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Iron isotopic analyses of geological reference materials on MC-ICP-MS with instrumental mass bias corrected by three independent methods

Chuanwei Zhu $^1\cdot$ Wenning Lu $^1\cdot$ Yongsheng He $^1\cdot$ Shan Ke $^1\cdot$ Hongjie Wu $^1\cdot$ Linan Zhang 1

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Abstract Here we report iron (Fe) isotopic data of three pure Fe solution standards (IRMM-014, GSB Fe, and NIST 3126a) and five widely used geological reference materials (RMs) from the United States Geological Survey and Geological Survey of Japan obtained on a Neptune Plus multi-collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) in our laboratory over the past 3 years. The instrumental mass bias was corrected by three independent methods: sample-standard bracketing (SSB), Ni doping + SSB, and 57 Fe $-{}^{58}$ Fe double spike + SSB. Measurements reveal that both the Ni doping and double spike methods helped calibrate short-term fluctuations in mass bias. Collectively, almost all measurements of RMs yielded δ^{56} Fe within ± 0.05 of recommended values, provided that each sample was measured four times on MC-ICP-MS. For the first time, new recommended values for NIST SRM3126a are reported (δ^{56} Fe = 0.363 \pm 0.006, 2SE, 95% CI; and δ^{57} Fe = 0.534 ± 0.010, 2SE).

Keywords Iron isotopic analyses · Sample-standard bracketing · Double spike · Ni doping · Reference materials · Precision and accuracy

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⊠ Yongsheng He heys@cugb.edu.cn

1 Introduction

Iron (Fe), as a major element both in the superficial and inner part of Earth, naturally has 0, + 2, and + 3 valences and buffers the redox state of geologic systems (Beard and Johnson 2004; He et al. 2015b; Dauphas et al. 2017). Iron has four stable isotopes: ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe, and ⁵⁸Fe. With its potential to trace geologic processes ranging from planetary formation to inter-mineral diffusion, and in particular redox state change, Fe isotope geochemistry has gained intensive interest from the community in the last 20 years (He et al. 2015b; Dauphas et al. 2017).

Precise and accurate isotopic analyses are required to reveal the limited Fe isotope fractionation in many geologic samples (e.g., most igneous rocks have δ^{56} Fe in a range of 0.10 ± 0.20) (He et al. 2015b; Dauphas et al. 2017). Following Strelow (1980), Fe can be nearly quantitatively recovered from matrices using anion resins in most labs (He et al. 2015a; Dauphas et al. 2017; and references therein). The initial attempts on Fe isotopic analyses were conducted on a thermal ionization mass spectrometer (TIMS) using the double spike technique to correct instrumental mass bias (Johnson and Beard 1999; and references therein). Limited by the difficulty of ionization and non-ideal source evaporation, measurements on TIMS yield poor precision, typically \pm 0.6 (2SD) in δ^{56} Fe (Johnson and Beard 1999; Fantle and Bullen 2009). Currently, most reported Fe isotopic data are measured on a multi-collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) (Belshaw et al. 2000; Weyer and Schwieters 2003; Dauphas et al. 2009, 2017; Millet et al. 2012; He et al. 2015a; Chen et al. 2017), and the long-term reproducibility of δ^{56} Fe can be better than 0.03 (e.g., Dauphas et al. 2009; Millet et al. 2012; He et al. 2015a). For Fe isotopic analyses on MC-ICP-MS, isobaric

¹ State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

interference and mass bias correction are the two major factors that limit precision and accuracy (e.g., Dauphas et al. 2009; He et al. 2015a). The argon plasma source produces intensive argide inference (e.g., ⁴⁰Ar¹⁴N, ⁴⁰Ar¹⁶O, ⁴⁰Ar¹⁶O¹H) on the mass spectrum near Fe isotopes. Pseudo high-resolution (e.g., on Neptune Plus and Nu II/III) is widely used and allows Fe ions to be partially discriminated from argide inference and measured on narrow low-mass-shoulders ($\Delta_{mass} < 0.010$ atomic mass unit) (Weyer and Schwieters 2003). The new generation of MC-ICP-MS (e.g., Nu Plasma 1700) can allow complete resolution of Fe ions from argide interference (Chen et al. 2017). To correct instrumental mass bias, sample-standard bracketing (SSB) is routinely used (Dauphas et al. 2017). The SSB method assumes that mass bias during sample measurements is the same as that during bracketing standard measurements, an assumption that is valid only when conditions between sample and standard solutions (e.g., concentration, purity, and acidity) are perfectly matched (He et al. 2015a; Dauphas et al. 2017; and references therein). Such matching and stability of instrumental mass bias is occasionally difficult to achieve, especially when special samples (e.g., seawater) are treated or MC-ICP-MS is aging. In this case, double spike or elemental doping in combination with SSB can be adopted (e.g., Malinovsky et al. 2003; Weyer and Schwieters 2003; Arnold et al. 2004; Poitrasson and Freydier, 2005; Lacan et al. 2008; Millet et al. 2012; Conway et al. 2013; Finlayson et al. 2015; Chen et al. 2017).

