	a, d	
			0.082	0.031	0.063	0.056	a, d	
			0.098	0.031	0.136	0.049	a, d	
			0.072	0.036	0.151	0.069	a, d	
			0.085	0.031	0.116	0.049	a, d	
			0.093	0.034	0.144	0.047	a, d	
	BCR-2 (recommended)	9.65	0.091	0.011	0.126	0.017		
	BCR-2 (literature)		0.077	0.126	0.135	0.215		Sharma <i>et al.</i> (2001)
	BCR-2 (literature)		0.054	0.077	0.159	0.212		Dauphas <i>et al.</i> (2004)
	BCR-2 (literature)		0.079	0.043				Weyer <i>et al.</i> (2005)
	BCR-2 (literature)		0.091	0.025	0.133	0.031		Dauphas <i>et al.</i> (2009a)
BE-N	Basalt, Nancy, Meurthe-et- Moselle, France (SARM)		0.141	0.030	0.235	0.057	a, d	
			0.154	0.031	0.224	0.043	a, d	
			0.135	0.031	0.192	0.045	a, d	
			0.162	0.039	0.242	0.060	a, d	
			0.192	0.036	0.317	0.047	a, d	
	BE-N (recommended)	8.98	0.154	0.015	0.241	0.022		
	BE-N (literature)				0.180	0.060		Rouxel <i>et al.</i> (2003)
	BE-N (literature)		0.113	0.058	0.187	0.086		Schoenberg and von Blanckenburg (2006)
BHVO-1	Basalt, Kilauea, Hawaii, USA (USGS)		0.091	0.028	0.150	0.040	a, d	
			0.124	0.027	0.169	0.040	a, d	
			0.104	0.032	0.149	0.043	a, d	
			0.107	0.027	0.169	0.042	a, d	
			0.099	0.029	0.150	0.044	a, d	
			0.102	0.031	0.149	0.046	a, d	
			0.101	0.032	0.171	0.045	a, d	
			0.097	0.034	0.164	0.063	a, d	
			0.107	0.027	0.167	0.045	a, d	
			0.103	0.030	0.154	0.057	a, d	
			0.118	0.031	0.133	0.083	a, d	
			0.109	0.034	0.163	0.054	a, d	
			0.112	0.032	0.188	0.079	a, d	
			0.096	0.030	0.160	0.053	a, e	
			0.108	0.034	0.189	0.047	a, e	
	BHVO-1 (recommended)	8.55	0.105	0.008	0.161	0.012		

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
	BHVO-1 (literature)	8.55	0.066	0.098	0.164	0.032		Poitrasson <i>et al.</i> (2004)
	BHVO-1 (literature)		0.085	0.050	0.111	0.086		Schoenberg and von Blanckenburg (2006)
	BHVO-1 (literature)		0.106	0.108	0.150	0.133		Rouxel <i>et al.</i> (2005)
	BHVO-1 (literature)		0.109	0.021	0.154	0.033		Teng <i>et al.</i> (2008)
	BHVO-1 (literature)		0.109	0.020	0.169	0.023		Schuessler <i>et al.</i> (2009)
BHVO-2	Basalt, Kilauea, Hawaii, USA (USGS)		0.096	0.032	0.153	0.079	a, d	
			0.137	0.041	0.211	0.072	a, d	
			0.084	0.034	0.147	0.054	a, d	
			0.137	0.030	0.207	0.048	a, d	
			0.093	0.035	0.142	0.043	a, d	
			0.127	0.029	0.181	0.043	a, d	
			0.124	0.035	0.171	0.047	a, d	
			0.120	0.052	0.173	0.055	a, d	
			0.111	0.048	0.195	0.064	a, d	
			0.123	0.042	0.197	0.064	a, d	
			0.100	0.041	0.157	0.063	a, d	
			0.119	0.076	0.178	0.108	c, d	
	BHVO-2 (recommended)	8.60	0.114	0.011	0.174	0.016		
	BHVO-2 (literature)		-0.030	0.046				Dideriksen <i>et al.</i> (2006)
BIR-1a	Basalt, Reykavik Dolerite, Iceland (USGS)		0.063	0.041	0.089	0.072	a, d	
			0.053	0.037	0.087	0.046	a, d	
			0.055	0.029	0.106	0.050	a, d	
			0.055	0.039	0.065	0.052	a, d	
			0.046	0.029	0.086	0.048	a, d	
	BIR-1a (recommended)	7.90	0.053	0.015	0.087	0.023		
	BIR-1 (literature)		0.063	0.012	0.102	0.015		Poitrasson <i>et al.</i> (2004)
	BIR-1 (literature)		0.055	0.036				Weyer <i>et al.</i> (2005)
	BIR-1 (literature)		0.120	0.060				Dideriksen <i>et al.</i> (2006)
	BIR-1 (literature)		0.051	0.046	0.063	0.073		Schoenberg and von Blanckenburg (2006)
	BIR-1 (literature)		0.053	0.019	0.085	0.033		Schuessler <i>et al.</i> (2009)
DTS-2b	Dunite, Twin Sisters Mtn., Washington, USA (USGS)		0.017	0.028	0.047	0.043	a, d	
			0.059	0.040	0.078	0.061	a, d	
			0.028	0.029	0.038	0.043	a, d	
			0.027	0.029	0.040	0.050	a, d	
			-0.002	0.043	0.009	0.067	a, d	
			0.042	0.038	0.062	0.056	b, d	
	DTS-2b (recommended)	5.43	0.028	0.013	0.045	0.021		
	DTS-2 (literature)		0.022	0.041	-0.058	0.072		Dauphas <i>et al.</i> (2004)

