

Characterization of a New Iron Isotopic Reference Material Using Two Independent Methods for Instrumental Mass Bias Correction

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ABSTRACT: Isotopic reference materials are crucial to the development of non-traditional stable isotope systems for both securing accurate and precise isotope ratio measurements and enabling comparison of isotope ratio data obtained at different laboratories. In this study, a new iron isotopic reference material, NIM-RM 2712, has been developed to fulfill the demand of reliable Fe isotopic data in geochemical, environmental and biological researches. This reference material exhibits sufficient homogeneity and stability for application in Fe isotopic analysis. The property values of NIM-RM 2712 were characterized as (U , $k=2$): $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.461 \pm 0.043\text{‰}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 0.693 \pm 0.064\text{‰}$ by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) on the use of two independent instrumental mass bias correction models: the standard-sample bracketing method and the double spike approach. This new Fe isotopic reference material can be recommended as a secondary isotopic standard or as a replacement for the conventional reference material IRMM-014 when it becomes exhausted.

INTRODUCTION

The isotopic reference materials are a vital part for the isotope ratio measurement of non-traditional stable isotopic systems, which are essential for securing accurate and precise measurement results as well as enabling the inter-laboratory comparisons.¹⁻³ Classical isotopic reference materials are certified for one or more isotope amount ratio, which apply traceable values accompanied by a sophisticated uncertainty statement.^{4,7} Wherein, the isotopic reference materials certified by applying the gravimetric isotope mixture approach with SI-traceable quantity values represent the highest metrological quality and have been defined as primary reference materials.^{8,9} By the advances of modern mass spectrometers, the isotope δ (relative difference of an isotope ratio to a specific standard),¹⁰ a traditional notation in the geological

sciences, has been adopted in many other areas for conveniently and accurately expressing of small differences in their isotopic composition between samples.¹¹⁻¹⁴ Apart from the high cost and labor of the gravimetric isotope mixture approach, the uncertainties of the isotope amount ratios obtained via this method are currently limited to approximately 0.01%, which is too high for some applications in isotope research.⁸ To bypass these problems, the isotopic reference material that certified for δ values have been proposed, which are indispensable for method development, validation and quality checks for determining small isotope variations.¹⁵⁻¹⁷

In the recent decades, the natural distribution and mass-fractionation mechanisms of iron isotopic compositions have gained particular interest due to its relatively high abundance, redox-sensitive property and biological utilization.^{18, 19} Iron has

four stable isotopes: ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe , with natural abundances of 5.845%, 91.754%, 2.119% and 0.282%, respectively. The isotopic compositions of Fe are conventionally expressed as $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values relative to IRMM-014 that produced by the Institute for Reference Materials and Measurements (Belgium).^{9,20,21} The natural Fe isotopic variations cover a range from -3.0‰ to +2.5‰ on the $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ scale.²² Since the IRMM-014 is exhausted, the characterization of new Fe isotopic reference material becomes urgent for Fe isotopic investigations. Single elemental standard solutions, as GSB Fe (Iron and Steel Research Institute, China) and JMC Fe (Johnson Matthey, UK) have been used as in-house reference solutions for Fe isotopic determinations in several laboratories.²³⁻²⁵ However, these solutions are only certified for the mass fraction of Fe. The consistency of Fe isotopic compositions in different batches of GSB Fe and JMC Fe are not necessarily be ensured by the manufacturers, which might hinder their long-term application. More recently, Li *et al.*²⁶ has developed the CAGS-Fe (Chinese Academy of Geological Sciences, China) reference solution with $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.83 \pm 0.06\%$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 1.20 \pm 0.12\%$, respectively. The fact that this material is not commercially available potentially limits its extensive use.³

To address the above issues, the main aim of this study was to develop and characterize a new Fe isotopic reference material (NIM-RM 2712) that certified for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values in relative to IRMM-014. Efforts have been made in the following aspects to improve the quality of this isotopic reference material: i) high-purity iron metal are selected as the raw material of this reference material to reduce interferences from Cr and Ni on Fe isotopic measurement; ii) a large enough stock of the raw material were preserved in proper condition so that the reference material can be applied for decades; iii) two independent characterization methods have been carried out to ensure the reliability of the certified $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ values; iv) the uncertainties on this isotopic reference material have been rigorously assessed including the uncertainties associated with characterization, isotopic homogeneity and stability.

