Check for updates

View Article Online
View Journal

# JAAS

Journal of Analytical Atomic Spectrometry

## Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: K. Yang, H. Zhang, J. Zhou, X. Wei, S. Zhou, Y. Cheng, Q. Ying, X. Gu, Q. Xia and J. Liu, *J. Anal. At. Spectrom.*, 2025, DOI: 10.1039/D5JA00225G.

Volume 32
Number 1
January 2017
Pages 1-202

JAAS
Journal of Analytical Atomic Spectrometry
rsc.li/jaas

ISSN 0267-9577

ROYAL SOCIETY OF CHEMISTRY

PAPER
José-Luis Todolí *et al.*
Analysis of whole blood by ICP-MS equipped with a high temperature total sample consumption system

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/jaas

View Article Online
DOI: 10.1039/D5JA00225G

# High-precision Fe isotope analysis for low contents by a Nu Sapphire instrument

Kai Yang *, Hongfu Zhang *, Jinjun Zhou, Qiwen Ying, Shenghua Zhou, Yishan Cheng, Xiping Wei, Xiaoyan Gu, Qunke Xia, Jia Liu

Research Center for Earth and Planetary Material Sciences, School of Earth Sciences, Zhejiang University, Hangzhou 310058, China

Abstract: 225 words

Text: 3033 words

Figures: 6

Tables: 2

Supplementary Tables: 2

Submit to Journal of Analytical Atomic Spectrometry

July. 2025

---

*Corresponding author: Kai Yang, Hongfu Zhang

Email: kai.yang@zju.edu.cn, hfzhang@mail.igcas.ac.cn

View Article Online
DOI: 10.1039/D5JA00225G

# Abstract

Iron (Fe) isotopes serve as a powerful tracer for studying planetary evolution, magmatic processes, redox conditions, biological activities, and other key geological processes. However, the application of stable Fe isotopes in low-Fe samples has been significantly constrained by pervasive argon-related isobaric interferences inherent to conventional multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). This study purified rock samples with varying Fe concentrations and precisely measured Fe isotope ratios using the collision cell pathway in the low-resolution mode of the Nu Sapphire instrument. We systematically evaluated the effects of total Fe concentration in solution, Fe signal intensity mismatch between samples and standards, and $HNO_3$ molarity differences on measurement precision and accuracy. For precise Fe isotope ratio measurements using sapphire, strict analytical conditions must be met: (1) matched nitric acid concentrations between sample and bracketing standard (1% deviation induces 0.2‰ Fe isotope offset); (2) consistent Fe signal intensities (5% concentration mismatch introduces 0.05‰ bias); and (3) suppression of matrix interferences to minimize isotopic fractionation. The results demonstrate that the Nu Sapphire can achieve precise measurements with as little as 1 µg of Fe, representing a tenfold improvement relative to conventional instruments. The Fe isotopic data obtained for 13 previously published geological references show good agreement with previous studies. Therefore, the exceptional sensitivity of Nu Sapphire facilitates high-precision Fe isotope ratio measurements for iron-depleted samples, offering broad application potential.

**Keywords:** Iron isotope; high precision; Fe depleted sample; Nu Sapphire instrument

View Article Online
DOI: 10.1039/D5JA00225G

# 1. Introduction

Iron (Fe) is widely utilized in industrial, agricultural, and medical applications, making it an indispensable element for human survival. It has three oxidation states 0, +2, and +3, and four stable isotopes: $^{54}$Fe, $^{56}$Fe, $^{57}$Fe, and $^{58}$Fe.

Iron and its isotopes have become powerful tracers for various processes, such as the formation and evolution of the Earth and other planets, the behavior of magma/melt/fluids in geological processes, redox states, and early life evolution [1–7]. Currently, Fe isotope analysis mainly relies on multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), which uses dry introduction systems, high-resolution modes, and cold plasma techniques to reduce interferences from Ar-plasma [8–11]. The testing is challenging and requires relatively high sample concentrations (usually in the ppm range). With the widespread use of the Sapphire system by Nu Instruments, which is equipped with a collision cell, for the analysis of K, Ca, and other isotopes, it has proven effective in removing intermediate products formed by reactions between the analyte and carrier gas [12,13]. This development is expected to bring similar benefits to Fe isotope ratio measurement.

This study employs Nu Sapphire for the Fe isotopic analysis at ultra-low contents, achieving high analytical precision. This approach offers a feasible method for high-precision Fe isotope ratio analysis of rare samples, such as planetary materials, high-temperature and high-pressure experimental samples, as well as biomedical applications.

# 2. Reference materials

The reference materials used here are JA-1 (andesite, Geological Society of Japan, GSJ), JA-2 (andesite, GSJ), JA-3 (andesite, GSJ), GSR-2 (andesite, National Research Center for Certified Reference Materials, NRCCRM), JB-1b (basalt, GSJ), JB-3 (basalt, GSJ), BHVO-2 (basalt, United States Geological Survey, USGS), BCR-2 (basalt, USGS), GBW07122 (gabbro, National Research Center for Geoanalyses of China, NRCG), GSR-9 (diorite, NRCG), DNC-1 (dolerite, USGS), DR-N (diorite, Centre de Recherches Petrographiques et Geochimiques, CRPG), JR-1 (rhyolite, GSJ). These materials vary greatly in matrix types, ranging from mafic to felsic rocks. Moreover, their Fe isotopic compositions have been previously analyzed in multiple laboratories, making them ideal for evaluating the accuracy of the Nu Sapphire installed at the Research Center for Earth and Planetary Material Sciences (RCEPMS), Zhejiang

DOI: 10.1039/D5JA00225G

University (ZJU). To evaluate the long-term reproducibility of the method, we analyzed three pure Fe solution standards (NWU-Fe, IGGCAS-Fe, ZJU-Fe, IRMM014, and JMC-Fe) and two geological reference materials (BCR-2 and BHVO-2) over a period of six months.

## 3. Experimental methods

### 3.1 Dissolution and chemical purification

The column chemistry was conducted in the ultra-clean Lab at the RCEPMS, ZJU. The geological reference powder was dissolved using ultrapure concentrated HF and HCl (1:1 vol./vol.) in 15-mL screw-top PTFE square digestion vials and heated in an oven at 180 °C for three days. After evaporation on a hotplate, the samples were refluxed with concentrated HCl and $HNO_3$ (3:1 vol./vol.) at 120 °C overnight. The samples were then evaporated and refluxed twice with HCl to ensure complete evaporation of residual $HNO_3$ and HF. We conducted Fe chemical separation on BHVO-2 and BCR-2 sample solutions with varying volumes. The Fe contents were 1 µg, 3 µg, 6 µg, 20 µg, and 100 µg for both BHVO-2 and BCR-2.