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
	DTS-2 (literature)		0.010	0.050				Dideriksen <i>et al.</i> (2006)
	DTS-2 (literature)		-0.006	0.022	-0.004	0.040		Teng <i>et al.</i> (2008)
	DTS-2 (literature)		0.017	0.025	0.023	0.031		Dauphas <i>et al.</i> (2009a)
DNC-1	Dolerite, Durham, N. Carolina, USA (USGS)		0.037 0.050 0.065 0.056 0.039	0.028 0.039 0.039 0.030 0.042	0.027 0.079 0.106 0.152 0.086	0.047 0.054 0.059 0.106 0.064	a, d a, d a, d a, d b, d	
	DNC-1 (recommended)	6.97	0.049	0.015	0.074	0.027		
	DNC-1 (literature)		0.017	0.046	0.028	0.073		Schoenberg and von Blanckenburg (2006)
	DNC-1 (literature)		0.000	0.050				Dideriksen <i>et al.</i> (2006)
GBW-07101	Ultramafic Rock, Qinhai, China (IGGE)		0.070 0.051 0.081	0.039 0.082 0.038	0.098 0.089 0.110	0.054 0.074 0.046	a, d a, d a, d	
	GBW-07101 (recommended)	4.82	0.073	0.026	0.102	0.032		
GBW-07102	Ultramafic Rock, Tibet Province (IGGE)		-0.006 -0.025 0.011	0.030 0.069 0.041	-0.007 0.001 0.010	0.044 0.064 0.063	a, d a, d a, d	
	GBW-07102 (recommended)	4.92	-0.003	0.023	-0.001	0.032		
GBW-07105	(GSR-3) Basalt, Zhangjiakou, Hebei, China (IGGE)		0.148 0.174 0.136	0.030 0.040 0.060	0.220 0.249 0.219	0.044 0.044 0.064	a, d a, d a, d	
	GBW-07105 (recommended)	9.37	0.154	0.022	0.232	0.028		
GBW-07112	(GSR-10) Gabbro, Panzhihua, Sichuan, China (IGGE)		0.080 0.091 0.072	0.039 0.040 0.060	0.110 0.120 0.119	0.054 0.044 0.064	a, d a, d a, d	
	GBW-07112 (recommended)	20.42	0.083	0.025	0.117	0.030		
PCC-1	Peridotite, Austin Creek, California, USA (USGS)		0.041 0.021 0.035 0.021 0.025 0.037 0.013 0.013 0.003	0.031 0.028 0.031 0.028 0.038 0.051 0.028 0.041 0.053	0.065 0.055 0.080 0.055 0.063 0.043 0.023 0.029 0.007	0.049 0.044 0.056 0.044 0.044 0.133 0.047 0.063 0.071	a, d a, d a, d a, d a, d a, d a, d b, d c, d	

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
	PCC-1 (recommended)	5.78	0.025	0.012	0.053	0.018		
	PCC-1 (literature)		0.030	0.156	0.020	0.184		Beard <i>et al.</i> (2003a)
	PCC-1 (literature)	5.83	0.033	0.030	0.034	0.038		Poitrasson <i>et al.</i> (2004)
	PCC-1 (literature)	6.26	0.043	0.023				Weyer <i>et al.</i> (2005)
PM-S	Microgabbro, Pitscurrie, Scotland (SARM)		0.070	0.031	0.104	0.083	a, d	
			0.041	0.034	0.064	0.047	a, d	
			0.040	0.028	0.063	0.037	a, d	
			0.051	0.026	0.071	0.040	a, d	
			0.044	0.031	0.091	0.058	a, d	
			0.042	0.040	0.056	0.059	b, d	
	PM-S (recommended)	7.06	0.048	0.013	0.070	0.020		
	PM-S (literature)		0.095	0.068	0.168	0.044		Poitrasson <i>et al.</i> (2004)
W-2	Diabase, Bull Run Quarry, Virginia, USA (USGS)		0.050	0.030	0.100	0.044	a, d	
			0.046	0.041	0.070	0.053	a, d	
			0.106	0.028	0.140	0.052	a, d	
			0.044	0.028	0.048	0.039	a, d	
			0.039	0.032	0.058	0.062	a, d	
			0.040	0.031	0.046	0.053	b, d	
	W-2 (recommended)	7.57	0.056	0.013	0.076	0.020		
	W-2 (literature)		0.036	0.093	0.026	0.089		Schoenberg and von Blanckenburg (2006)
WS-E	Dolerite, Whin Sill, County Durham, England (SARM)		0.095	0.038	0.176	0.044	a, d	
			0.089	0.034	0.136	0.047	a, d	
			0.104	0.028	0.166	0.037	a, d	
			0.079	0.031	0.128	0.060	a, d	
			0.071	0.040	0.087	0.059	b, d	
	WS-E (recommended)	9.20	0.089	0.015	0.148	0.021		
	WS-E (literature)		0.167	0.164	0.132	0.071		Poitrasson <i>et al.</i> (2004)
Intermediate and felsic rocks								
AC-E	Granite, Ailsa Craig Island, Scotland (SARM)		0.311	0.027	0.471	0.037	a, d	
			0.311	0.026	0.487	0.039	a, d	
			0.314	0.033	0.462	0.060	a, d	
			0.319	0.029	0.453	0.041	a, d	
			0.320	0.027	0.462	0.040	a, d	
			0.336	0.029	0.509	0.040	a, d	
			0.330	0.033	0.480	0.063	a, e	
	AC-E (recommended)	1.77	0.320	0.010	0.478	0.015		
	AC-E (literature)	1.76	0.289	0.024	0.353	0.044		Dauphas <i>et al.</i> (2007)
	AC-E (literature)		0.330	0.032	0.497	0.044		Teng <i>et al.</i> (2008)
	AC-E (literature)		0.322	0.025	0.461	0.031		Dauphas <i>et al.</i> (2009a)

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
AGV-2	Andesite, Guano Valley, Oregon, USA (USGS)	4.68	0.107	0.028	0.140	0.041	a, d	
			0.098	0.032	0.131	0.043	a, d	
			0.100	0.028	0.146	0.037	a, d	
			0.099	0.032	0.155	0.057	a, d	
			0.114	0.028	0.159	0.040	a, d	
			0.110	0.029	0.151	0.041	a, d	
			0.105	0.035	0.142	0.047	a, d	
	AGV-2 (recommended)		0.105	0.011	0.146	0.016		
	AGV-2 (literature)		0.112	0.081	0.165	0.275		Dauphas <i>et al.</i> (2004)
	AGV-2 (literature)		0.130	0.038				Dideriksen <i>et al.</i> (2006)
AN-G	Anorthosite, Fiskenaesset, Greenland (SARM)	2.35	0.056	0.037	0.090	0.056	a, d	
			0.099	0.036	0.118	0.047	a, d	
			0.122	0.039	0.187	0.073	a, d	
			0.083	0.030	0.086	0.047	a, d	
			0.078	0.033	0.108	0.054	a, d	
			0.078	0.033	0.102	0.054	a, e	
			0.085	0.032	0.080	0.062	a, e	
	AN-G (recommended)		0.085	0.014	0.109	0.022		
	AN-G (literature)		0.065	0.046	0.088	0.073		Schoenberg and von Blanckenburg (2006)
DR-N	Diorite, Massif Champ du Feu, Vosges, France (SARM)	6.78	0.052	0.037	0.083	0.056	a, d	
			0.126	0.039	0.202	0.059	a, d	
			0.067	0.028	0.087	0.037	a, d	
			0.079	0.039	0.100	0.073	a, d	
			0.070	0.030	0.134	0.047	a, d	
	DR-N (recommended)		0.076	0.015	0.115	0.023		
	DR-N (literature)		0.068	0.135	0.054	0.053		Poitrasson <i>et al.</i> (2004)
GA	Granite, Andlau, Alsace, France (SARM)	1.98	0.108	0.038	0.189	0.044	a, d	
			0.087	0.031	0.159	0.043	a, d	
			0.141	0.036	0.219	0.047	a, d	
			0.126	0.039	0.232	0.073	a, d	
			0.094	0.035	0.124	0.058	a, d	
	GA (recommended)		0.109	0.016	0.182	0.022		
	GA (literature)	1.98	0.110	0.027	0.243	0.027		Poitrasson and Freydier (2005)
	GA (literature)		0.120	0.085	0.185	0.124		Schoenberg and von Blanckenburg (2006)
GBW-07103	(GSR-1) Biotite granite, Binzhou, Hunan, China (IGGE)	1.50	0.167	0.030	0.261	0.044	a, d	
			0.181	0.042	0.275	0.072	a, d	
			0.184	0.066	0.261	0.062	a, d	
			0.160	0.041	0.255	0.063	a, d	
	GBW-07103 (recommended)		0.170	0.020	0.262	0.029		
	GBW- 07103/GSR-1 (literature)	1.50	0.170	0.040	0.243	0.049		Poitrasson and Freydier (2005)