EXPERIMENTAL

Reagents and materials. Raw material of the Fe isotopic reference material was high-purity iron blocks (99.999%) that purchased from China New Metal Company. The Fe isotopic reference material IRMM-014 (Institute for Reference Materials and Measurements, Belgium) was used throughout this study as bracketing standards. The CAGS-Fe solution that developed by the Institute of Geology (CAGS, China) was measured relative to IRMM-014 for δ -value measurement method verification. A set of multi-element certified reference materials GBW(E)082428 - GBW(E)082431 were produced by the National Institute of

Metrology (NIM, China), which were utilized as the calibration standards for impurity analysis. The isotopically enriched ^{57}Fe and ^{58}Fe iron sheets used as spikes were purchased from Cambridge Isotope Laboratories, Inc. (CIL, USA) and the Oak Ridge National Laboratory (ORNL, USA), respectively.

Nitric acid was purchased from Beijing institute of chemical reagents (China) and purified twice through a sub-boiling distillation system prior to use. Ultrapure water with a resistivity of 18.2 M Ω cm was obtained from a Milli-Q Integral 5 water purification system (Millipore Corp., USA). All the quartz or polyfluoralkoxy polymer (PFA) containers were cleaned by purified nitric acids and ultrapure water before use.

Preparation of the Fe isotopic reference material. The new Fe isotopic reference material NIM-RM 2712 was prepared from high-purity iron blocks. To ensure persistent supply of this isotopic reference material, a large quantity of the same batch of the high-purity iron blocks was purchased and sealed separately in bottles.

Each lot of the Fe isotopic reference material was prepared by dissolving one piece of iron block (~6 g). Firstly, the surface of an iron block was successively cleaned by rinsing in methanol, water and 1 mol L⁻¹ HNO₃ with ultrasound for 5 min, and then in water and methanol for three times with ultrasound for 3 min before drying in nitrogen gas. Secondly, the cleaned iron block was weighed on an analytical balance, and dissolved in a certain amount of 5 mol L⁻¹ HNO₃ under mild heating. The solution was then diluted by ultrapure water after complete dissolution, creating the Fe isotopic reference material with a concentration of 100 $\mu\text{g}\cdot\text{g}^{-1}$ Fe in 2% HNO₃. Finally, every 2 ml of solution was dispensed into pre-cleaned ampoule bottles and sealed for storage.

Chemical analysis. In total of 73 elemental impurities in the raw material of NIM-RM 2712 were determined using a high resolution double - focusing sector-field glow discharge mass spectrometry (GDMS, Element GD, Thermo Fisher Scientific, Germany). To reduce possible surface contaminations, the iron blocks were cleaned by the aforementioned processes before analysis. Typical discharge current and discharge gas flow rate were 35 mA and 430 mL/min, respectively. The calibration of GDMS was based on standard relative sensitivity factors (SRSFs) as supplied with the instrument.²⁷ Among them, K, Ru, Rh and Pd were measured in high resolution mode ($m/\Delta m \geq 10000$); while, the other 69 elements were measured in medium resolution mode ($m/\Delta m \geq 4000$).

In addition, since Cr and Ni are the main isobaric interferences on Fe isotopic analysis, the mass fractions of these elements in the new Fe isotopic reference material were measured using a high-resolution inductively coupled plasma mass spectrometer (HR-ICPMS, Element II, Thermo Fisher Scientific, Germany). The external calibration method was conducted with yttrium utilizing

Fig. 1 A mass scan showing the principle of medium resolution employed for Fe isotopic measurement with ideal magnet placement on interference-free peak flat.

as an internal standard for matrix correction.