This study reports Fe isotopic data of three solution standards (IRMM-014, GSB Fe, and NIST SRM3126a) and five widely distributed reference materials (BHVO-2, BCR-2, GSP-2, JP-1, and AGV-2) from the United States Geological Survey and Geological Survey of Japan during 2014–2018 at the Isotope Geochemistry Laboratory, China University of Geosciences, Beijing (CUGB). Mass bias was corrected through three independent methods: SSB, double spike + SSB, and elemental (Ni) doping + SSB. The long-term reproducibility of δ ⁵⁶Fe was better than 0.05, provided that each sample was measured four times on MC-ICP-MS, irrespective of the mass bias correction methods used. Except for a few outliers, standards measured in study yielded results consistent with updated recommended values (Craddock and Dauphas 2010; He et al. 2015a; Sossi et al. 2015). Compared to SSB alone, additional double spike and Ni doping corrections both helped overcome short-term fluctuations of the instrumental mass bias. For the first time, new reference values for NIST SRM3126a are given, facilitating future interlaboratory comparison.

2 Experiments

2.1 Chemical procedures

Sample dissolution and Fe purification procedures are after Dauphas et al. (2009) and have been reported elsewhere (He et al. 2015a). Only a brief description is given below. Sample powders containing about 250 µg Fe were dissolved in a mixture of concentrated HF-HNO₃ acids, and then refluxed in aqua regia and HNO₃-enriched aqua regia $(HNO_3:HCl = 2:1)$. The dissolved samples were dried and re-dissolved in 0.5 mL 6-N HCl, and an aliquot of each sample solution containing about 100 µg Fe was processed through the column chemistry. Iron was separated from matrices by 1 ml AG1-X8 resin (200-400 mesh chloride form, Bio-Rad, Hercules, CA, USA) in a HCl medium. Matrix elements were removed using 8 ml 6-N HCl, and then Fe was collected with 9 mL 0.4-N HCl. The same column chemistry was typically performed twice to ensure the purity of the collected Fe. Recovery of Fe was > 99.5%, and the whole procedure blank was routinely below 10 ng and rarely reached 50 ng-negligible compared to the 100 µg sample Fe processed. The purified samples were dried with drops of HNO₃ to reduce possible organic materials from resins, and dissolved in 3% HNO₃ (v/v) prior to isotopic analyses.

2.2 Mass spectrometry

Iron isotopic ratios were measured on a Thermo Fisher Neptune Plus MC-ICP-MS at CUGB on high-resolutions modes (also referred to as medium- and high-resolution modes, e.g., Weyer and Schwieters 2003). Samples were introduced through a Cetac auto sampler and Thermo Scientific Stable Introduction System (SIS) which combines quartz cyclonic and Scott type spray chambers and PFA Teflon self-aspirating micro-nebulizers with 50–100 μ l/min uptake. ⁵³Cr, (⁵⁴Cr + ⁵⁴Fe), ⁵⁶Fe, ⁵⁷Fe, $({}^{58}$ Fe + 58 Ni), and 60 Ni were measured at L3, L1, Central, H1, H2, and H4 respectively, with a ⁵⁶Fe intensity typically around 15 ± 5 V. Concentrations of unknown sample and bracketing standard solutions were well matched within 10%; the same batch of 3% HNO₃ was used to prepare all solutions to eliminate the effects of acid molarity mismatching. The same 3% HNO3 was measured at the beginning of each sequence, and signals were subtracted for all the standards and samples as "On Peak Zero" (OPZ) (Dauphas et al. 2009; He et al. 2015a). Each isotopic analysis consisted of a 30 s (s) baseline, 3 s idle time prior to integration, and 25 cycles with 8.389 s integration each. Data were deduced offline and reported

in the traditional δ notation relative to IRMM-014, δ^{i} Fe (‰) = [(ⁱFe/⁵⁴Fe)_{sample}/(ⁱFe/⁵⁴Fe)_{IRMM-014} - 1] × 1000, where i is 56 or 57.