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
GBW-07104	(SDR-2)		0.098	0.033	0.143	0.046	a, d	
	Andesite,		0.106	0.066	0.130	0.062	a, d	
	Meishan,		0.087	0.038	0.119	0.046	a, d	
	Nanjing, China (IGGE)							
	GBW-07104 (recommended)	3.43	0.095	0.023	0.131	0.029		
GBW-07109	(GSR-7)	0.181	0.039	0.268	0.054	a, d		
	Nepheline		0.203	0.040	0.294	0.044	a, d	
	Syenite,		0.187	0.058	0.283	0.092	a, d	
	Fengcheng,		0.128	0.057	0.184	0.076	a, d	
	Liaoning, China (IGGE)							
	GBW-07109 (recommended)	5.47	0.181	0.023	0.269	0.029		
GBW-07110	(GSR-8) Trachyte,		0.066	0.113	0.102	0.102	a, d	
	Fanchang,		0.052	0.038	0.087	0.046	a, d	
	Anhui, China (IGGE)		0.048	0.058	0.062	0.092	a, d	
	GBW-07110 (recommended)	3.34	0.052	0.031	0.085	0.038		
GBW-07111	(GSR-9)		0.098	0.033	0.154	0.046	a, d	
	Granodiorite,		0.110	0.038	0.171	0.046	a, d	
	Fangshan,		0.078	0.058	0.133	0.092	a, d	
	Beijing, China (IGGE)							
	GBW-07111 (recommended)	4.96	0.099	0.023	0.159	0.031		
GBW-07113	(GSR-11)		0.032	0.030	0.059	0.044	a, d	
	Rhyolite,		0.060	0.039	0.097	0.049	a, d	
	Shangyu,		0.031	0.082	0.039	0.074	a, d	
	Zhejiang, China (IGGE)							
	GBW-07113 (recommended)	2.68	0.042	0.023	0.070	0.030		
GS-N	Granite,		0.143	0.033	0.218	0.060	a, d	
	Senones,		0.149	0.030	0.198	0.046	a, d	
	Vosges, France		0.142	0.037	0.225	0.056	a, d	
	(SARM)		0.152	0.041	0.239	0.047	a, d	
			0.135	0.029	0.191	0.048	a, d	
	GS-N (recommended)	2.62	0.143	0.015	0.213	0.023		
	GS-N (literature)		0.129	0.046	0.177	0.073		Schoenberg and von Blanckenburg (2006)
GSP-2	Granodiorite,		0.184	0.029	0.244	0.051	a, d	
	Silver Plume,		0.146	0.031	0.240	0.046	a, d	
	Colorado, USA		0.136	0.031	0.198	0.043	a, d	
	(USGS)		0.154	0.030	0.226	0.048	a, d	
			0.154	0.030	0.213	0.106	a, d	
			0.180	0.032	0.264	0.057	a, d	
	GSP-2 (recommended)	3.43	0.159	0.013	0.230	0.021		

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
	GSP-1 (literature)		0.110	0.128	0.080	0.152		Beard <i>et al.</i> (2003a)
	GSP-2 (literature)		0.030	0.050				Dideriksen <i>et al.</i> (2006)
MDO-G	Trachyte, Mont-Dore, Massif Central, France (SARM)		0.266 0.246 0.247 0.229 0.229 0.220	0.037 0.028 0.039 0.035 0.031 0.031	0.376 0.379 0.376 0.329 0.347 0.337	0.056 0.037 0.073 0.058 0.060 0.053	a, d a, d a, d a, d a, d a, d	
	MDO-G (recommended)	4.33	0.238	0.013	0.360	0.021		
RGM-2	Rhyolite, Glass Mtn., California, USA (USGS)		0.188 0.235 0.209 0.223 0.261 0.211	0.030 0.039 0.029 0.029 0.050 0.042	0.278 0.356 0.312 0.342 0.408 0.339	0.044 0.054 0.049 0.041 0.077 0.048	a, d a, d a, d a, d b, d b, d	
	RGM-2 (recommended)	1.40	0.216	0.014	0.329	0.020		
	RGM-1 (literature)	1.30	0.180	0.220	0.290	0.100		Beard <i>et al.</i> (2003a)
Metamorphic, sedimentary and other rocks								
IF-G	Iron Formation, Isua, Greenland (SARM)		0.640 0.633 0.660 0.629 0.652 0.642 0.622	0.031 0.030 0.034 0.033 0.029 0.060 0.032	0.972 0.945 0.971 0.961 0.949 0.916 0.917	0.083 0.050 0.054 0.063 0.043 0.072 0.044	a, d a, d a, d a, e a, d a, d a, d	
	IF-G (recommended)	39.80	0.639	0.013	0.945	0.020		
	IF-G (literature)		0.640	0.058	0.957	0.087		Rouxel <i>et al.</i> (2005)
	IF-G (literature)		0.633	0.030	0.945	0.050		Teng <i>et al.</i> (2008)
	IF-G (literature)		0.647	0.025	0.939	0.031		Dauphas <i>et al.</i> (2009a)
SoNE-1	Sharpsburg Soil, Lancaster County, Nebraska, USA (USGS)		0.020 0.010 -0.011	0.028 0.082 0.113	0.021 0.004 -0.004	0.041 0.074 0.102	a, d a, d a, d	
	SoNE-1 (recommended)	2.73	0.017	0.026	0.015	0.034		
SGR-1b	Shale, Green River Formation, Colorado, USA (USGS)		0.047 0.030 0.029 0.033 0.043	0.041 0.029 0.034 0.038 0.030	0.051 0.051 0.042 0.055 0.051	0.072 0.051 0.047 0.065 0.047	a, d a, d a, d a, d b, d	
	SGR-1b (recommended)	2.12	0.036	0.015	0.049	0.024		
	SGR-1 (literature)		-0.270	0.316	-0.390	0.519		Beard <i>et al.</i> (2003a)
	SGR-1 (literature)		0.150	0.035				Dideriksen <i>et al.</i> (2006)

Table 3 (continued).