The solutions were purified using 2 mL of Bio-Rad AG1-X8 (200–400 mesh) packed in 10 mL Bio-Spin© chromatography columns. After cleaning the resin with alternating cycles of 6 N HCl, 3 N $HNO_3$, 0.5 N HCl, and MQ water, the samples were loaded onto the columns in 1 mL of 6 mol/L HCl. Matrix elements were eluted with 32 mL of 6 mol/L HCl acid. The Fe fraction was collected with 10 mL 0.5 mol/L HCl (Fig. 1).

Sub-boiling distilled acids and purity Milli-Q® water (18.2 MΩ・cm resistivity) were used to minimize the procedural blank, which was <5 ng for Fe, and is negligible (<0.001%) compared to the amounts of Fe present in the samples. The whole procedural Fe blank is <10 ng throughout dissolution, chemical purification, and analysis, which is negligible relative to the 1-100 µg of Fe processed. In addition, the chemical purification developed in this study ensured that the average recovery of Fe is better than 99 % (Fig. 1).

The separation of Fe element is essential for high-precision Fe isotopes analysis. Although multiple methods currently exist for isolating Fe from natural samples, most require either multi-column procedures or consume large volumes of acid and prolonged processing times [13–15]. In this study, by optimizing reagent selection, resin type, and column dimensions, we achieved effective separation of ultra-trace Fe from the sample matrix while significantly reducing procedural blanks. Notably, our method requires only a single, short-duration column pass to obtain solutions suitable for Fe isotopic analysis.

View Article Online
DOI: 10.1039/D5JA00225G

### 3.2 Iron isotopic measurements on a Nu Sapphire instrument

Iron isotopic ratios were measured on a Nu Sapphire instrument at ZJU. The collision reaction cell path (low energy) was used to resolve polyatomic interferences of $^{40}Ar^{16}O^{1}H$, $^{40}Ar^{16}O$, and $^{40}Ar^{14}N$ on $^{57}Fe$, $^{56}Fe$, and $^{54}Fe$, respectively. Collision cell technology has been well known for its effectiveness in eliminating Ar-based molecular interferences. However, traditional quadrupole-based collision cells may introduce complications in isotopic measurement systems due to multipole mass discrimination effects and inherent instrumental isotopic fractionation characteristics. The Nu Sapphire instrument employs a radio frequency hexapole collision cell, which features a wider mass transmission window compared to quadrupole systems, significantly reducing mass discrimination effects. Within the gas-filled collision cell, ions undergo collisional thermalization through interactions with He buffer gas, substantially enhancing transmission efficiency through the hexapole ion guide. Simultaneously, charge-exchange reactions with $H_2$ gas reduce $Ar^+$ signal intensity by >9 orders of magnitude, achieving near-complete elimination of all Ar-based interfering species. Through multiple adjustments of the He and $H_2$ flow rate and other parameters, we selected an optimal set of collision cell parameters that maximizes the Fe ion beam intensity while effectively suppressing interferences from $ArO^+$, $ArN^+$, and $ArOH^+$ beams. The detailed parameters are presented in Table 1. Samples and standard solutions were using a cyclonic spray chamber (wet plasma) fitted with a 100 µl/min quartz nebulizer in low energy mode (300 µm source slit), achieving a sensitivity of 80 V/1 ppm. For comparative analysis, we also employed an Airdus 3 desolvating system with standard Ni cones in dry plasma mode, which demonstrated approximately 10-fold higher sensitivity than conventional wet plasma operation. Sample and standard solutions were diluted to 20-200 ppb Fe in 2% $HNO_3$ for analysis. Between each sample and standard analysis, an 80-110 s wash with 2 % $HNO_3$ and 50-70 s transfer time were applied. The instrument settings remained unchanged throughout the sequence, and each sample was measured at least 3 times. The operating parameters are provided in Table 1.

The sample-standard bracketing (SSB) technique was used to correct instrumental isotope fractionation. An in-house Fe solution (GSB04) from the China Iron and Steel Research Institute was used as the bracketing standard for Fe (named ZJU-Fe), and the Fe isotopic compositions of the samples are reported relative to the IRMM014 Fe standard:

$$\delta^{56}\text{Fe}\ (‰) = \left[\frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{ZJU}}} - 1\right] \times 1000 + \delta^{56}\text{Fe}_{\text{ZJU}}$$

View Article Online
DOI: 10.1039/D5JA00225G

where $\delta^{56}Fe_{ZJU}$ describes the Fe isotopic difference between the IRMM014 and ZJU-Fe standards. The $\delta^{56}Fe$ value of ZJU-Fe compared to IRMM014 is $\delta^{56}Fe_{ZJU} = +0.696 \pm 0.023‰$ (n=70), and the error represents two standard deviations (2SD) uncertainties.

## 4. Results and discussion

This study systematically investigated chemical purification and isotopic ratio measurements of ultra-low content (1-100 μg) Fe using the Nu Sapphire MC-ICP-MS system installed in ZJU. The obtained Fe isotopic data were subject to superimposed interferences from multiple factors, necessitating precise quantification of each interference source to ensure accuracy. We comprehensively evaluated critical parameters affecting measurement fidelity, including acid concentration mismatch between samples and standards, Fe concentration mismatch effects, matrix element interferences, and long-term instrumental stability. Specific tolerance ranges were established for these parameters to guarantee reproducible high-precision Fe isotopic data. The systematic methodology provides essential guidelines for reliable Fe isotope ratio measurements in MC-ICP-MS applications.

### 4.1 Effect of acid molarity mismatching

The impact of $HNO_3$ concentration mismatch on $\delta^{56}Fe$ accuracy variations in the molarity of $HNO_3$ in analyzed solutions has been shown to influence mass bias in Fe isotope ratio measurements [9,10,13]. To assess this effect, a pure ZJU-Fe solution was dissolved in $HNO_3$ at concentrations ranging from 0.5% to 5% and analyzed against the same solution prepared in 2% $HNO_3$ (Fig. 2). The results reveal a strong linear correlation ($R^2 = 0.99$) between the $\delta^{56}Fe$ values and the $HNO_3$ concentration mismatch. The derived relationship for the pure standard is $\delta^{56}Fe \approx 0.44 - 19.94 \times Fe_{sample}/Fe_{2\%HNO3}$. This indicates that a 1% discrepancy in $HNO_3$ concentration introduces an isotopic bias of ≈ 0.2‰, representing a significant limitation in Fe isotope ratio measurements using the Nu Sapphire instrument. To ensure measurement accuracy, it is therefore critical to prepare all samples and standards in solutions of identical acid concentrations. In this study, all samples and standards were diluted using the same batch of 2% $HNO_3$ to minimize this source of error.