MC-ICPMS analysis. The Neptune Plus multi-collector ICPMS (MC-ICPMS, Thermo Fisher Scientific, Germany) was used for Fe isotope ratio measurements. Sample solutions were injected into the plasma through a self-aspiration glass nebulizer with an uptake rate of 0.1 mL min⁻¹ using an ASX-112FR autosampler (Teledyne CETAC Technologies, USA). The cup configurations and instrument parameters are displayed in Table S1. Static measurements of the Fe isotope mass along with masses of 53 and 60 were conducted using a Faraday collector array equipped with 10¹¹ Ω resistors. The contributions of ⁵⁴Cr⁺ on the ⁵⁴Fe⁺ signal and ⁵⁸Ni⁺ on the ⁵⁸Fe⁺ signal was corrected based on a natural ⁵⁴Cr/⁵³Cr ratio of 0.2489 and a natural ⁵⁸Ni/⁶⁰Ni ratio of 2.5961, respectively,²⁸ if the signal intensities of ⁵³Cr⁺ and ⁵⁸Ni⁺ were above 0. As displayed in Fig. 1, the measurements were performed at medium mass resolution (m/Δm ≥ 3000) on the interference-free plateau of the peak shoulder.

Typically, the signal intensity of ⁵⁶Fe⁺ in 750 ng·g⁻¹ of Fe solution could reach 20 V. Concentrations of the solutions of sample and bracketing standard were well matched within 10%. And, the same batch of 2% HNO₃ was used to prepare all solutions to eliminate the effects of acid molarity mis-matching. At the beginning of each sequence, the signal of 2% HNO₃ was recorded and subtracted for all the standards and samples. And after each measurement, the nebulizer and spray chamber were rinsed with 5% HNO₃ until the signal intensity had dropped to the background level. Data were deduced offline. The Fe isotopic composition in NIM-RM 2712 was reported using δⁱFe notation in permil (‰) relative to IRMM-014, where *i* denotes 56 or 57.

Instrumental mass bias correction. Instrumental mass bias correction for Fe isotopic analysis commonly uses the SSB

method. To ensure accuracy of the results, we also introduced the double spike method in addition to SSB to overcome the mass bias fluctuations during MC-ICPMS measurements. The Fe isotopic compositions of CAGS-Fe and NIM-RM 2712 were measured in relative to IRMM-014 using both methods.

For SSB method, the δⁱFe was calculated through Equation 1.

$$\delta^i\text{Fe} = \frac{r_{i/54,\text{sample}}}{r_{i/54,\text{IRMM-014}}} - 1 \quad (1)$$

where $r_{i/54,\text{sample}}$ represents the measured ⁱFe/⁵⁴Fe ratio in sample, and $r_{i/54,\text{IRMM-014}}$ represents the mean value of ⁱFe/⁵⁴Fe ratios in IRMM-014 that measured before and after sample solution.

For the double spike method, a ⁵⁷Fe-⁵⁸Fe double spike solution was prepared using ⁵⁷Fe and ⁵⁸Fe single spikes in accordance with the optimized proportion calculated by Rudge *et. al.* (~48% ⁵⁷Fe in a ⁵⁷Fe-⁵⁸Fe double spike).²⁹ The Fe isotopic composition in the double spike solution was determined by the SSB method using IRMM-014 as bracketing standard to obtain (amount fraction%, 2SD): $x_{54\text{Fe}} = 0.00102 \pm 0.00004$, $x_{56\text{Fe}} = 2.1052 \pm 0.0005$, $x_{57\text{Fe}} = 48.213 \pm 0.005$ and $x_{58\text{Fe}} = 49.681 \pm 0.005$, respectively. Then, the double spike was mixed with the sample or standard solution in the optimized proportion of near 45%. The mathematical model used for calculation of corrected Fe isotope ratios in sample is described by Equation 2, which assumed that both natural and instrumental mass-dependent fractionation follow an exponential law.³⁰ Data were deduced offline using the Isolution software that developed by Lanping Feng from China University of Geosciences (Wuhan, China),³¹ as well as using a MATLAB[®] program. To achieve better precision, the double spike approach was performed plus SSB method. Thus, the δⁱFe values for samples were obtained in relative to the corrected Fe isotopic composition of IRMM-014.

$$F_i(q, f_N, f_M) = qR_{S,i} + (1 - q)r_{N,i} \left(\frac{m_i}{m_{54}}\right)^{f_N} - r_{M,i} \times \left(\frac{m_i}{m_{54}}\right)^{f_M} = 0 \quad (2)$$

where $R_{S,i}$ is the corrected Fe isotope ratio in the spike, $r_{N,i}$ and $r_{M,i}$ are the measured Fe isotope ratios of sample and spike-sample mixture, respectively. The f_N and f_M are the isotopic fractionation factors for the natural sample and the mixture, respectively; and m_i and m_{54} are the atomic masses of the Fe isotopes. The q is related to the proportion of the spike in the mixture.

