

Recommendations of Stable Mg, Si, V, Fe, Cu, Zn, Rb, Sr, Ag, Cd, Ba, and U Isotope Compositions for Multiple Geological References

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ABSTRACT: The Metal Stable Isotope Geochemistry Laboratory (MSIGL) at the University of Science and Technology of China has developed state-of-the-art analytical methods for twelve stable isotope systems, including Mg, Si, V, Fe, Cu, Zn, Rb, Sr, Ag, Cd, Ba, and U. Geological and biological samples were first digested by acid dissolution or alkali dissolution. The target element was subsequently purified by the column chromatography method. A Neptune Plus MC-ICP-MS was used to measure isotope compositions and the isotope bias caused during measurements was calibrated by standard bracketing and/or the double spike method. The analytical procedure was carefully checked to ensure the high precision and accuracy of the data. Here, we summarized the protocol of these established methods and compiled the standard data measured at our lab as well as those reported in literature. This comprehensive dataset can serve as a reliable benchmark for calibration, method validation, and quality assurance in metal stable isotope analyses.

KEY WORDS: non-traditional stable isotope, metal stable isotope, analytical methods, MC-ICP-MS, standards, geological references.

0 INTRODUCTION

In the past two decades, advancements in isotope analytical techniques have driven the rise of numerous non-traditional stable isotope geochemical tracers. To further push the boundaries of these studies, the Metal Stable Isotope Geochemistry Laboratory (MSIGL) was established at the University of Science and Technology of China (USTC) at 2013. Owing to the combined efforts of our dedicated students and staff, we developed a suite of high-precision and accurate analytical methods using Neptune Plus multi-collector inductively coupled mass spectrometry (MC-ICP-MS). The MSIGL now can analyze over twelve isotope systems, including Mg, Si, V, Fe, Cu, Zn, Rb, Sr, Ag, Cd, Ba, and U, in both geological and biological materials. The laboratory's rigorous and accurate isotope measurements have significantly enhanced

our understanding across various fields such as geosciences, archaeology, anthropology, medicine, materials science, and food science. This paper provides a concise review of these analytical methods and summarizes the standard data analyzed since 2013. Our extensive standard compilations can provide a robust benchmark for calibration, method validation, quality control, and quality assurance in the expanding field of non-traditional stable isotope research.

1 METHODS

1.1 Sample Digestion

Sample digestion and column chemistry were performed in a class 1 000 clean laboratory. The nitric acid (HNO₃), hydrochloric acid (HCl), and hydrofluoric acid (HF) used in chemical procedures are all ultra-pure acids produced through double sub-boiling distillation. Samples were first grounded into powders that were finer than 200 mesh. Routine digestion for rocks with few organic components used a mixing acid of concentrated HF-HNO₃ (about 3 : 1, volume/volume, simplified as v/v hereafter) in Teflon Savillex beakers and placed on 120–140 °C hot plate for 3–4 days. If samples contain acid-resistant sili-

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cates such as the Cr-Al spinel, the beaker needs to be embedded inside a steel bomb and placed into an oven at 190 °C for 3–4 days. After initial digestion, samples were evaporated to dryness, treated with aqua regia, and then dried again. Subsequently, samples were refluxed with concentrated HNO₃ to remove residual fluorides and dry down in preparation for column procedures.

Alkali fusion digestion was applied for silicon isotope analysis. 2–5 mg of sample powder was weighed into a 10 mL silver crucible containing 200 mg of high-purity NaOH powder. After that, the crucible was heated in a muffle furnace for ten minutes at 720 °C with a cap on. The outside of the crucible was cleaned several times with Milli-Q water before it was allowed to cool to room temperature and then submerged in 15 mL Milli-Q water in a Teflon beaker. Until the black precipitates at the crucible's bottom were fully digested, the beaker containing the crucible was kept at ~25 °C for twenty-four hours. The sample solution was then moved to an additional Teflon beaker. After using ~25 mL of Milli-Q water to clean the Teflon beaker containing the crucible three times, the rinsed solution was moved into a new Teflon beaker. In preparation for subsequent column chemistry, the pH of the final solution was adjusted to be between 1 and 2 by adding concentrated HNO₃.