### 4.2 Effect of concentration mismatching between sample and standard

To evaluate the influence of signal intensity mismatch on Fe isotope ratio measurements, a series of experiments were conducted using a ZJU-Fe bracketing standard maintained at a constant concentration of 200 ppb Fe, while the ZJU-Fe as the samples were varied from 30% lower to 110% higher concentrations to measurement (Fig. 3). There is a clear linear correlation ($R^2 = 0.96$) between the $\delta^{56}$Fe values and the intensity mismatch. For the pure Fe solution, the measured $\delta^{56}$Fe offset follows a linear relationship of $\delta^{56}\text{Fe} \approx -0.98 + 0.96 \times \text{Fe}_{\text{sample}}/\text{Fe}_{\text{standard}}$. This indicates that a 5% deviation in signal intensity introduces an isotopic bias of ≈ 0.05‰ fractionation, highlighting a critical limitation in high-precision Fe isotope ratio measurement. To mitigate this effect and ensure data accuracy, it is essential to maintain sample and standard intensities within 5% of each other during analysis on the Nu Sapphire instrument. In this study, all measurements adhered strictly to this protocol.

## 4.3 Matrix elements effect

The SSB method operates under the fundamental assumption that both sample and standard solutions are chemically pure, rendering it particularly vulnerable to matrix effects. Previous studies have demonstrated that these matrix effects originate from the residual cationic impurities in sample solutions, and organic compounds leached from chromatographic resins [3,8,9,13,16]. Both matrix effects and isobaric interferences can induce significant mass bias in Fe isotopic measurements. Notably, certain matrix elements, while not contributing to isobaric interference, can still substantially alter instrumental mass bias behavior for Fe isotopes. Most major and trace elements show significant effects on Fe isotopic ratios when their concentrations exceed certain thresholds. Specifically, accurate Fe isotoic data can be obtained when the concentration ratios of Al, As, and K to Fe are < 0.1; Cd, Cu, Na, and Ni to Fe are < 0.5; and Ca, Mg, Mn, Pb, Sb, S, Ti, V to Fe are < 1; and Co, and Zn to Fe are < 2 [10,13]. The column chromatography procedure used in this study efficiently purifies Fe, reducing residual matrix element concentrations in the final solution to levels significantly below the established threshold ratios (Fig. 1). Notably, chromium concentrations in the Fe-purified solutions were consistently below the method detection limit (Fig. 1), confirming effective separation of this isobaric interferent. This minimizes spectral and non-spectral interferences, ensuring high-precision Fe isotope ratios by MC-ICP-MS measurements.

## 4.4 Consistency and long-term reproducibility

The analytical accuracy and long-term reproducibility of our protocol were evaluated by repeated measurements of in-house standards and self-bracketing pure Fe standards. We measured two in-house JMC-Fe and ZJU-Fe standards, which yielded $\delta^{56}$Fe values of 0.404 ±

View Article Online
DOI: 10.1039/D5JA00225G

0.029‰ (2SD, n=29) for JMC-Fe, and 0.696 ± 0.023‰ (2SD, n=70) for ZJU-Fe, consistent with those measured on a same instrument at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS, Fig. 4 a-b)[16]. In addition, two international rock standards (BHVO-2 and BCR-2) were processed and analyzed. We obtained an average $\delta^{56}$Fe of 0.097 ± 0.024‰ (2SD, n = 59) for BCR-2, and 0.121 ± 0.023‰ (2SD, n = 62) for BHVO-2 (Fig. 4 c-d), which are consistent with the previous studies[10,13]. Furthermore, five pure Fe solutions were taken to test self-bracketing that had expected $\delta^{56}$Fe values of 0 ‰ (Fig. 4e) during more than ten sessions over six months. Our results reveal a long-term reproducibility of 0.025‰ (2SD).

To comprehensively demonstrate the consistency and reproducibility of our method, we additionally incorporated Fe isotopic data obtained from an identical instrument model (Nu Sapphire) at the IGGCAS for comparison (Fig. 4a, c-d). The results indicate that the Fe isotopic ratios of the calibration solution JMC-Fe and rock reference materials BHVO-2 and BCR-2 exhibit excellent agreement with previously reported values. Moreover, our instrument demonstrates remarkable stability across multiple batches over extended periods, achieving significantly smaller analytical uncertainties.

### 4.5 Effect of Fe content on consistency

Two rock standards, BHVO-2 and BCR-2, have been analyzed using steps with Fe contents from 1 to 100 μg, and tests have been performed to evaluate the accuracy of the measurements. The $\delta^{56}$Fe values from different Fe abundances for BHVO-2 and BCR-2 are well consistent with literature data (Fig. 5) [7,9,11,13,15,17,18]. Therefore, ultra-low contents of Fe can be measured for the Fe isotope ratios with the Nu Sapphire instrument. It is a remarkable gain in comparison to previous methods that needed several micrograms of Fe to yield similar qualitative data, which means that high-precision Fe isotope ratio measurements for rare samples or samples with minimal Fe content are entirely feasible.

Recent studies have successfully integrated machine learning with experimental isotopic measurements to predict the heavy metal isotopic composition (e.g., Pb) of microscale samples (e.g., industrial smoke particles), thereby facilitating health risk assessments and pollution control [19]. In this study, the precise measurement of Fe isotopic ratios in ultra-trace samples may similarly support the analysis of aerosol-like samples and could potentially serve as a novel indicator for environmental evaluation.