2.3 Instrumental mass bias correction

Instrumental mass bias correction for Fe isotopic analyses relies on the SSB method (Dauphas et al. 2017). For the measurements in our lab before April 2016, we commonly adopted the SSB method alone for mass bias correction, details of which have been previously reported (He et al. 2015a). After April 2016, short-term fluctuation in instrumental mass bias became frequent, due to aging of the MC-ICP-MS and/or failure of the temperature control system of the lab. To ensure accuracy and facilitate efficient measurements, we attempted to overcome these mass bias fluctuations by introducing the ⁵⁷Fe-⁵⁸Fe double spike and Ni doping methods in addition to SSB.

2.3.1 Double spike method

The ⁵⁷Fe-⁵⁸Fe double spike used in this study was prepared by mixing ⁵⁷Fe and ⁵⁸Fe single spikes from the Oak Ridge National Laboratory (USA) according to the optimized proportion calculated by Rudge et al. (2009). The prepared double spike was measured for its isotopic composition on MC-ICP-MS by SSB (Table S1). The double spike was typically mixed with unknown samples after purification, as in previous studies (Millet et al. 2012; Finlayson et al. 2015). Given the near complete recovery of Fe in the column chemistry (He et al. 2015a), there was no artifact on measured isotopic ratios. The optimized proportion of double spike (q) in the mixed Fe solutions was near 50%(Rudge et al. 2009). We adopted $q \sim 20\%$ to reduce consumption of double spike. The few sessions with q ranging from 20% to 50% indicate this compromise had little effect on the precision and accuracy of Fe isotopic data (Table S3). Double spiked IRMM-014 solutions were measured bracketing every three to five unknown samples. The data were deduced offline using an Excel macro modified after He et al. (2017) that can be provided by the authors upon request. Typically, deduced ⁵⁶Fe/⁵⁴Fe ratios for IRMM-014 in a single session were consistent within \pm 0.10‰ (Fig. 1). $\delta^{56}\text{Fe}$ values were calculated for unknown samples relative to the mean ⁵⁶Fe/⁵⁴Fe ratio of IRMM-014 in each session. Occasionally, time-related shifting in deduced ⁵⁶Fe/⁵⁴Fe ratios for IRMM-014 was observed. If such shifting was < 0.10% between each two adjacent measurements on bracketing IRMM-014 in the whole session, δ values were calculated for unknown samples relative to the mean ratios of their bracketing IRMM-014. Otherwise, the data were rejected, and the



Fig. 1 Mass bias correction by the ⁵⁷Fe-⁵⁸Fe double spike method illustrated by two representative sessions (Fe20160112 and Fe20160113). Every four GSB measurements were bracketed by one IRMM-014 measurement. δ^{56} Fe values for GSB Fe (open symbols) were calculated using ⁵⁶Fe/⁵⁴Fe ratios with mass bias corrected by the double spike method relative to IRMM014. For a comparison, the mass bias (β) shifting during the sessions (filled symbols) is also shown in corresponding δ values relative to the β value of the first measurement of each session. The red line represents the recommended δ^{56} Fe value of GSB Fe (0.729) (He et al. 2015a)

samples were reanalyzed after optimizing MC-ICP-MS conditions.

2.3.2 Ni doping method

Elemental doping is widely used for isotopic measurements on MC-ICP-MS to overcome short-term fluctuations in instrumental mass bias (Marechal et al. 1999; Arnold et al. 2004; Poitrasson and Freydier 2005; Dauphas et al. 2017). This method assumes that the mass bias factor for isotopes of the target element is the same as, or in linear covariation with, isotopes of doped element. Copper and Ni were used in previous studies to correct mass bias for Fe isotopic analyses (Dauphas et al. 2009). Given that ⁶³Cu and ⁶⁵Cu cannot be measured simultaneously with Fe ions, peak jumping is required; the duration of the measurements is significantly extended. Therefore, we adopted Ni doping with mass bias corrected by ⁶⁰Ni/⁵⁸Ni after Oeser et al. (2014) and Chen et al. (2017). The single element GSB Ni solution (1000 ppm) from China Iron and Steel Research Institute was dried and dissolved in 3% HNO₃ (v/v) as a 100 ppm solution. This diluted GSB Ni solution was mixed with purified unknown samples and bracketing standards targeting Ni:Fe of 1:1. In this condition, the doped Ni does not significantly affect the mass bias for Fe isotopic analyses (He et al. 2015a). GSB Fe solutions doped with Ni were measured bracketing every two or three unknown samples.