Samples containing small proportions of organic components such as soils need to be treated with concentrated HNO₃ (~15.4 N) and H₂O₂ (30%) at least three times to remove organic components. Then, dried samples were processed with the routine HF-HNO₃ digestion procedure. Regarding those containing a high proportion of organic components such as biological samples, high-pressure Asher is required for sample digestion. As described in Guo et al. (2023), sample powder was processed with 4.8 mL ultra-pure H₂O₂ and 1.6 mL concentrated HNO₃ in a polytetrafluoroethylene vessel and was subsequently held at 25 °C for 24 h, the vessel was heated on a hotplate at 100 °C for 24 h to remove part of organic materials. To eliminate part of the biological materials, the vessel was first left at 25 °C for 24 h and then was heated on a hotplate at 100 °C, kkk for 24 h. The solution was evaporated to dryness and then the vessel was refilled with a mixture of 1 mL concentrated HF, 1 mL concentrated HNO₃, and 3 mL concentrated HCl. The vessel was subsequently placed into a microwave digestion instrument of which running temperature and pressure stepwise increased to 200 °C and 40 atm and maintained for 30 min. Then, the sample was heated up to 225 °C and 45 atm for 30 min. Finally, the solution was transferred into a 30 mL PFA beaker and evaporated to dryness, waiting for column chemistry.

Barite (BaSO₄) has low dissolubility in H₂O and most inorganic acids such as HNO₃. Two methods were used to dissolve barite: (1) the Na₂CO₃ exchange method (Sun et al., 2022; Tian et al., 2019) and (2) the rapid water-extraction method (Tian et al., 2020). The Na₂CO₃ exchange method is according to the reaction: BaSO₄ + Na₂CO₃ = BaCO₃ + Na₂SO₄. Carbonate and organic com-

pounds in natural barite were first removed by concentrated HNO₃ and 30% H₂O₂. The 7 mL Teflon beaker containing 2 mg barite powder was heated up at 70–90 °C for 24 h. After dryness, a mixture of concentrated HF and HNO₃ was added into the beaker and then was placed on a hot plate at 130 °C. Aqua regia and 3 N HCl were added into the beaker alternately to remove undissolved CaF₂. Then, 1 mL of Na₂CO₃ solution (20 mg/mL) was added to the undissolved residue (i.e., pure barite) and was ultrasonicated for 30 min. The suspension was heated at 95 °C on the hot plate for > 4 h. The residue aqueous (Na₂SO₄) was pipetted out from the solid residue (BaCO₃). This Na₂CO₃ exchange procedure was repeated twice to ensure a complete reaction. Milli-Q water was used to rinse the solid residue several times and the solution was pipetted out. Finally, the solid residue (i.e., BaCO₃) was dissolved by 3 N HCl in preparation for chemical purification.

The rapid water-extraction method used H₂O to produce a barite suspension including barite microparticles and dissolved Ba. 10 mg barite powder with a grain size smaller than 0.074 mm was weighed into a 7 mL centrifuge tube. The centrifuge tube was added with 4 mL H₂O, then ultrasonicated and centrifuged. The supernatant was subsequently pipetted out and evaporated to dryness, and then further dissolved in 1 mL 3 N HCl in preparation for chemical purification.

1.2 Magnesium Isotope Analysis

Magnesium (Mg) is an alkali earth element that has three stable isotopes ²⁴Mg (79.0%), ²⁵Mg (10.0%), and ²⁶Mg (11.0%). Its isotope composition is usually reported in delta notation relative to standard DSM-3 as, δ^xMg (‰) = [(^xMg/²⁴Mg)_{sample} / (^xMg/²⁴Mg)_{DSM-3} - 1], x represents 25 or 26. Notably, geological samples show a large variation in their MgO content, such as ultramafic rocks usually larger than 40 wt.%, and felsic rocks possibly smaller than 0.5 wt.%. Because of the extremely higher matrix/Mg ratios, purification of low-Mg samples is more challenging than that of high-Mg ones. Therefore, purification for Mg used two different protocols, a high-Mg procedure for samples with MgO > 1 wt.% and a low-Mg procedure for those with MgO < 1 wt.%.