Recommended iron isotopic compositions of geological and other reference materials relative to IRMM-014

Sample/ Name	Description	[Fe] (% m/m)	$\delta^{56}\text{Fe}$ (‰)	95% c.i.*	$\delta^{57}\text{Fe}$ (‰)	95% c.i.*	Protocol [†]	Reference
GBW-07122	(GSR-15)		0.052	0.030	0.081	0.044	a, d	
	Amphibolite,		0.034	0.113	0.053	0.102	a, d	
	Benxi, Liaoning,		-0.019	0.057	-0.043	0.076	a, d	
	China (IGGE)		0.048	0.057	0.087	0.077	a, d	
			0.074	0.058	0.064	0.092	a, d	
	GBW-07122 (recommended)	10.35	0.043	0.022	0.057	0.031		
UB-N	Serpentine,		0.066	0.031	0.089	0.083	a, d	
	Vosges, France		0.035	0.031	0.069	0.046	a, d	
	(SARM)		0.055	0.045	0.100	0.063	a, d	
			0.062	0.028	0.100	0.039	a, d	
			0.067	0.032	0.124	0.062	a, d	
			0.068	0.032	0.134	0.048	a, d	
	UB-N (recommended)	5.83	0.059	0.013	0.102	0.021		
COQ-1	Carbonatite,		-0.124	0.042	-0.188	0.072	a, d	
	Oka Complex,		-0.117	0.067	-0.110	0.064	a, d	
	Lake Two Mtns,		-0.104	0.054	-0.199	0.053	a, d	
	Montreal,							
	Canada (USGS)							
	COQ-1 (recommended)	2.06	-0.117	0.030	-0.169	0.036		
	COQ-1 (literature)		0.000	0.060				Dideriksen <i>et al.</i> (2006)
Organic materials								
SRM-1577c	Bovine		-1.314	0.053	-1.947	0.079	a, d	
	Liver (NIST)		-1.341	0.053	-1.949	0.079	a, d	
			-1.375	0.055	-2.045	0.082	a, d	
	SRM-1577c (recommended)	0.02	-1.343	0.031	-1.979	0.046		

* Reported analytical uncertainties. The uncertainties on iron isotopic measurements performed in this study are 95% confidence intervals. Uncertainties for previously published iron isotopic data are typically 2 standard deviation or 2 standard error.

[†] Protocols used for sample preparation: **a**, hot-plate digestion; **b**, Parr bomb digestion; **c**, flux fusion; **d**, short-column purification; **e**, long-column purification.

error arising from unaccounted analytical fractionation. The working estimates of σ_{Unknown} at the Origins Laboratory are $\pm 0.011\%$ for $\delta^{56}\text{Fe}$ and $\pm 0.012\%$ for $\delta^{57}\text{Fe}$ (Dauphas *et al.* 2009b), but these should be calculated independently in all laboratories. Accounting for all sources of errors, the analytical uncertainties for iron isotopic measurements obtained in our laboratory are typically $\pm 0.03\%$ and $\pm 0.05\%$ (95% c.i.) for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, respectively.

The long-term external reproducibility of iron isotopic measurements can be assessed from replicate data for the same material that has been independently processed (i.e., digested and purified) and analysed over several analytical sessions. Our best estimate for the iron isotopic compositions of geological and other reference materials

analysed in this study was calculated as a weighted average of independent analyses:

$$\bar{x} = (x_1/e_1^2 + x_2/e_2^2 + \dots + x_n/e_n^2) / (1/e_1^2 + 1/e_2^2 + \dots + 1/e_n^2), \quad (3)$$

where e_n is the 95% confidence interval of an independent analysis n . Uncertainty is calculated accordingly:

$$95\% \text{ c.i.} = 1/\sqrt{(1/e_1^2 + 1/e_2^2 + \dots + 1/e_n^2)}. \quad (4)$$

The uncertainties calculated for weighted average iron isotopic compositions were $\pm 0.008\text{--}0.024\%$ for $\delta^{56}\text{Fe}$ and $\pm 0.012\text{--}0.034\%$ for $\delta^{57}\text{Fe}$, although it should be noted that accuracy has only been tested down to a level of $\sim 0.03\%$ (Dauphas *et al.* 2009b).

Iron isotopic compositions of chondrites, geological and other reference materials

Iron isotopic compositions of chondrites, geological and other reference materials with a wide range of compositions and iron concentrations are reported (Tables 2 and 3; Figures 2 and 3). The iron isotopic compositions of independent replicate analyses of each reference material measured over a period of ~ 12 months were identical within uncertainties ($\pm 0.03\text{‰}$ and $\pm 0.05\text{‰}$ on $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, respectively) confirming the long-term reproducibility of our analytical routine. Recommended iron isotopic ($\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$) compositions and associated uncertainties are reported for all geological and other reference materials; typically at least five independent analyses were used to estimate error-weighted average iron isotopic compositions. To assess that uncertainties were adequately estimated, reduced- χ^2 statistics were calculated for geological reference materials with a least five independent analyses using the following equation:

$$\chi_{\text{red}}^2 = \frac{1}{n-1} \sum \frac{(x_i - \bar{x})^2}{\sigma_{\text{Data}}^2} \quad (5)$$

The reduced- χ^2 calculated for geological and other reference materials was within the 95% confidence interval specified by reduced- χ^2 statistics for the appropriate number of independent sample analyses. In a single case (reference material W-2), the reduced- χ^2 fell outside the 95% confidence limit, resulting from a single datum outlier.