Uncertainty estimation. The uncertainties of δ⁵⁶Fe and δ⁵⁷Fe values were evaluated following the recommendations of the ‘Reference Materials - Guidance For Characterization And Assessment Of Homogeneity And Stability’ (ISO Guide 35, 2017).³² The combined standard uncertainty (u_{CRM}) on the reference material was obtained by the standard uncertainty associated with characterization of the property value (u_{char}),

between-unit variability (u_{bb}) and the long-term stability (u_{lts}) through Equation 3:

$$u_{CRM} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2} \quad (3)$$

Among them, the basic principles for the evaluation of characterization uncertainty were in accordance with the ‘Guide to Expression of Uncertainty in Measurement of ISO/BIPM’ (ISO Guide 98-3, 2008).³³ To be specific: i) The uncertainty on the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values obtained by the SSB method were estimated by the terms contributing to the isotopic variability, including the uncertainty of both the measured isotope ratios of the sample $u(r_{i/54, \text{sample}})$ and that of the standard $u(r_{i/54, \text{IRMM-014}})$ through Equation 4. ii) The uncertainty provided by the double spike approach encompassed all potential sources of uncertainty which can influence the reproducibility of the Fe isotopic composition results, as the reference material data used, the analysis of the ^{57}Fe - ^{58}Fe double spike as well as the measurement of the standard, sample, spike-standard and spike-sample mixtures. Their uncertainty propagations were assessed using the Monte Carlo simulation. iii) As the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values of NIM-RM 2712 were repeatedly measured using the SSB method and the double spike approach, their combined measurement uncertainties were obtained by the square sum of the uncertainty for a single δ measurement and the standard deviation of the mean of all measurement results through Equation 5.³⁴

$$u_c(\delta^i\text{Fe}) = \sqrt{\left(\frac{1}{r_{i/54, \text{IRMM-014}}}\right)^2 u^2(r_{i/54, \text{sample}}) + \left(-\frac{r_{i/54, \text{sample}}}{(r_{i/54, \text{IRMM-014}})^2}\right)^2 u^2(r_{i/54, \text{IRMM-014}})} \quad (4)$$

$$u_{char} = \sqrt{\left(\frac{s}{\sqrt{N}}\right)^2 + \frac{u_c^2(\delta^i\text{Fe})}{N}} \quad (5)$$

where $u_c(\delta^i\text{Fe})$ is the measurement uncertainty for a single δ measurement, s is the standard deviation of N replicate measurements.

The uncertainties associated with between-unit variability and long-term stability of NIM-RM 2712 were evaluated using Equations 6 and 7 based on the homogeneity and stability test data.

$$u_{bb} = S_{bb} = \sqrt{\frac{M_{\text{between}}^2 - M_{\text{within}}^2}{n}} \quad (6)$$

$$u_{lts} = s(b_1) \cdot X \quad (7)$$

where S_{bb} donates the between-bottle variance; M_{between} donates the between-unit mean square; M_{within} donates the within-unit mean square; n donates the number of subsamples measured for each unit. The $s(b_1)$ is the standard deviation of the estimated slope obtained by regression analysis of the stability test data; X is the shelf life of 15 months.

RESULTS AND DISCUSSION

Chemical purity of NIM-RM 2712. The chemical purity of the reference material is crucial to the Fe isotope ratio measurements using MC-ICPMS. For this purpose, the purity of the raw material of NIM-RM 2712 was well established based on analytical results of GDMS (Table S2) as Fe mass fraction of $99.9973\% \pm 0.0003\%$ (2SD). The isobaric elements Cr and Ni in the solution of NIM-RM 2712 were further determined using external calibration assays by HR-ICPMS. The results revealed that Cr was nearly undetectable with a $^{54}\text{Cr}/^{54}\text{Fe}$ value of 9×10^{-7} and Ni was absent in the NIM-RM 2712 solution with a $^{58}\text{Ni}/^{58}\text{Fe}$ value of $< 2 \times 10^{-5}$ (below the detection limit of Ni). These contents of Cr and Ni were at similar level to those in IRMM-014, while superior to GSB Fe solution that contained detectable Ni with a $^{58}\text{Ni}/^{58}\text{Fe}$ ratio of 6.5×10^{-2} .³⁵ In this circumstance, the isobaric elements Cr and Ni in NIM-RM 2712 could not affect the Fe isotope data since they were too low to be detected by the Faraday cups in MC-ICPMS when the stock solution was diluted more than 100 times for measurement.