The high-Mg procedure is modified after the protocol in Huang et al. (2009). Briefly, fully digested samples (containing ~40 µg Mg) were redissolved by 0.1 mL 1.2 N HNO₃. Chemical purification of Mg used a microcolumn (0.64 cm ID × 6.8 cm bed height, Savillex) containing 2 mL AG50-X12 resin (Bio-Rad, 200–400 mesh). The resin was washed with 8 N HNO₃ and H₂O alternatively for > 3 times and was kept in Milli-Q water. Before chemical separation, the column with resin was pre-cleaned with a 12 mL mixture of 0.5 N HF + 4 N HNO₃, then by 4 mL Milli-Q H₂O, and followed by adding 3 mL 1.2 N HNO₃ twice for condition. All columns were routinely calibrated using two pure Mg standards (IGG and IEE). The magnesium was eluted by 1.2 N HNO₃, with 16 mL for eluting matrix elements, and then 23 mL for collection of pure Mg solu-

tions. The same procedure was conducted twice to ensure complete purification of Mg. Two 1 mL solutions before and after the Mg cut were collected and analyzed by ICP-MS as a check for the Mg yield.

The low-Mg procedure at the MSIGL is developed by An et al. (2014). The resin used is the same as Nanjing Binzhenghong Instrument). The fully digested sample (containing ~20 µg Mg) is redissolved by 1 mL 2 N HNO₃ and the cleaned resin is conditioned by 3 mL 2 N HNO₃ twice. The matrix was eluted with a 5 mL mixture of 2 N HNO₃ + 0.5 N HF and followed by 6 mL 1 N HNO₃. Subsequently, 22 mL 1 N HNO₃ elution was used to collect the pure Mg solution. Similar to the high-Mg procedure, two 1 mL solutions before and after were collected to check the Mg yield. The blank level for both high-Mg and low-Mg procedures is > 99%. The total procedural Mg blank is < 10 ng, which is much smaller than the 20–40 µg loaded Mg.

Magnesium isotope compositions were measured on the MC-ICP-MS (Neptune Plus, Thermo Scientific) at the MSIGL. The instrument measurement was carried out using a quartz dual cyclonic spray chamber, a Jet sample cone, and an H-skimmer cone. ²⁴Mg, ²⁵Mg, and ²⁶Mg are set at L3, C, and H3 Faraday cups, respectively. Measurements were conducted under low-resolution mode and the instrument bias was corrected by the standard-sample bracketing (SSB) method. A block includes 30 cycles with an integration time of 2.097 s per cycle. 3–6 repeated measurements were conducted for one sample. An on-peak baseline was measured using 30 cycles and 1 second integration time each cycle. To avoid potential cross-contamination, 5% and 2% HNO₃ were used to wash the sample-introduction system to reduce the ²⁴Mg signal to < 1 mV. No isobaric interferences were observed.

1.3 Silicon Isotope Analysis

Silicon (Si) has three stable isotopes: ²⁸Si (92.23%), ²⁹Si (4.67%), and ³⁰Si (3.10%), and its isotope composition is expressed as δ³⁰Si, i. e., per mille deviation of ³⁰Si/²⁸Si ratio of a sample relative to those of NBS28. The purification of silicon at MSIGL follows the protocol modified after Georg et al. (2006). Briefly, the chromatography used a 10 mL polypropylene column (0.8 cm ID × 2 cm bed height, Bio-Rad) containing 2 mL of AG50W-X12 resin (Bio-Rad, 200–400 mesh). Before purification, the resin was washed with 6 N HNO₃ and Milli-Q water. Then, about 50 µg Si dissolved in 3 mL sample solution was loaded onto the column. After sample loading, silicon was collected immediately, and 5 mL of H₂O was used to elute Si. The yield of Si was higher than 99%, and the total procedural blank was < 70 ng, negligible relative to the ~50 µg loaded Si.

Silicon isotope analysis on MC-ICP-MS using nickel Jet cone and H skimmer cone, an ESI PFA microflow nebulizer (aspiration rate: ~50 µL/min), and a quartz dual cyclonic spray chamber. L3, C, and H3 Faraday cups were used to measure the ²⁸Si, ²⁹Si, and ³⁰Si, respectively.