View Article Online
DOI: 10.1039/D5JA00225G

### 4.6 Iron isotopic compositions of reference materials

To evaluate the reliability of our analytical protocol, from chemical separation to mass spectrometric measurement, we analyzed 13 widely used geological reference materials (from mafic to felsic in lithology) with well-documented Fe isotopic compositions in previous studies. The results confirm that our method not only offers a straightforward and robust approach but also delivers high-precision Fe isotopic data, even at ultra-trace concentrations (Fig. 5). The various materials measured in this study cover the $\delta^{56}$Fe values range from 0.041 to 0.178‰ (Fig. 6, Table S1), with rhyolite being the heaviest ($\delta^{56}Fe_{JR-1}$ = 0.178 ± 0.03‰, 2SD, n = 3) and andesite being the lightest ($\delta^{56}Fe_{JA-1}$ = 0.041 ± 0.02‰, 2SD, n = 4). Specifically, the andesite samples JA-1, JA-2, JA-3, and GSR-2 yielded $\delta^{56}$Fe values of +0.04 ± 0.02‰, +0.109 ± 0.03‰, +0.095 ± 0.026‰, and +0.081 ± 0.002‰, respectively. For the basalts JB-1b, JB-3, BHVO-2, and BCR-2, the $\delta^{56}$Fe values were +0.089 ± 0.008‰, +0.063 ± 0.022‰, +0.122 ± 0.02‰, and +0.097 ± 0.025‰, respectively. The diorite samples GSR-9, DNC-1, and DR-N displayed $\delta^{56}$Fe values of +0.105 ± 0.022‰, +0.065 ± 0.027‰, and +0.091 ± 0.026‰, respectively, while the rhyolite JR-1 showed a value of +0.178 ± 0.029‰. These results are in good agreement with the previous studies acquired in pseudo-high resolution mode on a Neptune, Neptune Plus, Nu Plasma II, or Nu Plasma 1700 [8,9,11,13,16,20–28]. Fig. 6 illustrates the sensitivity performance of the Nu Sapphire instrument's low-energy collision cell path for Fe isotopic measurements, in comparison with conventional single-focusing collision cell MC-ICP-MS and double-focusing MC-ICP-MS without a collision cell. Compared to all previous methods, the Nu Sapphire instrument exhibits superior reproducibility in both wet and dry plasma modes (Fig. 6). Even when operating solely in wet plasma mode, its sensitivity significantly surpasses that of traditional MC-ICP-MS in high-resolution/dry plasma mode.

Alongside geological reference materials, we characterized the ZJU-Fe standard solution as an additional quality control. Seventy analyses over 6 months yielded a reproducible $\delta^{56}$Fe value of 0.696 ± 0.023‰ (2SD), demonstrating measurement stability. These results demonstrate that our optimized Fe isotope analytical protocol, from column purification to high-precision measurement using a Sapphire MC-ICP-MS at ZJU, provides reliable and reproducible data for geological samples spanning a wide range of Fe concentrations and lithologic types.

View Article Online
DOI: 10.1039/D5JA00225G

## 5. Conclusion

The chromatographic column separation method developed in this study combines high efficiency with operational simplicity for Fe purification, while the Nu Sapphire instrument delivers high-precision Fe isotopic data ($\delta^{56}$Fe reproducibility ±0.03‰, 2SD). Compared to the conventional high-resolution modes employed on Neptune series instruments, the Nu Sapphire's low-resolution mode with collision cell technology improves analytical efficiency for Fe isotope ratio measurements. This configuration effectively suppresses polyatomic interferences (e.g., $^{40}Ar^{16}O^{+}$) while maintaining flat-topped peaks critical for high-accuracy measurements. Capitalizing on the superior sensitivity of the Nu Sapphire (10× signal enhancement vs. conventional instruments), we achieved high-precision Fe isotope ratio measurements at ultralow concentrations using wet plasma conditions. Method validation analyzed BCR-2 and BHVO-2 reference materials with five different Fe concentration tiers (1–100 μg), with BCR-2 processed replicate full-process analyses for reproducibility. Results demonstrate that our method reliably achieves high-purity extraction and accurate Fe isotopic determination for samples containing >1 μg Fe. This optimized approach is particularly valuable for analyzing rare geological materials (e.g., Lunar basalts, Martian meteorites, or other extraterrestrial samples) with limited sample availability, and depleted Fe materials (e.g., feldspars, carbonates) where traditional methods face sensitivity limitations.

Although the geological reference materials analyzed in this study did not include organic-rich biological or sedimentary samples, the distinct elution profiles observed for each element demonstrate well-resolved purification intervals. This suggests the potential applicability of our method to such complex matrices, though further experimental validation remains necessary. Precision in situ isotopic analysis has emerged as a pivotal focus in modern geochemical investigations. While laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) has been applied to Fe isotope ratio measurements, the analytical accuracy remains significantly compromised by mineral-scale elemental heterogeneity and matrix-induced interferences. Here we present an optimized protocol for high-precision Fe isotope analysis of ultra-low abundance samples, achieving robust microanalytical characterization of geological materials. This advancement not only provides a novel approach for spatially resolved isotopic analysis but also establishes a verification benchmark for evaluating and enhancing the accuracy of LA-based in situ techniques. Our methodological breakthrough carries fundamental implications for advancing microanalytical capabilities in isotope geochemistry, serving as a crucial reference for future high-resolution isotopic studies.

## Author contributions

The study was conceptualized by K. Yang., and H. F. Zhang. Column procedures were performed by K. Yang., and Y. S. Cheng. Data collection and analysis were performed by K. Yang., J. J Zhou., and X. P. Wei. All authors contributed to writing and revising the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This study was supported by funding from the "Double First-Class" Academic Masters Gathering Initiative 2025 (No. 107400*1942225R2/001@916295). We are grateful to Yongsheng He for supporting Fe Solutions.

## References:

1 X. K. Zhu, Y. Guo, R. K. O'Nions, E. D. Young, R. D. Ash. 2001.
2 K. A. Kelley, E. Cottrell. Science, 2009, 325(5940): 605-607.
3 N. Dauphas, P. R. Craddock, P. D. Asimow, V. C. Bennett, A. P. Nutman, D. Ohnenstetter. Earth and Planetary Science Letters, 2009, 288(1): 255-267.
4 B. Debret, M. A. Millet, M. L. Pons, P. Bouilhol, E. Inglis, H. Williams. Geology, 2016, 44(3): 215-218.
5 B. Debret, P. Bouilhol, M. L. Pons, H. Williams. Journal of Petrology, 2018, 59(6): 1145-1166.
6 B. Debret, C. J. Garrido, M. L. Pons, P. Bouilhol, E. Inglis, V. López Sánchez-Vizcaíno, H. Williams. Geochimica et Cosmochimica Acta, 2021, 296: 210-225.
7 B. Debret, C. Caurant, B. Ménez, V. Busigny, F. Moynier. Earth and Planetary Science Letters, 2024, 642: 118855.
8 R. Schoenberg, F. V. Blanckenburg. Earth and Planetary Science Letters, 2006, 252(3-4): 342-359.
9 Y. He, S. Ke, F. Teng, T. Wang, H. Wu, Y. Lu, S. Li. Geostandards and Geoanalytical Research, 2015, 39(3): 341-356.
10 K. Chen, Z. Bao, H. Yuan, N. Lv. Journal of Analytical Atomic Spectrometry, 2022, 37(2): 249-263.
11 Y. Feng, W. Zhang, Z. Hu, T. Luo, M. Li, Y. Liu, H. Liu, Q. Li. Journal of Analytical Atomic Spectrometry, 2022, 37(3): 551-562.