Fe isotopic composition in NIM-RM 2712. The Fe isotopic composition of the isotopic reference material NIM-RM 2712 was expressed as δ -values relative to IRMM-014. The characterization of $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ was carried out by both the SSB method and the double spike approach. Before that, the precision and accuracy of these methods had been verified using IRMM-014 and CAGS-Fe as measurement samples. As results, replicate measurement of IRMM-014 given mean values ($N=20$, 2SD) of $\delta^{56}\text{Fe}_{\text{IRMM-014}} = -0.002 \pm 0.068\%$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = -0.001 \pm 0.092\%$ using the SSB method, and $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.003 \pm 0.060\%$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 0.004 \pm 0.090\%$ via the double spike approach. Meanwhile, the Fe isotopic composition of CAGS-Fe was determined as ($N=8$, 2SD): $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.820 \pm 0.060\%$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 1.218 \pm 0.090\%$ by the SSB mass bias correction model, and $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.787 \pm 0.054\%$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 1.178 \pm 0.082\%$ by the double spike approach in this study. These results are in good agreement with the reference values of CAGS-Fe within uncertainties.

Figure 2 shows the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values of NIM-RM 2712 relative to IRMM-014 measured in a period of 15 months. The mean Fe isotopic composition in NIM-RM 2712 was $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.464 \pm 0.066\%$ ($N = 66$, 2SD) and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 0.698 \pm 0.090\%$ ($N = 66$, 2SD) obtained by the SSB method; and $\delta^{56}\text{Fe}_{\text{IRMM-014}} = 0.458 \pm 0.058\%$ ($N = 20$, 2SD) and $\delta^{57}\text{Fe}_{\text{IRMM-014}} = 0.687 \pm 0.086\%$ ($N = 20$, 2SD) determined using the double spike approach. The comparison on the Fe isotopic compositions obtained using the SSB method and the double spike approach are displayed in Fig. 3, together with the respective kinetic and equilibrium fractionation lines. The values were in good agreement, which ensured the accuracy and reliability of the δ -values obtained by this study. This also suggested that the isotopic

Fig. 2 The $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (a) and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ (b) of NIM-RM 2712 measured during a period of 15 months. Instrumental mass bias was corrected via SSB method and the double spike (DS) approach, respectively. The error bars represented the measurement uncertainty for a single δ measurement. The solid lines represented the certified values of NIM-RM 2712 with the dash lines were their expanded uncertainty of $k=2$.

Fig. 3 Comparison of the Fe isotopic compositions of NIM-RM 2712 as obtained by the SSB and double spike (DS) approaches. TFL referred to terrestrial fractionation line. The error bars represented the standard deviation of each measurement method.

variation of the new Fe isotopic reference material follows the rules of mass-dependent fractionation.

Homogeneity of NIM-RM 2712. To assess the homogeneity of the Fe isotopic composition in the new reference material, fifteen bottles of NIM-RM 2712 were randomly selected. Three subsamples from each bottle were measured independently by MC-ICPMS. The whole homogeneity test was performed under strictly the same instrumental conditions within the same session. The mass bias was corrected using SSB method. A one-way analysis of variance (ANOVA) approach was applied for the homogeneity assessment of all the samples in accordance with the ISO Guide 35: 2017.³² The results were acquired using ExcelTM and summarized in Table 1. The F -testing value indicated that the between-unit terms was insignificant at the 95% level of

confidence ($F < F_{\text{critical}}(V_{\text{between}}, V_{\text{within}})$), demonstrating sufficient homogeneity of Fe isotopic composition in NIM-RM 2712.