The sensitivity of the ²⁸Si ion beam is ~5 V/(µg·g) under high-resolution mode (> 6 000 M/ΔM) and the running solution was at ~3 µg/g. A 0.05% HNO₃ was used to clean the sample introduction system twice between each two analyses to eliminate potential cross-contamination. The SSB method was applied to correct the instrumental bias, and the bracketing standard NBS-28 needed to be purified through the same chemical procedure.

1.4 Vanadium Isotope Analysis

Vanadium (V) has one stable isotope ⁵¹V (99.76%) and one radioactive isotope ⁵⁰V (0.24%). ⁵⁰V has a very long half-life (108 Ga), which makes it to be considered as a stable isotope. Its isotope composition is expressed as δ⁵¹V relative to the Alfa Aesar standard (AA). Routine V isotope analysis for mafic rocks is a four-step procedure combining cation- and anion-exchange columns and the detailed procedure has been described in Wu et al. (2016). Briefly, the purification of V first used a pre-cleaned Bio-Rad polypropylene chromatography column (0.8 cm ID × 2 cm bed height, Bio-Rad) loaded with 2 mL of AG50W-X12 cation resin. The cation-exchange resin column is used to separate matrix elements (e.g., Fe, Al, Ca, Ti, Cr, and Mn). The resin was cleaned with 6 N HCl and H₂O alternately before loading, and then was washed with 1 N HNO₃ and H₂O, alternately. The resin was subsequently rinsed with 20 mL 6 N HCl and 10 mL H₂O alternately and then was conditioned by 3 mL 1 N HNO₃ twice. 1 mL solution dissolving 5 to 10 µg of V was then loaded onto the column. Ti and Al were eluted off by 4 mL of 1 N HNO₃ + 0.1 N HF and 1 mL of 1.2 N HNO₃. 19 mL of 1.2 N HNO₃ was eluted to collect V. This procedure was conducted twice to ensure the complete separation of Fe and Ti from V. Two 1 mL solutions before and after V cut were collected to check the V yield. After dryness, the obtained solution was redissolved in 1 mL dilute HCl (< 0.01 N) in preparation for the next column procedure.

Vanadium is further purified through an anion exchange column, modified after the procedure in Nielsen et al. (2011). A pre-cleaned Bio-Rad polypropylene column (0.8 cm ID × 2 cm bed height, Bio-Rad) was filled with 1.4 mL of AG1-X8 anion resin (Bio-Rad, 200–400 mesh). 1 N HNO₃ and Milli-Q H₂O were alternately used to wash the resin. After loading onto the column, the resin was rinsed with 10 mL 6 N HCl, 10 mL 1 N HNO₃, and 10 mL Milli-Q water in sequence, and then was conditioned by a 3 mL mixture of diluted HCl (< 0.01 N) + 1% H₂O₂ twice. Then, 1 mL dilute (< 0.01 N) HCl with 33 µL 1% H₂O₂ were used to re-dissolve the sample and immediately loaded onto the column. Residual matrix elements were eluted off by 15 mL dilute HCl (< 0.01 N) + 1% H₂O₂. Then, 17 mL 1 N HCl and 3 mL 6 N HCl were eluted to collect V cut.

A clipped PE pipet (0.4 cm ID × 1.2 cm bed height) containing 100 µL AG1-X8 (Bio-Rad, 200–400 mesh) resin was used to fully remove the residual Cr. After loading onto the column, the resin was rinsed with 2 mL 6 N HCl,

2 mL 1 N HNO₃ and 2 mL Milli-Q water in sequence, and then was conditioned by 0.5 mL diluted HCl (< 0.01 N) + 1% H₂O₂. The sample was re-dissolved in 1 mL diluted HCl (< 0.01 N) + 1% H₂O₂ and loaded on the column and then rinsed with 2 mL diluted HCl (< 0.01 N) + 1% H₂O₂. Then, 1.7 mL 1 N HCl and 0.3 mL 6 N HCl were eluted to collect V cut. The collected V solution was evaporated to dryness and dissolved in 2% HNO₃ in preparation for measurements. The whole procedure blank was < 1.5 ng and the yield for V was > 99%.