For data deduction, mass basis on MC-ICP-MS is assumed to follow the exponential law:

$$\beta_{Fe} = \ln\left(\frac{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{measured}}{({}^{56}\text{Fe}/{}^{54}\text{Fe})_{true}}\right) / \ln\left(\frac{Mass_{56}\text{Fe}}{Mass_{54}\text{Fe}}\right)$$
(1)

$$\beta_{\mathrm{Ni}} = \ln\left(\frac{({}^{60}\mathrm{Ni}/{}^{58}\mathrm{Ni})_{measured}}{({}^{60}\mathrm{Ni}/{}^{58}\mathrm{Ni})_{ture}}\right) / \ln\left(\frac{Mass_{{}^{60}\mathrm{Ni}}}{Mass_{{}^{58}\mathrm{Ni}}}\right)$$
(2)

The ⁵⁸Fe interference on ⁵⁸Ni was corrected based on ⁵⁴Fe signals, assuming 58 Fe/ 54 Fe = 0.0480734 given β_{Fe} calculated from measured ⁵⁶Fe/⁵⁴Fe against 15.6986 (Taylor et al. 1992). It has been noted that such correction works well only for terrestrial samples, for which no mass-independent isotopic variation has been observed (Dauphas et al. 2017). Natural mass-dependent Fe isotopic variations were compensated during the correction and will not cause ⁶⁰Ni/⁵⁸Ni. measured deviation on А true 60 Ni/ 58 Ni = 0.385199 was adopted after (Gramlich et al. 1989). In reality, β_{Fe} is usually not the same as β_{Ni} (e.g., Malinovsky et al. 2003; Poitrasson and Freydier 2005; Chen et al. 2017). β_{Fe} and β_{Ni} for bracketing standards were calculated for each measured session. In the case that variation between β_{Fe} and β_{Ni} was > ~0.016 (e.g., > 0.60 measured by δ^{56} Fe), a linear regression between them was performed and used to calculate β_{Fe} for unknown samples. Otherwise, $\beta_{Fe} = \beta_{Ni}$ was adopted, due to the large uncertainty for the linear regression. Calculations demonstrate that such approximation had negligible effect on Fe isotopic compositions measured for unknown samples, e.g., < 0.01 in δ^{56} Fe. Data were treated offline; δ values were calculated relative to bracketing GSB Fe standards and reported relative to IRMM-014 (He et al. 2015a).

2.4 Internal errors

Each unknown sample was duplicately measured on MC-ICP-MS, typically four or nine times; Fe isotopic data are reported as mean values of the results. Internal errors are given in 2 standard errors of the mean in 95% CI after Dauphas et al. (2009), except for runs measured by the double spike + SSB method. Briefly, δ values of each bracketing standard relative to their neighboring standards were calculated for each sequence, and 2 standard deviations of these δ values for bracketing standards were given to represent the reproducibility of single time MC-ICP-MS measurements $(2SD_{MC}). 2\sigma = \sqrt{(2SD_{MC}/\sqrt{n})^2 + (2\sigma_{Chem})^2}$, where *n* represents the number of duplicate measurements on each sample and σ_{Chem} represents errors that may arise from the chemical procedures. Based on duplicate measurements of prepared solutions with variable matrices and known Fe isotopic compositions, $2\sigma_{Chem}$ has been estimated to be 0.005 and 0.013 in our lab for δ^{56} Fe and δ^{57} Fe, respectively (He et al. 2015a). $2\sigma_{Chem}$ values were not integrated into final errors for natural samples, because GSB Fe was used as the bracketing standard for the SSB and SSB + Ni doping methods, and calibration from $\delta^{56}Fe_{GSB}$ to $\delta^{56}Fe_{IRMM-014}$ ($\delta^{56}Fe_{IRMM-014} = \delta_{56}Fe_{GSB} + \delta^{56}Fe_{IRMM-014}$ (GSB) + $\delta^{56}Fe_{GSB} \times \delta^{56}$ - Fe_{IRMM-014}(GSB)/1000), for example, had already included an extra uncertainty of 0.005 (He et al. 2015a). Such calibration may cause a systematic bias rather than an increase in the dispersion of the data. As to the SSB + double spike method, internal errors were directly given as 2 standard errors of mean of duplicate results for each sample because the number of bracketing standard measurements in each sequence was low.