Stability of NIM-RM 2712. The long-term stability of NIM-RM 2712 was evaluated relative to IRMM-014 over a period of 15 months. In the meantime, the $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ values were determined for five times, and each time three bottles were selected for analysis (Fig. S1). The stability was assessed based on Student's t test. As shown in Table 2, the Fe isotopic composition in NIM-RM 2712 displayed no statistically significant instability in the elapsed time of 15 months. In addition, to detect potential contaminants from the containers during storage, the ampoule bottles for packaging the Fe isotopic reference materials were filled with 2% HNO_3 and preserved at the storage condition for 4 years. The mass fractions of Fe, Cr and Ni in the soaking solution were determined as $< 1 \text{ ng g}^{-1}$, 0.05 ng g^{-1} ($^{54}\text{Cr}/^{54}\text{Fe} = 2 \times 10^{-7}$) and $< 0.01 \text{ ng g}^{-1}$ ($^{58}\text{Ni}/^{58}\text{Fe} < 2 \times 10^{-5}$) by HR-ICPMS. These dissolved elements would cause negligible influence to the property values of NIM-RM 2712. To ensure its quality, the stability of Fe isotopic composition in NIM-RM 2712 will be continually monitored by our laboratory within the lifetime of this reference material.

Uncertainty of the Fe isotopic composition in NIM-RM 2712. The combined uncertainties of the $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ values were estimated to be 0.010‰ and 0.017‰ for SSB method; while those obtained using the double spike approach were 0.010‰ and 0.021‰, given the characterization uncertainties of $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ and $\delta^{57}\text{Fe}_{\text{IRMM-014}}$ values in NIM-RM 2712 as 0.013‰ and 0.027‰, respectively. The uncertainties associated with between-unit variability and long-term stability were evaluated as 0.014‰ and 0.009‰ for $\delta^{56}\text{Fe}_{\text{IRMM-014}}$, and 0.013‰ and 0.011‰ for $\delta^{57}\text{Fe}_{\text{IRMM-014}}$, respectively. Thus, the property values of NIM-

Table 1. ANOVA analysis results for homogeneity test of NIM-RM 2712

NIM-RM 2712	n^a	m	M_{between}	M_{within}	ν_{between}	ν_{within}	F	$F_{0.05}(14, 30)$
$\delta^{56}\text{Fe}$	3	15	2.08×10^{-3}	1.49×10^{-3}	14	30	1.39	2.04
$\delta^{57}\text{Fe}$	3	15	3.35×10^{-3}	2.87×10^{-3}	14	30	1.17	2.04

^a n denotes the number of subsamples measured for each unit; m denotes the number of units; ν_{between} denotes the between-unit degrees of freedom; ν_{within} denotes the within-unit degrees of freedom.

Table 2. Assessment of long-term stability for NIM-RM 2712

NIM-RM 2712	b_0^a	b_1	$s(b_1)$	$t_{0.95, n-2}$	Conclusion
$\delta^{56}\text{Fe}$	0.467	-9.43×10^{-6}	2.03×10^{-5}	3.18	$ b_1 < t_{0.95, n-2} \times s(b_1)$
$\delta^{57}\text{Fe}$	0.703	6.51×10^{-6}	2.31×10^{-5}	3.18	$ b_1 < t_{0.95, n-2} \times s(b_1)$

^a b_0 and b_1 donate the interception and slope of the linear regression curve for the stability test data, respectively; $s(b_1)$ donates the standard deviation of b_1 .

RM2712 that calculated as the unweighted mean of the measurement results obtained using SSB and double spike approaches were as follows ($U, k=2$): $\delta^{56}\text{Fe} = 0.461 \pm 0.043\%$ and $\delta^{57}\text{Fe} = 0.693 \pm 0.064\%$.

CONCLUSION

In this study, we have performed the development and characterization of a new Fe isotopic reference material NIM-RM 2712. By the advantages of ultra-high purity, satisfactory homogeneity and stability, comprehensive uncertainty statement, as well as δ -values within natural variations and obey the mass-dependent fractionation law, this new Fe isotopic reference material was suitable for analytical validation and quality control for Fe isotopic measurements. Moreover, as a national metrology institute, NIM owned the capabilities of reproducing, storage and distribution of large quantities of reference materials, which could ensure the long-term supply of this reference material. Given that the previously used IRMM-014 is no longer available, it is also suggested that NIM-RM 2712 be used as a new isotopic reference material for precise cross-laboratory calibration of Fe isotope data in future studies. This reference material is commercially available through the National Sharing Platform for Reference Materials of China.

ASSOCIATED CONTENT

The supporting information (Tables S1-S2 and Fig. S1) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION



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Notes

The authors declare no competing financial interest.