For ultramafic samples with high Mg and Fe contents, two more columns are needed to reduce the Mg/V and Fe/V ratio prior to the four-step purification procedure (Qi et al., 2019). First, AG1-X8 (Bio-Rad, 200–400 mesh) resin was used to remove Fe. Then the sample collected in the previous column was dissolved in 1 mL 1 N HCl and then loaded on 2 mL columns. A mixture of 8 mL 0.01 N HCl + 1% H₂O₂ was applied to elute V. The V cut was then further purified by the four-step column procedure. More details can be found in the supplementary material of Qi et al. (2019).

The measurements of V isotopes were conducted with the SSB method for correction of the instrument bias. Concentration mismatching between a sample and bracketing standard should be less than 10%. Measurements were done with a dry plasma condition with an Aridus II (CETAC Technologies) desolvating nebulizer. Using a 10¹⁰ Ω amplifier, the signal sensitivity on the ⁵¹V ion beam is ~200 V/(μg·g) under medium resolution mode (M/ΔM > 5 500) with an uptake rate of ~50 μL/min. The running solution has a V concentration of ~800 ng/g, corresponding to a signal of ~0.4 V on the ⁵⁰V ion beam using a 10¹¹ Ω amplifier. Isobaric interferences from ⁵⁰Ti and ⁵⁰Cr masses were corrected by monitoring the signal of ⁴⁸Ti, ⁴⁹Ti, ⁵²Cr, and ⁵³Cr. The purified solutions generally have ⁴⁹Ti/⁵¹V and ⁵³Cr/⁵¹V ratios smaller than 4 × 10⁻⁵ during measurements.

1.5 Iron Isotope Analysis

Iron (Fe) has four stable isotopes: ⁵⁴Fe (5.85%), ⁵⁶Fe (91.75%), ⁵⁷Fe (2.12%), and ⁵⁸Fe (0.28%). Its isotope composition is expressed as δ⁵⁶Fe or δ⁵⁷Fe, i.e., the per mille deviation of the ⁵⁶Fe/⁵⁴Fe or ⁵⁷Fe/⁵⁴Fe ratio relative to IRMM-014. The analytical method for Fe isotopes follows the protocol in Qi et al. (2020) and An et al. (2017). A fully dissolved sample containing ~50 μg Fe was purified by passing through 2 mL PFA columns (0.8 cm ID × 2 cm bed height, Bio-Rad) filled with 0.5 mL AG1 X8 anion resin (200–400 mesh). Before sample loading, 6 N HCl was used for resin conditions. 4 mL 6 N HCl was eluted to remove matrix elements. The eluted solution was collected to assess the yield. Iron was then collected by eluting 4 mL 0.5 N HCl, 1 mL 8 N HNO₃, and 0.5 mL Milli-Q H₂O in sequence. The collected pure Fe solution was then evaporated to dryness and redissolved in 2% HNO₃ in preparation for measurements. The yield is higher than 99% and the total procedural blank is smaller than 40 ng, negligible relative to Fe loaded onto column (~50 μg).

Iron isotope compositions were measured on MC-ICP-MS with an electrospray ionization 50 μL/min PFA microflow nebulizer, a Jet sample cone, and an H skimmer cone. ⁵³Cr, ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe, ⁵⁸Fe, and ⁶⁰Ni were measured on L3, L1, C, H1, H2, and H4 Faraday cup, respectively. ⁵³Cr was monitored to correct for the interference of ⁵⁴Cr on ⁵⁴Fe. The measurement was conducted under high-resolution mode (M/ΔM > 8 000, ΔM represents the mass difference between 5% and 95% peak height) to avoid isobaric interferences, such as ⁴⁰Ar¹⁴N on ⁵⁴Fe and ⁴⁰Ar¹⁶O on ⁵⁶Fe. The sensitivity on the ⁵⁶Fe ion beam is ~10 V/(μg·g). Each analyzed block contains 60 cycles with 2.097 s integration time per cycle. An analytical session includes 3–6 repeated measurements on the same solution. The introduction system between each measurement was washed by 5% and 2% HNO₃ for > 4 min to ensure the ⁵⁶Fe blank signal was < 3 mV.