3 Results and discussion

3.1 Correction of short-term fluctuations in mass bias

The double spike technique has been considered to calibrate well for instrumental mass bias (Lacan et al. 2008; Rudge et al. 2009; Li et al. 2011; Millet et al. 2012; Conway et al. 2013; Finlayson et al. 2015; He et al. 2017). However, this may not always be true for Fe isotopic analyses, due to the narrow mass spectrum shoulder allowing accurate analyses, fluctuations of argide interference intensity, and difficulty in ⁵⁸Ni correction on ⁵⁸Fe (Millet et al. 2012; Finlayson et al. 2015). Mismatching of acidity between unknown samples and their bracketing standards can cause mass-independent measured δ^{56} Fe and δ^{57} Fe based on SSB measurements (He et al. 2015a), and thus may also lead to inaccurate results for Fe isotopic analyses using the double-spike technique. Furthermore, only one independent ratio can be obtained by doublespiked runs, given that Fe has only four isotopes; any massindependent effect on mass bias cannot be identified by raw data of unknown samples themselves. Special cautions on the reproducibility of measured isotopic ratios for geological reference materials with known isotopic composition and bracketing standards in each session are required to ensure accuracy.

As illustrated by two representative sessions measuring only GSB and IRMM-014 Fe (Fig. 1), we demonstrated that short-term fluctuations in mass bias can be well calibrated by the double-spike technique. Typically, measured ratios of GSB and IRMM-014 Fe are stable. Abrupt shifting in measured ratios observed in previous studies (e.g., Millet et al. 2012) due to argide interference burst was not observed in the present study. We attribute this to good resolution of Fe ions from argide interference and magnetic field stability on the Neptune Plus. Occasionally, smooth shifting in measured ratios of bracketing standards can be observed. In the same conditions, tests on unspiked GSB Fe solution also reveal shifting on (${}^{57}\text{Fe}/{}^{54}\text{Fe})_N$ with mass bias internally corrected by ${}^{56}\text{Fe}/{}^{54}\text{Fe} = 15.6986$ (Taylor et al. 1992), suggesting shifting of the magnetic field and gradual deviation from the optimized mass for Fe isotopic measurement. Except for a few cases, such shifting can be eliminated by calculation of δ values relative to bracketing standards as suggested by Millet et al. (2012). As shown previously (He et al. 2015a), the GSB Fe solution contains detectable Ni with ⁶⁰Ni/⁵⁴Fe = 0.000121 ± 5 (2SE), corresponding to ⁵⁸Ni/⁵⁸Fe ~ 0.0653. With ⁵⁸Ni interference being monitored by ⁶⁰Ni and corrected using ⁶⁰Ni/⁵⁸Ni measured on a 100 ppb GSB Ni at the beginning of each session, runs on double-spiked GSB Fe yielded accurate δ^{56} Fe. This confirms that ⁵⁸Ni correction is not a problem for double-spiked Fe isotopic analyses in our lab at the quoted precision level (see Sect. 3.2).

The double spike method has difficulty identifying mass-independent effects based on raw data of unknown samples themselves. To overcome this, we attempted to measure Fe isotopic ratios with the Ni doping method. As shown in Fig. 2, introduction of the Ni doping method can well calibrate the mass bias shifting on MC-ICP-MS. In the case of short-term fluctuations in mass bias during session measurements, the Ni doping method can significantly improve reproducibility and accuracy. As exemplified by the session Fe20170221 (Fig. 2), the reproducibility of δ^{56} Fe was poor ~ 0.37 (2SD) if calculated based on measured ⁵⁶Fe/⁵⁴Fe directly, relative to bracketing standards without mass bias correction, but the reproducibility was improved to an acceptable level < 0.05 (2SD) when mass bias was corrected by 60Ni/58Ni. Furthermore, both representative sessions (Fe20170221 and Fe20170223) yielded ⁵⁶Fe/⁵⁴Fe with mass bias corrected by ⁶⁰Ni/⁵⁸Ni constant within \pm 0.05 for bracketing Ni-doped GSB Fe solutions. This allows accurate measurement of several unknown samples between each two adjacent bracketing standards in routine sessions. δ^{57} Fe and δ^{56} Fe can be independently measured by the Ni-doping + SSB method (e.g., Fig. 3 and Table S3), which allows monitoring massindependent effects of all data.