Carbonaceous (CI, CM, CO and CV) and ordinary (H, L, LL) chondrites gave a uniform bulk composition, with average $\delta^{56}\text{Fe}$ values of $-0.010 \pm 0.010\text{‰}$ and $-0.013 \pm 0.010\text{‰}$, respectively (Table 2, Figure 2). These data are consistent with iron isotopic compositions reported previously for carbonaceous and ordinary chondrites (e.g., Zhu *et al.* 2001, Poitrasson *et al.* 2005, Schoenberg and von Blanckenburg 2006, Teng *et al.* 2008, Dauphas *et al.* 2009a). An exception was the ordinary chondrite Kelly, which had a low Fe isotopic composition ($\delta^{56}\text{Fe} = -0.117 \pm 0.022\text{‰}$). This chondrite has textural features suggestive of impact/shock metamorphism, melting and recrystallisation on the parent meteorite body and fragments of this chondrite have suffered terrestrial weathering and oxidation of Fe-bearing minerals (Bunch and Stöffler 1974). One or both of these processes may have affected the iron isotopic composition of this chondrite. Enstatite chondrites examined in this study showed a wider range of iron isotopic compositions, from $\delta^{56}\text{Fe} = -0.140 \pm 0.030\text{‰}$ (Blithfield EL6 breccia) to $\delta^{56}\text{Fe} = +0.121 \pm 0.034\text{‰}$ (Daniel's Kuil

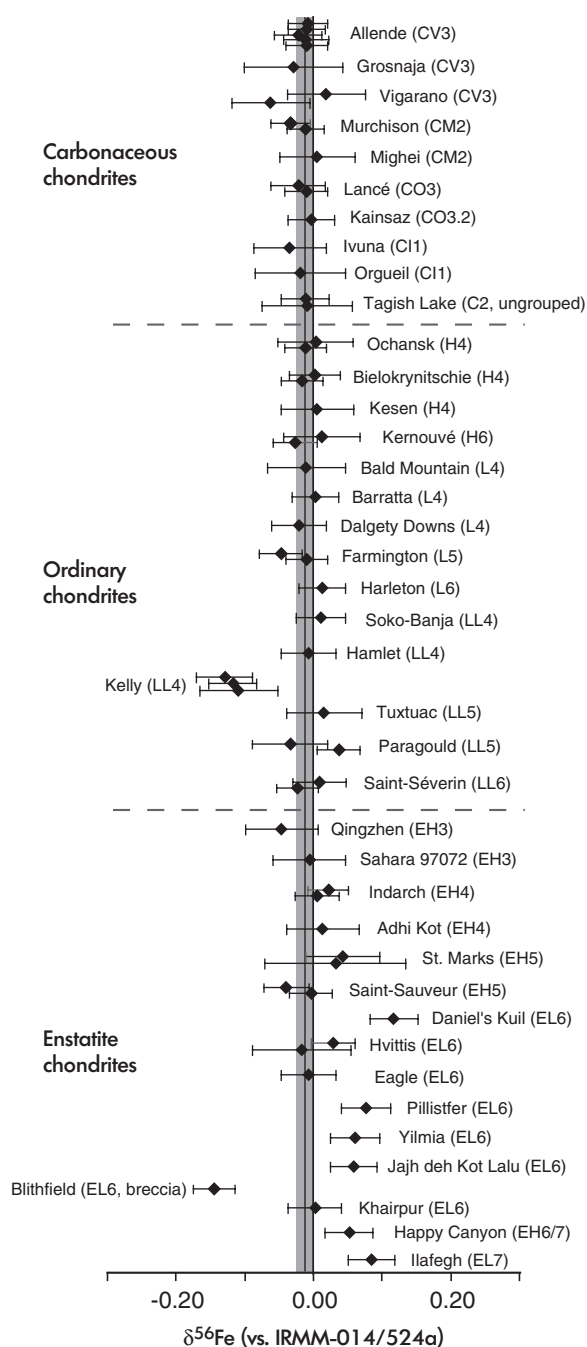


Figure 2. Summary of iron isotope ($\delta^{56}\text{Fe}$) compositions of chondrite meteorites. All iron isotopic data obtained at the University of Chicago (this study; Dauphas *et al.* 2009a). Error bars for data obtained in this study (typically $\pm 0.03\text{‰}$) are 95% confidence intervals.

EL6), but had an average $\delta^{56}\text{Fe} = +0.020 \pm 0.010\text{‰}$, similar to that of carbonaceous and ordinary chondrites (Table 2, Figure 2). The wider range of iron isotopic compositions measured in enstatite chondrites may reflect more extensive metamorphism and metal-silicate redistribution in