12 F. Moynier, Y. Hu, K. Wang, Y. Zhao, Y. Gérard, Z. Deng, J. Moureau, W. Li, J. I. Simon, F. Z. Teng. Chemical Geology, 2021, 571: 120144.
13 J. Wang, D. M. Tang, B. X. Su, Q. H. Yuan, W. J. Li, B. Y. Gao, K. Y. Chen, Z. A. Bao, Y. Zhao. Journal of Analytical Atomic Spectrometry, 2022, 37(9): 1869-1875.
14 P. A. Sossi, G. P. Halverson, O. Nebel, S. M. Eggins. Geostandards and Geoanalytical Research, 2015, 39(2): 129-149.
15 P. R. Craddock, N. Dauphas. Geostandards and Geoanalytical Research, 2011, 35(1): 101-123.
16 X. Li, Y. He, S. Ke, A. Sun, Y. Zhang, Y. Wang, R. Yang. Atomic Spectroscopy, 2022, 43(02).
17 P. R. Craddock, J. M. Warren, N. Dauphas. Earth and Planetary Science Letters, 2013, 365: 63-76.
18 B. Debret, H. Beunon, N. Mattielli, M. Andreani, I. Ribeiro da Costa, J. Escartin. Earth and Planetary Science Letters, 2018, 503: 170-180.
19 Y. Ye, N. Aizezi, J. Feng, B. Han, X. Li, Z. Su, L. Li, Y. Liu. Analytical Chemistry, 2025, 97(10): 5554-5562.
20 K. Dideriksen, J. A. Baker, S. L. S. Stipp. Geochimica et Cosmochimica Acta, 2006, 70(1): 118-132.
21 N. Dauphas, O. Rouxel. Mass Spectrometry Reviews, 2006, 25(4): 515-550.
22 S. Weyer, D. A. Ionov. Earth and Planetary Science Letters, 2007, 259(1-2): 119-133.
23 M. A. Millet, J. A. Baker, C. E. Payne. Chemical Geology, 2012, 304-305: 18-25.
24 M. Telus, N. Dauphas, F. Moynier, F. L. H. Tissot, F. Z. Teng, P. I. Nabelek, P. R. Craddock, L. A. Groat. Geochimica et Cosmochimica Acta, 2012, 97: 247-265.
25 S. A. Liu, D. Li, S. Li, F. Z. Teng, S. Ke, Y. He, Y. Lu. Journal of Analytical Atomic Spectrometry, 2014, 29(1): 122-133.
26 M. Oeser, S. Weyer, I. Horn, S. Schuth. Geostandards and Geoanalytical Research, 2014, 38(3): 311-328.
27 Y. He, H. Wu, S. Ke, S. A. Liu, Q. Wang. Geochimica et Cosmochimica Acta, 2017, 203: 89-102.
28 C. Zhu, W. Lu, Y. He, S. Ke, H. Wu, L. Zhang. Acta Geochimica, 2018, 37(5): 691-700.
29 K. Y. Chen, H. L. Yuan, P. Liang, Z. A. Bao, L. Chen. International Journal of Mass Spectrometry, 2017, 421: 196-203.

**Figures caption:**

Figure 1. Elution curves of Fe and matrix elements for mixed element solutions. Subplots (a) to (e) represent loading solutions with Fe contents of 1 μg, 3 μg, 6 μg, 20 μg, and 100 μg, respectively.

Figure 2. Effect of $HNO_3$ concentration mismatch between sample and standard on the $\delta^{56}$Fe ratios. The “sample” here represents the pure ZJU-Fe standard dissolved in acid with various molarities from 0.5 % to 5 % $HNO_3$. The bracketing standard is a pure ZJU-Fe solution in 2% $HNO_3$. Error bars represent 2SD uncertainties.

Figure 3. Iron isotopic variation of ZJU-Fe solutions with changing Fe concentrations compared to the bracketing ZJU-Fe solutions with 200 ppb Fe.

View Article Online
DOI: 10.1039/D5JA00225G

Figure 4. Iron isotopic compositions of geological standards over a six-month measurement period. (a-b) the pure Fe standard JMC-Fe, and ZJU-Fe; (c-d) the rock standard BCR-2, and BHVO-2; (e) long-term measurement of mono-element standard solutions (NWU-Fe, IGGCAS-Fe, ZJU-Fe, IRMM014-Fe, and JMC-Fe).

Figure 5. Iron isotopic compositions of BCR-2 and BHVO-2 with varying Fe contents after the same column procedure. Measurements are accurate lower than 25 ppb.

Figure 6. Composition of Fe isotopic data of geological reference materials in this study and from the literature. The Fe isotopic compositions of reference materials from various lithologies are referred to [3,7-11,13,15,17,18,20-29]

**Tables caption:**

Table 1. Operating parameters of the Nu Sapphire and the Aridus 3 introduction system.

Table 2. Iron isotopic compositions of geological standards over a six-month measurement period.

Table S1. Composition of Fe isotopic data of geological reference materials.

Table S2. Composition of Fe isotopic data of standard solutions and geological reference materials from previous studies and this study.