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REFERENCES

1. K. P. Jochum and S. M. Brueckner, *Geostand. Geoanal. Res.*, 2008, **32**, 405-542. <https://doi.org/10.1111/j.1751-908X.2008.00916.x>
2. J. Vogl and W. Pritzkow, *J. Anal. At. Spectrom.*, 2010, **25**, 923-932. <https://doi.org/10.1039/c000509f>
3. F. -Z. Teng, N. Dauphas, and J. M. Watkins, *Rev. Mineral. Geochem.*, 2017, **82**, 1-26. <https://doi.org/10.2138/rmg.2017.82.1>

4. C. S. J. W. Briche, A. Held, M. Berglund, P. D. Bièvre, and P. D. P. Taylor, *Anal. Chim. Acta.*, 2002, **460**, 41-47. [https://doi.org/10.1016/S0003-2670\(02\)00145-9](https://doi.org/10.1016/S0003-2670(02)00145-9)
5. T. Ren, J. Wang, H. Lu, T. Zhou, and Y. Zhou, *Geostand. Geoanal. Res.*, 2016, **40**, 227-238. <https://doi.org/10.1111/j.1751-908X.2015.00357.x>
6. P. S. Song, J. Wang, T. X. Ren, T. Zhou, S. Wang, and Y. J. Zhou, *Geostand. Geoanal. Res.*, 2020, **45**, 369-381. <https://doi.org/10.1111/jggr.12369>
7. L. Yang, B. Methven, Z. Mester, and J. Meija, *J. Anal. At. Spectrom.*, 2023, **38**, 2080-2086. <https://doi.org/10.1039/d3ja00212h>
8. J. Vogl, M. Rosner, and W. Pritzkow, *Anal. Bioanal. Chem.*, 2012, **405**, 2763-2770. <https://doi.org/10.1007/s00216-012-6605-3>
9. W. A. Brand, T. B. Coplen, J. Vogl, M. Rosner, and T. Prohaska, *Pure Appl. Chem.*, 2014, **86**, 425-467. <https://doi.org/10.1515/pac-2013-1023>
10. T. B. Coplen, *Rapid Commun. Mass Spectrom.*, 2011, **25**, 2538-2560. <https://doi.org/10.1002/rcm.5129>
11. P. Zuo, Y. Huang, J. Bi, W. Wang, W. Li, D. Lu, Q. Zhang, Q. Liu, and G. Jiang, *TrAC Trends in Analytical Chemistry*, 2023, **158**, 116866-116882. <https://doi.org/10.1016/j.trac.2022.116866>
12. J. Irgeher and T. Prohaska, *Anal Bioanal Chem*, 2016, **408**, 369-385. <https://doi.org/10.1007/s00216-015-9025-3>
13. F. Albarède, P. Télouk, and V. Balter, *Rev. Mineral. Ceochem.*, 2017, **82**, 851-885. <https://doi.org/10.2138/rmg.2017.82.20>
14. F. Vanhaecke and M. Costas-Rodríguez, *View*, 2020, **2**, 20200094. <https://doi.org/10.1002/viw.20200094>
15. H. Wen, J. Carignan, C. Cloquet, X. Zhu, and Y. Zhang, *J. Anal. At. Spectrom.*, 2010, **25**, 716-721. <https://doi.org/10.1039/b921060a>
16. Q. Hou, L. Zhou, S. Gao, T. Zhang, L. Feng, and L. Yang, *J. Anal. At. Spectrom.*, 2016, **31**, 280-287. <https://doi.org/10.1039/c4ja00488d>
17. C. González de Vega, S. M. Chernonozhkin, R. Grigoryan, M. Costas-Rodríguez, and F. Vanhaecke, *J. Anal. At. Spectrom.*, 2020, **35**, 2517-2529. <https://doi.org/10.1039/d0ja00225a>
18. N. Dauphas, S. G. John, and O. Rouxel, *Rev. Mineral. Ceochem.*, 2017, **82**, 415-510. <https://doi.org/10.2138/rmg.2017.82.11>
19. J. N. Fitzsimmons and T. M. Conway, *Ann. Rev. Mar. Sci.*, 2023, **15**, 383-406. <https://doi.org/10.1146/annurev-marine-032822103431>