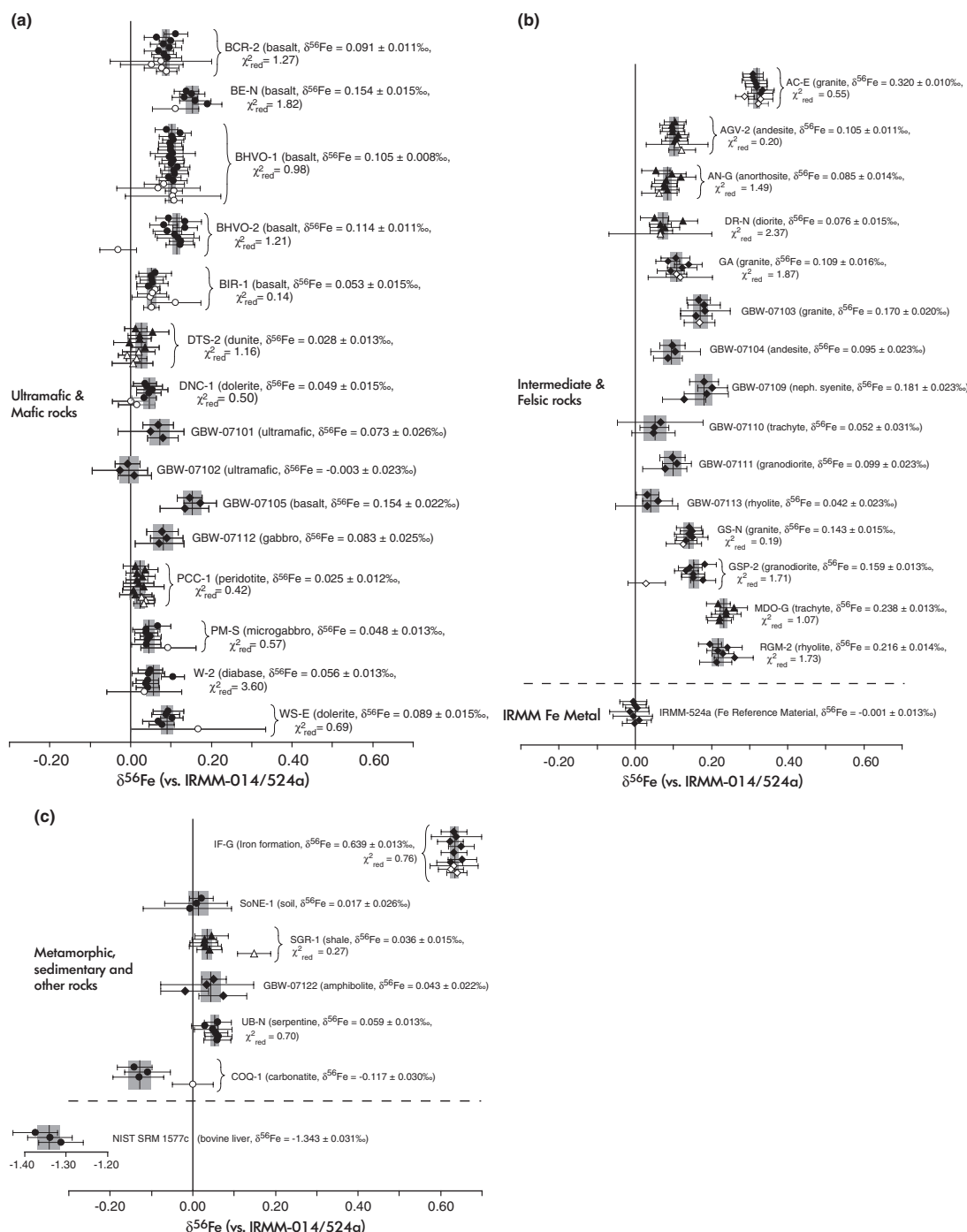


Figure 3. Summary of iron isotope ($\delta^{56}\text{Fe}$) compositions of geological and other reference materials issued by NIST, USGS, IRMM, SARM and IGGE. Iron isotopic data obtained in this study (filled symbols) were compared against literature data for the same samples (open symbols). Iron isotopic compositions reported in the literature normalised to 'igneous Fe' were corrected to the IRMM-014 scale using $\delta^{56}\text{Fe}_{\text{igneous-Fe}} = +0.09\text{‰}$ relative to IRMM-014 (Beard *et al.* 2003a). Error bars for data obtained in this study (typically $\pm 0.03\text{‰}$) are 95% confidence intervals. Recommended iron isotopic compositions and related uncertainties for all geological reference materials are reported as an error-weighted mean of independent replicate isotopic data obtained in this study only and are shown by the grey bars (previously published data are not included in weighted mean calculations). Calculated reduced χ^2 statistics (χ^2_{red}) are also reported for each geological reference material with five or more replicate analyses to assess the adequacy of uncertainty estimations (for well behaved data χ^2_{red} is ~ 1).

the parent bodies of EH and EL meteorites relative to that experienced by carbonaceous and ordinary chondrites (e.g., Rubin 1984, Rubin *et al.* 1997).

Recommended iron isotopic compositions are reported for a wide range of geological and other reference materials issued by NIST, USGS, IRMM, SARM and IGGE (Table 3; Figure 3). Where available, the iron isotopic data obtained in this study were compared with those published previously for the same reference materials. Overall, the agreement between iron isotopic compositions from this and other studies was very good. However, analytical uncertainties were significantly reduced. Most igneous and metamorphic reference materials had $\delta^{56}\text{Fe}$ ratios between 0.00 and +0.32‰. While the range of iron isotopic variations in igneous rocks was restricted, different igneous rocks showed different iron isotopic compositions. In general, more evolved and differentiated rocks had heavier iron isotopic compositions, similar to those observed by Poitrasson and Freydier (2005), Heimann *et al.* (2008) and Schuessler *et al.* (2009). Ultramafic and mafic rocks showed an iron isotopic composition closer to chondritic. The iron isotopic composition of Fe-rich chemical sediment IF-G was significantly fractionated relative to igneous rocks with $\delta^{56}\text{Fe} = +0.639 \pm 0.013\text{‰}$. The biological reference material NIST SRM 1577c (bovine liver) showed a very low iron isotopic composition ($\delta^{56}\text{Fe} = -1.34 \pm 0.03\text{‰}$). There are no previously reported iron isotopic compositions of bovine liver reference materials that enable a direct comparison with the iron isotopic composition of NIST SRM 1577c reported here. However, the iron isotopic composition of NIST SRM 1577c is similar to that of non-specific bovine liver samples reported previously by Schoenberg and von Blanckenburg (2005), who measured a $\delta^{56}\text{Fe}$ value of $-1.833 \pm 0.036\text{‰}$. The iron isotopic composition of herbivore mammalian tissues is significantly lighter than that of plants, by up to 2–3‰ (e.g., Walczyk and von Blanckenburg 2002, 2005, Guelke and von Blanckenburg 2007), suggesting extensive iron isotopic fractionation during mammalian uptake of plant-derived iron (Walczyk and von Blanckenburg 2002).

This study demonstrated that iron isotopic compositions could be accurately and reproducibly determined in a wide range of Fe-bearing materials and matrices, including igneous silicates, clays, oxides, organic-bearing sediments (e.g., shale, soil) and biological materials. Our research demonstrated that $\delta^{56}\text{Fe}$ ratios can be measured accurately within analytical uncertainties of $\pm 0.03\text{‰}$ (Dauphas *et al.* 2009b). The geological reference materials reported in this research are well-suited for sample calibration and quality assurance for future iron isotopic studies in the geological and biological sciences.

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References

- Balci N., Bullen T.D., Witte-Lien K., Shanks W.C., Motelica M. and Mandernack K.W. (2006) Iron isotope fractionation during microbially stimulated Fe(II) oxidation and Fe(III) precipitation. *Geochimica et Cosmochimica Acta*, 70, 622–639.
- Beard B.L. and Johnson C.M. (1999) High precision iron isotope measurements of terrestrial and lunar materials. *Geochimica et Cosmochimica Acta*, 63, 1653–1660.
- Beard B.L. and Johnson C.M. (2004) Fe isotope variations in the modern and ancient Earth and other planetary bodies. *Reviews in Mineralogy and Geochemistry*, 55, 319–357.
- Beard B.L., Johnson C.M., Cox L., Sun H., Nealson K.H. and Aguilar C. (1999) Iron isotope biosignatures. *Science*, 285, 1889–1892.
- Beard B.L., Johnson C.M., Skulan J.L., Nealson K.H., Cox L. and Sun H. (2003a) Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology*, 195, 87–117.
- Beard B.L., Johnson C.M., Von Damm K.L. and Poulson R.L. (2003b) Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans. *Geology*, 31, 629–632.
- Belshaw N.S., Zhu X.K., Guo Y. and O’Nions R.K. (2000) High precision measurement of iron isotopes by plasma source mass spectrometry. *International Journal of Mass Spectrometry*, 197, 191–195.
- Bullen T.D., White A.F., Childs C.W., Vivit D.V. and Schulz M.S. (2001) Demonstration of significant abiotic iron isotope fractionation in nature. *Geology*, 29, 699–702.