View Article Online
DOI: 10.1039/D5JA00225G

Figure 1

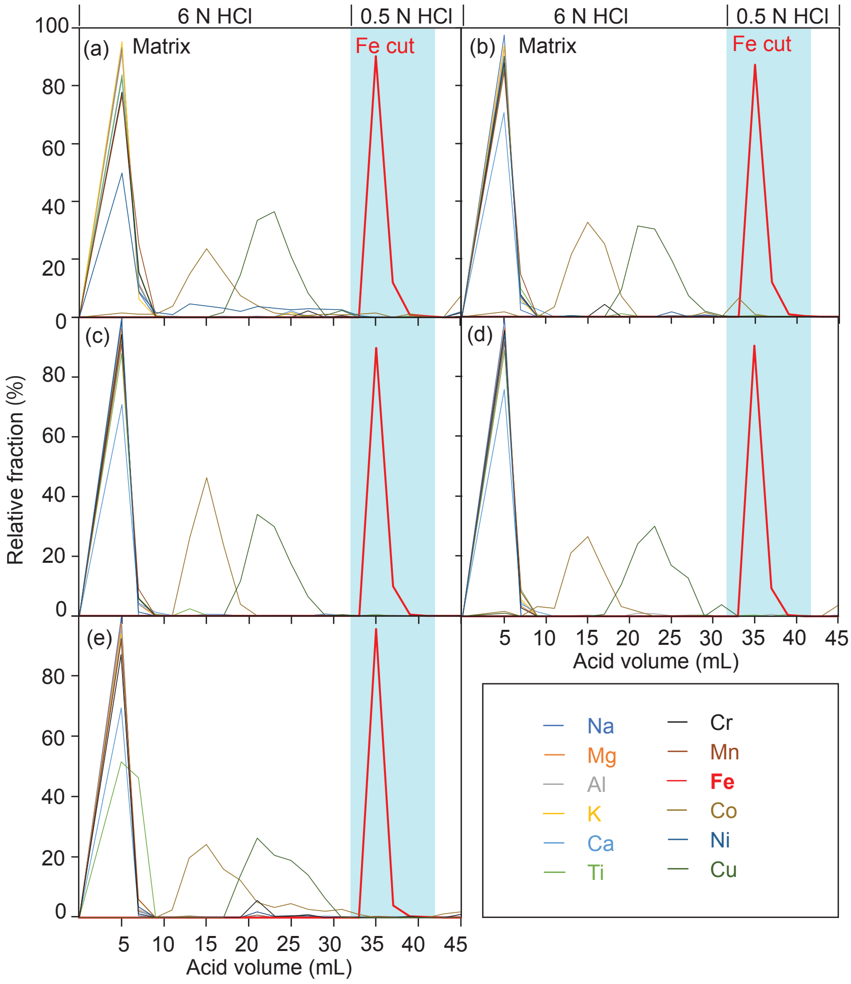


Figure 2

View Article Online
DOI: 10.1039/D5JA00225G

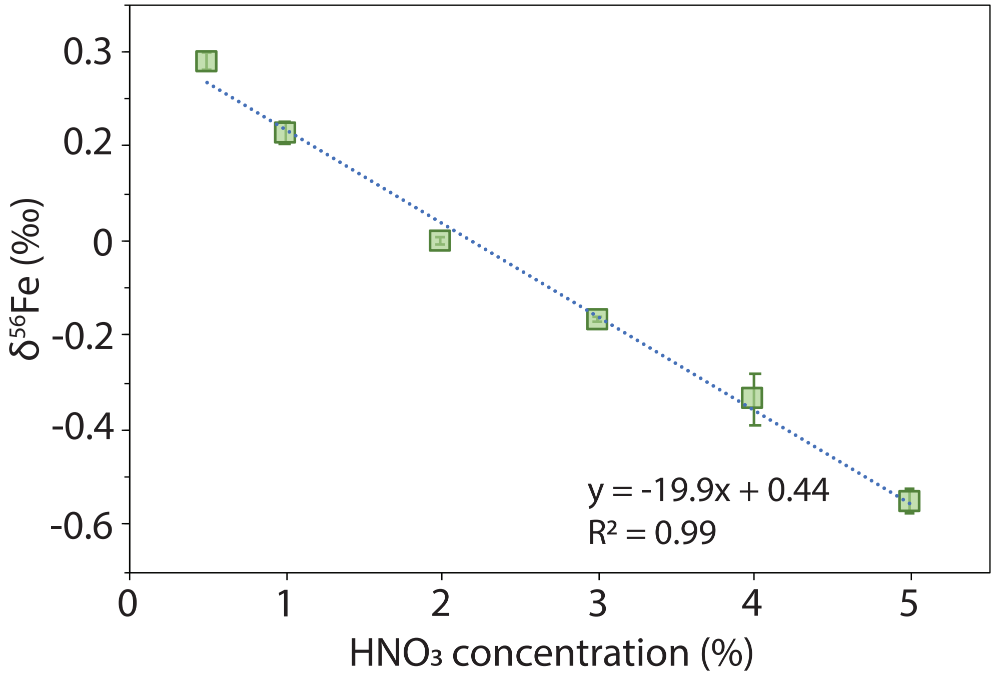
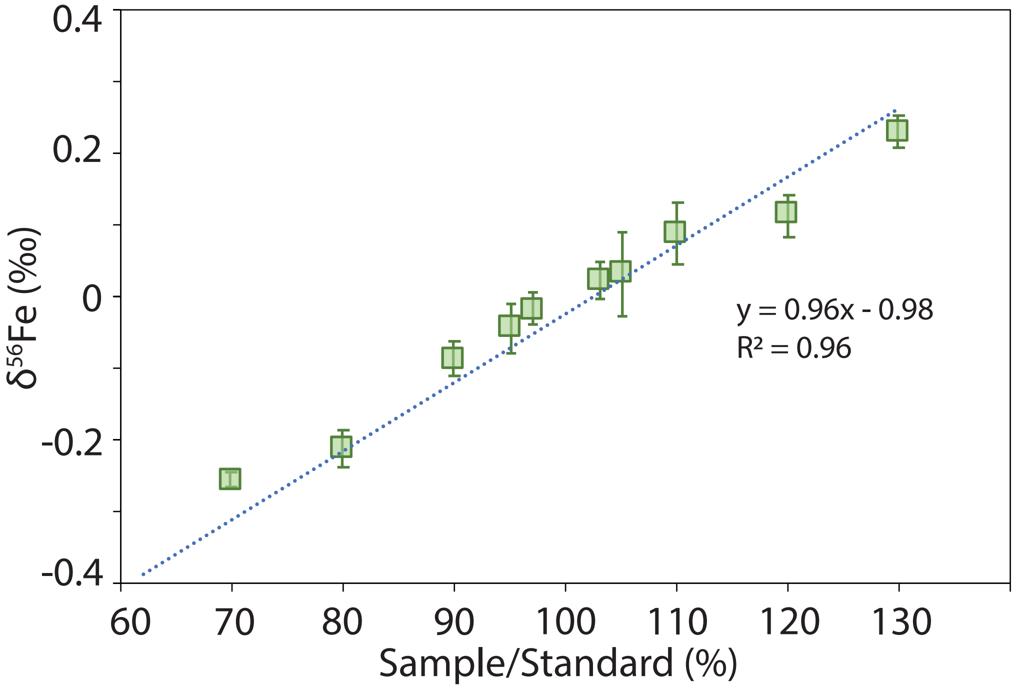