20. Y. Lei, M. Li, Z. Wang, Y. Zhu, Z. Hu, Y. Liu, and X. Chai, *Atom. Spectrosc.*, 2022, **43**, 214-222. <https://doi.org/10.46770/as.2022.111>
21. X. Li, Y. S. He, S. Ke, A. -Y. Sun, Y. -C. Zhang, Y. Wang, R. -Y. Yang, and P. -J. Wang, *Atom. Spectrosc.*, 2022, **43**, 164-173. <https://doi.org/10.46770/as.2022.062>
22. N. E. Holden, T. B. Coplen, J. K. Böhlke, L. V. Tarbox, J. Benefield, J. R. de Laeter, P. G. Mahaffy, G. O'Connor, E. Roth, D. H. Tepper, T. Walczyk, M. E. Wieser, and S. Yoneda, *Pure Appl. Chem.*, 2018, **90**, 1833-2092. <https://doi.org/10.1515/pac-2015-0703>
23. Y. He, S. Ke, F. Z. Teng, T. Wang, H. Wu, Y. Lu, and S. Li, *Geostand. Geoanal. Res.*, 2015, **39**, 341-356. <https://doi.org/10.1111/j.1751-908X.2014.00304.x>
24. R. M. Kettler, Y. He, S. Ke, F.-Z. Teng, and D. B. Loope, *Chem. Geol.*, 2022, **612**, 121146-121187. <https://doi.org/10.1016/j.chemgeo.2022.121146>
25. J. Wang, D.-M. Tang, B.-X. Su, Q.-H. Yuan, W.-J. Li, B.-Y. Gao, K.-Y. Chen, Z.-A. Bao, and Y. Zhao, *J. Anal. At. Spectrom.*, 2022, **37**, 1869-1875. <https://doi.org/10.1039/d2ja00084a>
26. J. Li, S. H. Tang, X. K. Zhu, Z. H. Li, S. Z. Li, B. Yan, Y. Wang, J. Sun, Y. Shi, A. Dong, N. S. Belshaw, X. Zhang, S. A. Liu, J. H. Liu, D. Wang, S. Y. Jiang, K. Hou, and A. S. Cohen, *Geostand. Geoanal. Res.*, 2018, **43**, 163-175. <https://doi.org/10.1111/jggr.12241>
27. J. Zhang, T. Zhou, Y. Tang, Y. Cui, and J. Li, *J. Anal. At. Spectrom.*, 2016, **31**, 2182-2191. <https://doi.org/10.1039/c6ja00172f>
28. J. R. D. LAETER, J. K. BÖHLKE, P. D. BIÈVRE, H. HIDAKA, H. S. PEISER, K. J. R. ROSMAN, and P. D. P. TAYLOR, *Pure Appl. Chem.*, 2003, **75**, 683-800. <https://doi.org/10.1351/pac200375060683>
29. J. F. Rudge, B. C. Reynolds, and B. Bourdon, *Chem. Geol.*, 2009, **265**, 420-431. <https://doi.org/10.1016/j.chemgeo.2009.05.010>
30. L. Yang, S. Tong, L. Zhou, Z. Hu, Z. Mester, and J. Meija, *J. Anal. At. Spectrom.*, 2018, **33**, 1849-1861. <https://doi.org/10.1039/c8ja00210j>
31. L. Feng, Goldschmidt 2023 Abstract. <https://doi.org/10.7185/gold2023.18858>
32. ISO Guide 35, 2017: Reference materials - Guidance for characterization and assessment of homogeneity and stability. International Organization for Standardization (Geneva), 20-42.
33. ISO Guide 98-3, 2008: Evaluation of measurement data - Guide to the expression of uncertainty in measurement. *JCGM 100:2008*. International Organization for Standardization (Geneva), 18-23.
34. J. Vogl, M. Rosner, S. A. Kasemann, R. Kraft, A. Meixner, J. Noordmann, S. Rabb, O. Rienitz, J. A. Schuessler, M. Tatzel, and R. D. Vocke, *Geostand. Geoanal. Res.*, 2020, **44**, 439-457. <https://doi.org/10.1111/jggr.12327>
35. C. Zhu, W. Lu, Y. He, S. Ke, H. Wu, and L. Zhang, *Acta Geochimica*, 2018, **37**, 691-700. <https://doi.org/10.1007/s11631-018-0284-5>