references

- Bunch T.E. and Stöckler D. (1974)**
The Kelly chondrite: a parent body surface metabreccia. *Contributions to Mineralogy and Petrology*, 44, 157–171.
- Butler I.B., Archer C., Vance D., Oldroyd A. and Rickard D. (2005)**
Fe isotope fractionation on FeS formation in ambient aqueous solution. *Earth and Planetary Science Letters*, 236, 430–442.
- Croal L.R., Johnson C.M., Beard B.L. and Newman D.K. (2004)**
Iron isotope fractionation by Fe(II)-oxidizing photoautotrophic bacteria. *Geochimica et Cosmochimica Acta*, 68, 1227–1242.
- Crosby H.A., Roden E.E., Johnson C.M. and Beard B.L. (2007)**
The mechanisms of iron isotope fractionation produced during dissimilatory Fe(III) reduction by *Shewanella putrefaciens* and *Geobacter sulfurreducens*. *Geobiology*, 5, 169–189.
- Dauphas N. (2007)**
Diffusion-driven kinetic isotope effect of Fe and Ni during formation of the Widmanstätten pattern. *Meteoritics and Planetary Science*, 42, 1–17.
- Dauphas N. and Rouxel O.J. (2006)**
Mass spectrometry and natural variations of iron isotopes. *Mass Spectrometry Reviews*, 25, 515–550.
- Dauphas N., Janney P.E., Mendenybaev R.A., Wadhwa M., Richter F.M., Davis A.M., van Zuilen M., Hines R. and Foley C.N. (2004)**
Chromatographic separation and multicollection-ICP-MS analysis of iron: investigating mass-dependent and independent isotope effects. *Analytical Chemistry*, 76, 5855–5863.
- Dauphas D., Cates N.L., Mojzsis S.J. and Busigny V. (2007)**
Identification of chemical sedimentary protoliths using iron isotopes in the >3750 Ma Nuvvuagittuq supracrustal belt, Canada. *Earth and Planetary Science Letters*, 254, 358–376.
- Dauphas N., Cook D.L., Sacarabany A., Fröhlich C., Davis A.M., Wadhwa M., Pourmand A., Rauscher T. and Gallino R. (2008)**
Iron 60 evidence for early injection and efficient mixing of stellar debris in the protosolar nebula. *Astrophysical Journal*, 686, 560–569.
- Dauphas N., Craddock P.R., Asimow P.D., Bennett V.C., Nutman A.P. and Ohnenstetter D. (2009a)**
Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters*, 288, 255–267.
- Dauphas N., Pourmand A. and Teng F.-Z. (2009b)**
Routine isotopic analysis of iron by HR-MC-ICP-MS: how precise and how accurate? *Chemical Geology*, 257, 175–184.
- Dauphas N., Teng F.-Z. and Arndt N.T. (2010)**
Magnesium and iron isotopes in 2.7 Ga Alexo komatiites: mantle signatures, no evidence for Soret diffusion, and identification of diffusive transport in zoned olivine. *Geochimica et Cosmochimica Acta*, 74, 3274–3291.
- Dideriksen K., Baker J.A. and Stipp S.L.S. (2006)**
Iron isotopes in natural carbonate minerals determined by MC-ICP-MS with a ^{58}Fe - ^{54}Fe double spike. *Geochimica et Cosmochimica Acta*, 70, 118–132.
- Fantle M.S. and DePaolo D.J. (2004)**
Iron isotopic fractionation during continental weathering. *Earth and Planetary Science Letters*, 228, 547–562.
- Guelke M. and von Blanckenburg F. (2007)**
Fractionation of stable iron isotopes in higher plants. *Environmental Science and Technology*, 41, 1896–1901.
- Heimann A., Beard B.L. and Johnson C.M. (2008)**
The role of volatile exsolution and sub-solidus fluid/rock interactions in producing high $^{56}\text{Fe}/^{54}\text{Fe}$ ratios in siliceous igneous rocks. *Geochimica et Cosmochimica Acta*, 72, 4379–4396.
- Icopini G.A., Anbar A.D., Ruebush S.S., Tien M. and Brantley S.L. (2004)**
Iron isotope fractionation during microbial reduction of iron: the importance of adsorption. *Geology*, 32, 205–208.
- Johnson C.M., Roden E.E., Welch S.A. and Beard B.L. (2005)**
Experimental constraints on Fe isotope fractionation during magnetite and Fe carbonate formation coupled to dissimilatory hydrous ferric oxide reduction. *Geochimica et Cosmochimica Acta*, 69, 963–993.
- Malinovsky D., Stenberg A., Rodushkin I., Andrén H., Ingri J., Öhlander B. and Baxter D.C. (2003)**
Performance of high resolution MC-ICP-MS for Fe isotope ratio measurements in sedimentary geological materials. *Journal of Analytical Atomic Spectrometry*, 18, 687–695.
- Maréchal C.N., Télouk P. and Albarède F. (1999)**
Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chemical Geology*, 156, 251–273.
- Needham A.W., Porcelli D. and Russell S.S. (2009)**
An Fe isotope study of ordinary chondrites. *Geochimica et Cosmochimica Acta*, 73, 7399–7413.
- Poitras F. and Frey R. (2005)**
Heavy iron isotope composition of granites determined by high resolution MC-ICP-MS. *Chemical Geology*, 222, 132–147.
- Poitras F., Halliday A.N., Lee D.-C., Levasseur S. and Teutsch N. (2004)**
Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth and Planetary Science Letters*, 223, 253–266.