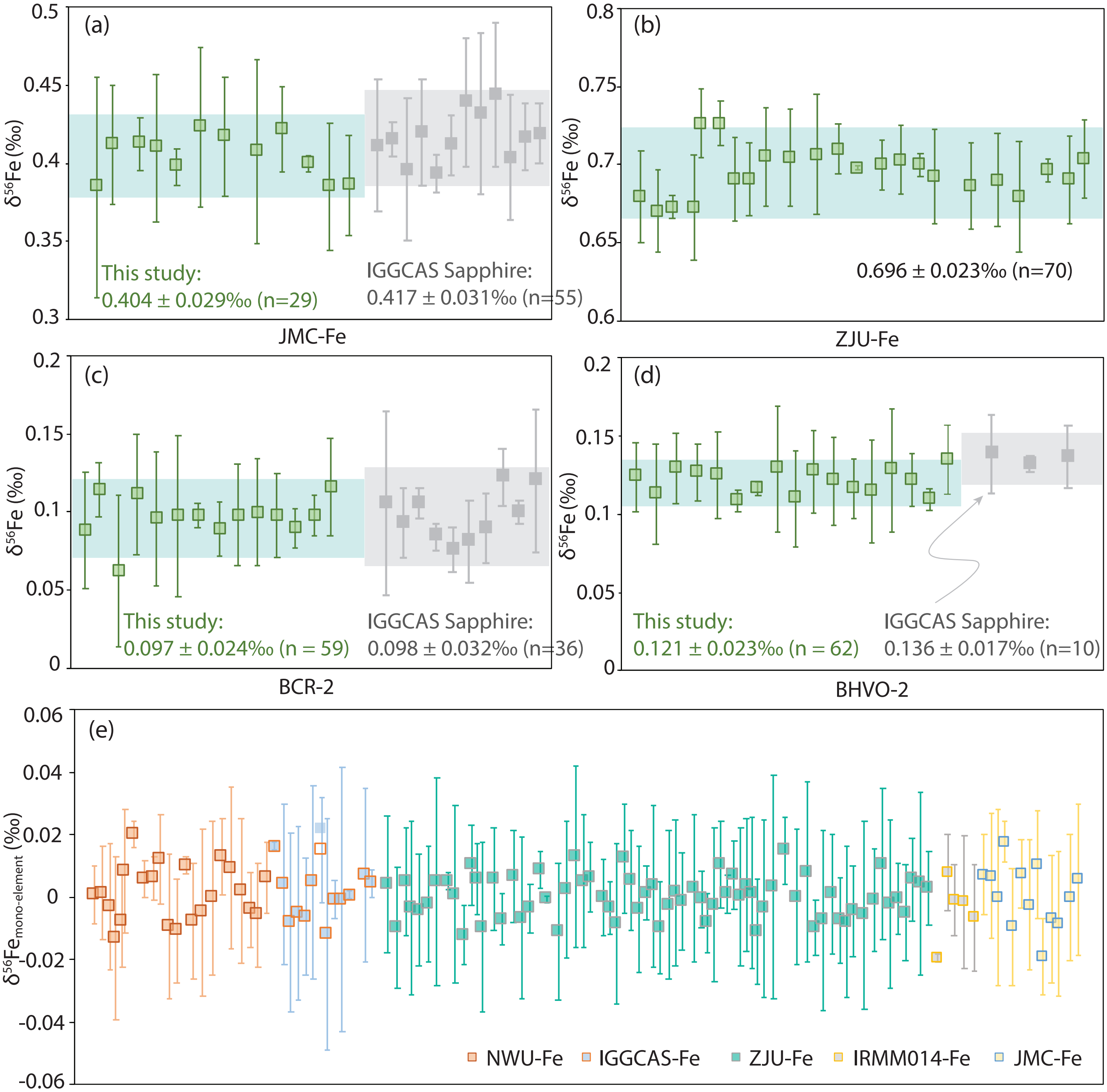
Figure 3

View Article Online
DOI: 10.1039/D5JA00225G



View Article Online
DOI: 10.1039/D5JA00225G

Figure 4



View Article Online
DOI: 10.1039/D5JA00225G

Figure 5

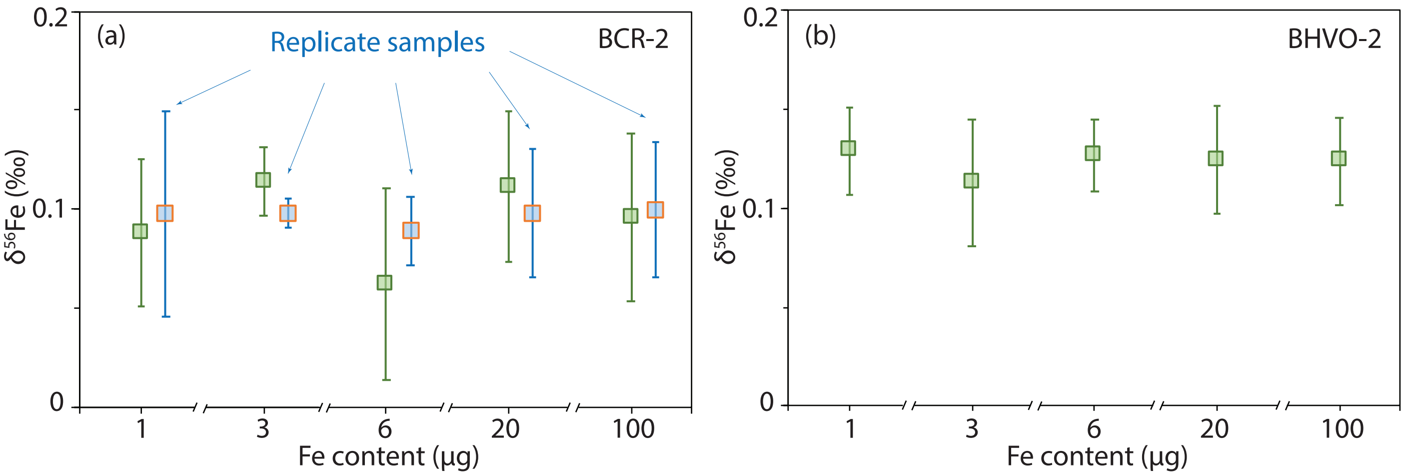
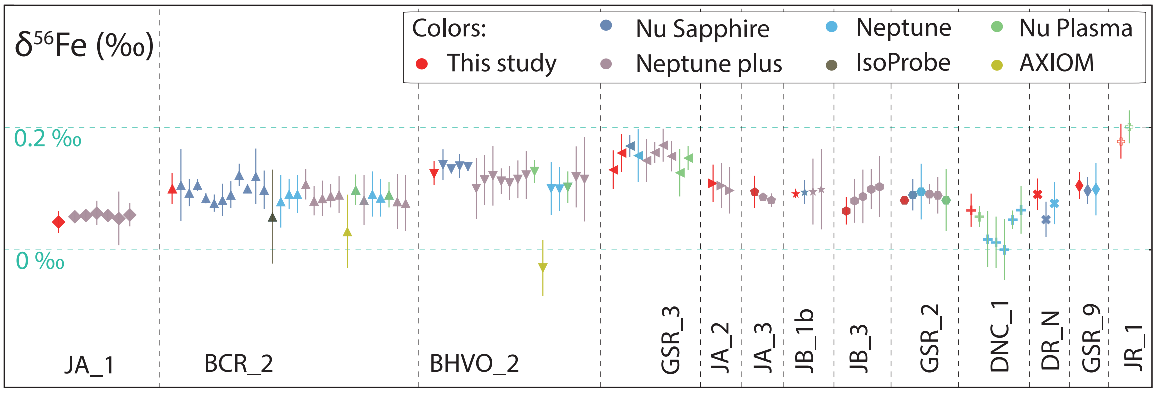