3.2 Precision and accuracy

Results of three pure Fe solution standards (IRMM-014, GSB Fe, and NIST 3126a) and five widely used geological reference materials (RMs) from the United States Geological Survey and Geological Survey of Japan obtained in our laboratory over the past 3 years are reported in Table S2-3, summarized in Table 1, and shown in Figs. 3 and 4. No significant interference can be identified in the three-isotope diagram (Fig. 3). The long-term reproducibility of δ^{56} Fe for almost all standards, measured by 2SD, was better than ± 0.05 (Table 1), provided that each duplicate measurement consisted of multiple analyses (see Table S2–3) on MC-ICP-MS. The only exception was



Fig. 2 Mass bias correction by Ni doping + SSB illustrated by two representative sessions (Fe20170221 and Fe20170223) and only the results of bracketing Ni-doped GSB Fe solutions are shown. In Fig. 2a, the shifting of mass bias was expressed as δ^{56} Fe values (filled symbols) relative to the first measured ratio, e.g., δ^{56} Fe = [(56 Fe/ 54 Fe)_{measured}/(56 Fe/ 54 Fe)_{first} - 1] * 1000. For comparison, δ^{56} Fe values (open symbols) relative to the first measured ratio with Ni-doping correction are also plotted. In Fig. 2b, we compare δ^{56} Fe values relative to the average 56 Fe/ 54 Fe ratios of the bracketing measurements with or without mass bias correction by Ni-doping



Fig. 3 Three isotope plot of Fe isotopic data obtained in this study. The regression slope between the measured δ^{57} Fe and δ^{56} Fe is 1.472, consistent with what is expected by the equilibrium fractionation law (1.475) (Young et al. 2002) within uncertainty

Table 1Average iron isotopiccompositions of standardsmeasured during Sept. 2014 toJan. 2018

Standards	FeO(t) (wt%)	δ ⁵⁶ Fe	2SD	2SE#	δ ⁵⁷ Fe	2SD	N
SSB							
BHVO-2, Basalt, USGS	11.15	0.115	0.031	0.033	0.165	0.046	44
BCR-2, Basalt, USGS	12.39	0.088	0.019	0.032	0.128	0.048	14
GSP-2, Granodiorite, USGS	3.93	0.158	0.023	0.031	0.233	0.038	17
JP-1, Peridotite, GSJ	7.51	0.018	0.022	0.027	0.022	0.053	9
AGV-2, Andesite, USGS	6.10	0.109	0.001	0.030	0.150	0.035	2
IRMM-014, IRMM		0.004	0.016	0.023	- 0.003	0.032	20
GSB Fe, CISRI		0.735	0.031	0.023	1.067	0.063	6
$SSB + double \ spike$							
BHVO-2, Basalt, USGS	11.15	0.122	0.039	0.037			11
BCR-2, Basalt, USGS	12.39	0.081	0.041	0.032			8
GSP-2, Granodiorite, USGS	3.93	0.154	0.060	0.034			3
JP-1, Peridotite, GSJ	7.51	0.005	0.033	0.025			3
IRMM-014, IRMM		0.011	0.039	0.039			11
SRM3126a, NIST		0.350	0.028	0.034			6
GSB Fe, CISRI		0.725	0.030	0.030			45
SSB + Ni doping							
BHVO-2, Basalt, USGS	11.15	0.119	0.050	0.029	0.170	0.100	16
BCR-2, Basalt, USGS	12.39	0.079	0.045	0.032	0.113	0.027	6
GSP-2, Granodiorite, USGS	3.93	0.149	0.030	0.040	0.208	0.062	7
AGV-2, Andesite, USGS	6.10	0.122	0.027	0.036	0.188	0.066	4
IRMM-014, IRMM		0.001	0.034	0.032	- 0.027	0.190	51
SRM3126a, NIST		0.365	0.047	0.034	0.534	0.065	45

Superscript # denotes 2SE as the mean of internal errors (95% CI) on δ^{56} Fe for individual measurements. FeO(t) (wt%) data are from http://georem.mpch-mainz.gwdg.de/

duplicate measurements on GSP-2 using the double spike + SSB method, which yielded a reproducibility of 0.060. Note that these duplicate double-spike measurements on GSP-2 yielded δ^{56} Fe consistent with the recommended value (He et al. 2015a) within \pm 0.04 (Table S2). The slightly large reproducibility for this standard (~ 0.06) may be due to the low number of duplicate measurements. The mean δ^{56} Fe values of all solution and rock standards are consistent with updated recommended values (He et al. 2015a) within \pm 0.02, ensuring the accuracy of data obtained here.