references

- Poitrasson F., Levasseur S. and Teutsch N. (2005)**
Significance of iron isotope mineral fractionation in pallasites and iron meteorites for the core-mantle differentiation of terrestrial planets. *Earth and Planetary Science Letters*, 234, 151–164.
- Pourmand A. and Dauphas N. (2010)**
Distribution coefficients of 60 elements on TODGA resin: application to Ca, Lu, Hf, U and Th isotope geochemistry. *Talanta*, 81, 741–753.
- Richter F.M., Dauphas N. and Teng F.-Z. (2009a)**
Non-traditional fractionation of non-traditional isotopes: evaporation, chemical diffusion and Soret diffusion. *Chemical Geology*, 258, 92–103.
- Richter F.M., Watson E.B., Mendybaev R., Dauphas N., Georg B., Watkins J. and Valley J. (2009b)**
Isotopic fractionation of the major elements of molten basalt by chemical and thermal diffusion. *Geochimica et Cosmochimica Acta*, 73, 4250–4263.
- Roskosz M., Luais B., Watson H.C., Toplis M.J., Alexander C. and Mysen B.O. (2006)**
Experimental quantification of the fractionation of Fe isotopes during metal segregation from a silicate melt. *Earth and Planetary Science Letters*, 248, 851–867.
- Rouxel O.J., Bekker A. and Edwards K.J. (2005)**
Iron isotope constraints on the Archean and Paleoproterozoic ocean redox state. *Science*, 307, 1088–1091.
- Rouxel O.J., Dobbek N., Ludden J. and Fouquet Y. (2003)**
Iron isotope fractionation during oceanic crust alteration. *Chemical Geology*, 202, 155–182.
- Rubin A.E. (1984)**
The Blithfield meteorite and the origin of sulfide-rich, metal-poor clasts and inclusions in brecciated enstatite chondrites. *Earth and Planetary Science Letters*, 67, 273–283.
- Rubin A.E., Scott E.R.D. and Keil K. (1997)**
Shock metamorphism of enstatite chondrites. *Geochimica et Cosmochimica Acta*, 61, 847–858.
- Russell W.A., Papanastassiou D.A. and Tombrello T.A. (1978)**
Ca isotope fractionation on the Earth and other solar system materials. *Geochimica et Cosmochimica Acta*, 42, 1075–1090.
- Schoenberg R. and von Blanckenburg F. (2005)**
An assessment of the accuracy of stable Fe isotope ratio measurements on samples with organic and inorganic matrices by high-resolution multicollector ICP-MS. *International Journal of Mass Spectrometry*, 242, 257–272.
- Schoenberg R. and von Blanckenburg F. (2006)**
Modes of planetary-scale Fe isotope fractionation. *Earth and Planetary Science Letters*, 252, 342–359.
- Schuessler J.A., Schoenberg R., Behrens H. and Blanckenburg F. (2007)**
The experimental calibration of the iron isotope fractionation factor between pyrrhotite and peralkaline rhyolitic melt. *Geochimica et Cosmochimica Acta*, 71, 417–433.
- Schuessler J.A., Schoenberg R. and Sigmarsson O. (2009)**
Iron and lithium isotope systematics of the Hekla volcano, Iceland – Evidence for Fe isotope fractionation during magma differentiation. *Chemical Geology*, 258, 78–91.
- Shahar A., Young E.D. and Manning C.E. (2008)**
Equilibrium high-temperature Fe isotope fractionation between fayalite and magnetite: an experimental calibration. *Earth and Planetary Science Letters*, 268, 330–338.
- Sharma M., Polizzotto M. and Anbar A.D. (2001)**
Iron isotopes in hot springs along the Juan de Fuca Ridge. *Earth and Planetary Science Letters*, 194, 39–51.
- Skulan J.L., Beard B.L. and Johnson C.M. (2002)**
Kinetic and equilibrium Fe isotope fractionation between aqueous Fe (III) and hematite. *Geochimica et Cosmochimica Acta*, 66, 2995–3015.
- Strelow F.W.E. (1980)**
Improved separation of iron from copper and other elements by anion-exchange chromatography on a 4% cross-linked resin with high concentrations of hydrochloric acid. *Talanta*, 27, 727–732.
- Tang H., Dauphas N. and Craddock P.R. (2009)**
High precision iron isotopic analyses of meteorites and terrestrial rocks: ^{60}Fe distribution and mass fractionation laws. *Proceedings of the Lunar Science Conference*, 40th, (The Woodlands, TX) 1903.
- Taylor P.D.P., Maeck R. and De Bièvre P. (1992)**
Determination of the absolute isotopic composition and atomic weight of a reference sample of natural iron. *International Journal of Mass Spectrometry and Ion Processes*, 121, 111–125.
- Teng F.Z., Dauphas N. and Helz R.T. (2008)**
Iron isotope fractionation during magmatic differentiation in Kilauea Iki lava lake. *Science*, 320, 1620–1622.
- Völkering J. and Papanastassiou D. (1989)**
Iron isotope anomalies. *Astrophysical Journal*, 347, L43–L46.
- Walczyk T. and von Blanckenburg F. (2002)**
Natural iron isotope variations in human blood. *Science*, 295, 2065–2066.
- Walczyk T. and von Blanckenburg F. (2005)**
Deciphering the iron isotope message of the human body. *International Journal of Mass Spectrometry*, 242, 117–134.
- Wang J., Davis A.M., Clayton R.N. and Mayeda T.K. (1994)**
Kinetic isotopic fractionation during the evaporation of the iron oxide from liquid state. *Lunar and Planetary Science*, 25, 1459–1460.

references

Weyer S. and Ionov D.A. (2007)

Partial melting and melt percolation in the mantle: the message from Fe isotopes. *Earth and Planetary Science Letters*, 259, 119–133.

Weyer S. and Schwieters J.B. (2003)

High precision Fe isotope measurements with high mass resolution MC-ICP-MS. *International Journal of Mass Spectrometry*, 226, 355–368.

Weyer S., Anbar A.D., Brey G.P., Münker C., Mezger K. and Woodland A.B. (2005)

Iron isotope fractionation during planetary differentiation. *Earth and Planetary Science Letters*, 240, 251–264.

Wiesli R.A., Beard B.L. and Johnson C.M. (2004)

Experimental determination of Fe isotope fractionation between aqueous Fe (II), siderite and “green rust” in abiotic systems. *Chemical Geology*, 211, 343–362.

Williams H.M., Peslier A.H., McCammon C., Halliday A.N., Levasseur S., Teutsch N. and Burg J.P. (2005)

Systematic iron isotope variations in mantle rocks and minerals: the effects of partial melting and oxygen fugacity. *Earth and Planetary Science Letters*, 235, 435–452.

Williams H.M., Nielsen S.G., Renac C., Griffin W.L., O'Reilly S.Y., McCammon C.A., Pearson N., Viljoen F., Alt J.C. and Halliday A.N. (2009)

Fractionation of oxygen and iron isotopes by partial melting processes: implications for the interpretation of stable isotope signatures in mafic rocks. *Earth and Planetary Science Letters*, 283, 156–166.

Zhu X.K., Guo Y., O'Nions R.K., Young E.D. and Ash R.D. (2001)

Isotopic homogeneity of iron in the early solar nebula. *Nature*, 412, 311–313.