Figure 6

View Article Online
DOI: 10.1039/D5JA00225G



View Article Online
DOI: 10.1039/D5JA00225G

Table 1. Operating parameters of the Nu Sapphire and the Aridus 3 introduction system.

| **Nu Sapphire instrument setting** | | **Airdus 3 parameters** | |
|---|---|---|---|
| RF power | 1300 W | Argon sweep gas flow | 6-8 L/min |
| Coolant gas flow | 13-14 L/min | Nebulizer pressure | 0.8-1 L/min |
| Auxiliary gas flow | 0.9-1.2 L/min | Peripump speed | 20 rpm |
| Cone material | Ni | Peripump flow | 15-20 rpm |
| He collision gas flow | 2 sccm | Spray chamber terperature | 110 ℃ |
| $H_2$ reaction gas flow | 5 sccm | Nebulizer uptake rate | 100 μL/min |
| Quad 1 | 21.3 | Peltier cooler temperature | 7 ℃ |
| Quad 2 | -42 | Desolvator temperature | 140 ℃ |

View Article Online
DOI: 10.1039/D5JA00225G

Table 2. Iron isotopic compositions of geological standards over a six-month measurement period.

| **Sample** | **$\delta^{56}$Fe (‰)** | **2SD (‰)** | **N** |
|---|---|---|---|
| JMC_Fe | 0.412 | 0.038 | 4 |
| | 0.412 | 0.017 | 3 |
| | 0.410 | 0.047 | 3 |
| | 0.398 | 0.012 | 3 |
| | 0.417 | 0.038 | 3 |
| | 0.422 | 0.027 | 4 |
| | 0.400 | 0.005 | 4 |
| | 0.385 | 0.041 | 3 |
| | 0.386 | 0.032 | 2 |
| **Average** | **0.404** | **0.029** | **29** |
| ZJU-Fe(GSB04) | 0.690 | 0.030 | 3 |
| | 0.670 | 0.027 | 3 |
| | 0.727 | 0.022 | 2 |
| | 0.673 | 0.034 | 3 |
| | 0.727 | 0.014 | 3 |
| | 0.691 | 0.027 | 3 |
| | 0.691 | 0.024 | 3 |
| | 0.705 | 0.031 | 3 |
| | 0.705 | 0.031 | 3 |
| | 0.707 | 0.038 | 3 |
| | 0.710 | 0.016 | 3 |
| | 0.698 | 0.001 | 2 |
| | 0.700 | 0.016 | 4 |
| | 0.703 | 0.022 | 3 |
| | 0.700 | 0.007 | 3 |
| | 0.692 | 0.031 | 3 |
| | 0.680 | 0.030 | 3 |
| | 0.686 | 0.028 | 4 |
| | 0.673 | 0.007 | 3 |
| | 0.679 | 0.036 | 3 |
| | 0.697 | 0.007 | 4 |
| | 0.691 | 0.028 | 3 |
| | 0.704 | 0.025 | 3 |
| **Average** | **0.696** | **0.023** | **70** |
| BCR 2 | 0.098 | 0.027 | 6 |
| | 0.088 | 0.037 | 4 |
| | 0.114 | 0.017 | 3 |
| | 0.062 | 0.028 | 3 |
| | 0.111 | 0.038 | 3 |
| | 0.096 | 0.023 | 5 |
| | 0.097 | 0.032 | 4 |
| | 0.098 | 0.007 | 6 |

View Article Online
DOI: 10.1039/D5JA00225G

| | | | |
|---|---|---|---|
| | 0.089 | 0.017 | 7 |
| | 0.098 | 0.032 | 3 |
| | 0.100 | 0.014 | 2 |
| | 0.090 | 0.013 | 3 |
| | 0.098 | 0.013 | 3 |
| | 0.116 | 0.031 | 3 |
| **Average** | **0.097** | **0.024** | **59** |
| BHVO-2 | 0.108 | 0.007 | 2 |
| | 0.116 | 0.004 | 3 |
| | 0.124 | 0.022 | 4 |
| | 0.113 | 0.032 | 6 |
| | 0.129 | 0.022 | 4 |
| | 0.126 | 0.018 | 4 |
| | 0.124 | 0.028 | 4 |
| | 0.129 | 0.040 | 3 |
| | 0.110 | 0.031 | 5 |
| | 0.127 | 0.026 | 4 |
| | 0.121 | 0.028 | 3 |
| | 0.116 | 0.019 | 3 |
| | 0.115 | 0.033 | 3 |
| | 0.128 | 0.039 | 3 |
| | 0.122 | 0.017 | 3 |
| | 0.110 | 0.007 | 4 |
| | 0.134 | 0.022 | 4 |
| **Average** | **0.121** | **0.023** | **62** |

View Article Online
DOI: 10.1039/D5JA00225G

# Data availability statements

The data supporting this article have been included as part of the Supplementary Information.