Previous studies have shown that the long-term reproducibility and accuracy for Fe isotopic analyses can be improved by increasing measurement times on MC-ICP-MS for each sample (Poitrasson and Freydier 2005; He et al. 2015a). He et al. (2015a) reported that the long-term reproducibility and accuracy for δ^{56} Fe were both better than 0.03 in our lab, provided that each sample was measured nine times on MC-ICP-MS with mass bias corrected by SSB. The data reported here demonstrate that accuracy at this level were routinely reached in our lab when the MC-ICP-MS was optimized and SSB was used (see the SSB data, summarized in Table 1 and shown in Fig. 4). It is difficult, however, to directly demonstrate whether δ^{56} Fe can be measured with a long-term reproducibility and accuracy of < 0.03 when mass bias of the MC-ICP-MS fluctuations and Ni-doping + SSB are used, given the limited dataset for standards with nine measurements each on MC-ICP-MS (Table S4). We assessed this issue using the Monte Carlo method. Nine "measured" δ^{56} Fe values were randomly collected from raw data for single measurement on each geological standard obtained by Nidoping + SSB (Table S5). The mean δ^{56} Fe of these nine measurements was then calculated. Such calculation was repeated 200 times, generating a representative dataset; the long-term reproducibility is given in Table 2 and predicted to be < 0.03. These calculations suggest that application of the Ni-doping method can improve the long-term reproducibility and accuracy for δ^{56} Fe to < 0.03 if each data consists of nine duplicate analyses on MC-ICP-MS, despite the fluctuating instrumental mass bias observed in our lab. This view is supported by the limited data with nine measurements each on MC-ICP-MS using Ni-doping + SSB, all of which give δ^{56} Fe consistent with updated recommended values within ± 0.03 (Table S4).



Fig. 4 Iron isotopic compositions of 3 pure Fe solution standards (IRMM-014, GSB Fe and NIST SRM3126a) and 5 geological reference materials (BHVO-2, BCR-2, GSP-2, JP-1, and AGV-2) measured during a period from Sept. 2014 to Jan. 2018. Instrumental mass bias was corrected via three independent techniques, including SSB, double Spike + SSB, and Ni doping + SSB. Recommended values (RV) are from He et al. (2015a), while the reference value for NIST SRM3126a is provided in this study. Note that recommended values from He et al. (2015a) were calculated by a compilation of Fe isotopic data from ten independent labs

As an important indicator of data quality for Fe isotopic data of individual unknown samples, internal errors should be properly reported. Internal errors are usually reported in different ways for Fe isotopic data. One way is to use 2 standard deviations of results of multiple analyses on each sample (e.g., Millet et al. 2012; Xia et al. 2017; Zhao et al. 2017). Another way is to report internal errors as 2 standard errors of the mean for multiple analyses on each sample



Fig. 4 continued

tandards	δ ⁵⁶ Fe	2SD	δ^{57} Fe	2SD	Ν

Table 2Mean andreproducibility (in 2SD) of Feisotopic analyses with each	Standards	δ^{56} Fe	2SD	δ^{57} Fe	2SD	Ν
	BHVO-2, Basalt, USGS	0.114	0.019	0.177	0.043	200
sample being measured nine	BCR-2, Basalt, USGS	0.093	0.017	0.117	0.026	200
by Monte Carlo calculations	GSP-2, Granodiorite, USGS	0.156	0.024	0.207	0.048	200
based on raw data obtained for	AGV-2, Andesite, USGS	0.124	0.022	0.189	0.044	200
each geological standard in our Lab using Ni-doping + SSB	IRMM-014, IRMM	-0.002	0.022	-0.002	0.034	200
	NIST 3126a, NIST	0.362	0.026	0.540	0.044	200

with or without the Student's t-correction (Poitrasson and Freydier 2005; Weyer and Ionov 2007). The routine way to report internal errors adopted in our lab is after Dauphas et al. (2009) and detailed in Sect. 2.4. Briefly, internal errors were calculated based on the reproducibility of measurements on a large number of bracketing standards in each session and on the number of multiple analyses on each sample, with errors arising from the chemical procedures considered. Note that we report internal errors for double-spiked runs as 2 standard errors of the mean for multiple analyses on each sample. Most standards plotted along a 1:1 line in long-term reproducibility (2SD) versus average 2SE, especially for representative samples with large numbers of duplicate measurements (Fig. 5). With accuracy given by the absolute difference between the measured and recommended δ^{56} Fe, internal errors reported here are larger than the accuracy for most (> 90%) measurements (Fig. 6). For the remaining measurements, internal errors largely agree well within the accuracy. Collectively, Figs. 5 and 6 demonstrate that internal errors reported in this study are proper and, in most cases, conservative.



Fig. 5 Summary of the relationship between the long-term reproducibility (2SD) and average 2SE of individual measurements for the same standard solutions and RMs. Most standards are plotted along a 1:1 line, especially for representative ones with large numbers of duplicate measurements, suggesting that internal errors reported in this study are proper. The larger bubble sizes reflect more duplicate measurements on individual samples



Acta Geochim (2018) 37(5):691-700

Fig. 6 Summary of the relationship between the absolute difference between the measured and recommended δ^{56} Fe values and internal errors (2SE) reported. MV, RV, and RMs refer to measured values, recommended value, and reference materials, respectively. RV is from He et al. (2015a). Except one outlier, all measured δ^{56} Fe for solution standards and RMs are consistent with RV within ± 0.05 , and thus ensure accuracy in the same level. Furthermore, internal errors reported are larger than the accuracy for most (>90%)measurements. For the rest measurements, internal errors largely agree well with the accuracy. Again, this plot demonstrates that internal errors reported in this study are proper and, in most cases, conservative. Results of NIST 3126a are not shown in this plot, since its RV only based on data from this study

3.3 New recommended values

Except for NIST SRM3126a, all solution standards and geological reference materials measured in this study yield mean δ^{56} Fe values consistent with the recommended values given by He et al. (2015a) within ± 0.01 (Fig. 4). Therefore, updating the recommended values for these standards is not necessary given the current analytical uncertainty. NIST SRM3126a has been previously measured at WHOI (δ^{56} Fe = 0.390 ± 0.130, 2SD, N = 10; Rouxel and Auro 2010) and IFREMER (Brest, France) $(\delta^{56}$ Fe = 0.420 ± 0.070, 2SD, N = 10; Chever et al. 2015). Six-month measurements in our lab using two independent mass bias correction methods yielded a mean δ^{56} Fe of 0.363 ± 0.046 (2SD, N = 51), consistent with literature values within uncertainty. Here, we provide new recommended values for NIST SRM3126a

 $(\delta^{56}\text{Fe} = 0.363 \pm 0.006, 2SE, 95\% \text{CI}; \delta^{57-}\text{Fe} = 0.534 \pm 0.010, 2SE, 95\% \text{CI})$ based on the large dataset from this study. Uncertainties are given by 2SD/ $\sqrt{\text{N}}$. Literature values are not included because of the lack of information on measurement details. Calibration of NIST SRM3126a can facilitate future inter-laboratory data comparison, given that the supply of IRMM-014 is exhausted (He et al. 2015a; Dauphas et al. 2017).

4 Conclusions

This study reports a large high-precision Fe isotopic dataset for three solution standards and five geological reference materials, obtained on MC-ICP-MS with mass bias corrected by SSB, 57 Fe– 58 Fe double spike + SSB, and Ni doping + SSB over the past 3 years in Isotope Geochemistry Lab, China University of Geosciences, Beijing. The dataset demonstrates that δ^{56} Fe can be routinely measured with an accuracy ≤ 0.05 or ≤ 0.03 , provided that each sample is measured on MC-ICP-MS for four or nine times, respectively. Of particular importance, we have illustrated our attempts to overcome short-term fluctuation in the instrumental mass bias using the double-spike and Nidoping methods. New recommended values for NIST SRM3126a are given, with δ^{56} Fe = 0.363 ± 0.006 (2SE) and δ^{57} Fe = 0.534 ± 0.010 (2SE).

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