1.6 Copper Isotope Analysis

Copper (Cu) is a chalcophile element that has two stable isotopes: ⁶³Cu (69.2%) and ⁶⁵Cu (30.8%). The isotope compositions are reported as δ⁶⁵Cu, i.e., ⁶⁵Cu/⁶³Cu of a sample relative to SRM 976. The Cu isotope analytical procedure at MSIGL is modified from the method in Maréchal et al. (1999) and has been described in Huang et al. (2017). Chromatographic purification of Cu was achieved by using a polypropylene column (0.8 cm ID × 2.0 cm bed height, Bio-Rad) with AG MP-1M (Bio-Rad, 100–200 mesh) resin by eluting with 6 N HCl + 0.001% H₂O₂ media. The column chemistry was conducted twice to ensure thorough separation of matrix elements (e.g., Na, Ti, Fe, Mg, and Al). The collected Cu cut was analyzed by ICP-MS to check remaining matrix elements if any. If the results show a higher value in any of the following ratios: Fe/Cu > 2, Ti/Cu > 0.1, Al/Cu > 2, Na/Cu > 0.5, and Mg/Cu > 4, one more column needs to be conducted. Two 1 mL solutions before and after the Cu cut were collected to check the yield of column chemistry, which is generally > 99%. The whole procedural blank is generally < 5 ng, which is negligible compared to ~1.2 μg Cu loaded on the column. Copper isotope compositions were analyzed under the low-resolution mode. ⁶³Cu and ⁶⁵Cu were located on the C and H₂ Faraday cup, respectively. A Jet sample cone and an H skimmer cone were used and the sensitivity of ⁶³Cu ion beam is ~33 V/(μg·g).

1.7 Zinc Isotope Analysis

Zinc (Zn) has five stable isotopes, ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn and ⁷⁰Zn and their abundances are 49.2%, 27.8%, 4.0%, 18.4%, and 0.6%, respectively. The isotope composition is expressed as δ⁶⁶Zn, i.e., ⁶⁶Zn/⁶⁴Zn ratio of the sample relative to that of JMC Lyon. The separation procedure for Zn at the MSIGL was modified after Chen et al. (2009) and has been described in Chen et al. (2016). Briefly, two columns are used to purify Zn. The first column used a polypropylene column (0.8 cm ID × 2.0 cm bed height, Bio-Rad) containing 2 mL of AG MP-1M resin (Bio-Rad, 100–200 mesh), and the second column (0.8

cm ID $\times$ 1.5 cm bed height, Bio-Rad) used 0.5 mL AG MP-1M resin (Bio-Rad, 100–200 mesh) to further purify Zn. Before loading, the resin was rinsed with 7 N HNO₃, Milli-Q water, 6 N HCl, and Milli-Q water, alternately. After loading, the resin was washed with 30 mL 0.5 N HNO₃ and 15 mL Milli-Q water. Then, the column is conditioned by 8 mL 6 N HCl. 1 mL solution dissolving 4 μ g Zn was loaded onto the column in 6 N HCl media. Matrix elements such as Na, Ti, Ni, and Ca were removed by elution of 4 mL of 6 N HCl. Then, Fe and Cu were removed with 6 mL of 0.5 N HCl. Then, 10 mL 0.5 N HNO₃ was eluted to collect the Zn cut. The collected Zn cut was evaporated to dryness and redissolved in 1 mL 6 N HCl in preparation for a second column. 0.5 mL of AG MP-1M resin (Bio-Rad, 100–200 mesh) was used as the second column to further purify the remaining matrix elements. After loading onto the column, the resin was rinsed with 8 mL 0.5 N HNO₃ and 4 mL Milli-Q water. Before sample loading, the column was conditioned with 2 mL 6 N HCl. 1 mL solution was loaded and eluted with 2 mL 6 N HNO₃ and 3 mL 0.5 N HCl. Then, pure Zn solution was collected by eluting with 5 mL 0.5 N HNO₃. The remaining Zn solution was evaporated to dryness in preparation for mass spectrometry analyses. The total procedural blank is about 7 to 12 ng, negligible relative to loaded Zn ($\sim$ 4 μ g).

The sample solutions were measured on MC-ICP-MS using a quartz dual cyclonic spray chamber, with a PFA microflow nebulizer (ESI) at an uptake rate of $\sim$ 50 μ L/min, X skimmer, and Jet sample cones. ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn and ⁷⁰Zn were measured at L2, C, H1, H3 and H4 cup, respectively. Mass-dependent isotope bias produced during measurements was corrected by the SSB method. In order to eliminate potential cross-contamination, $\sim$ 2% HNO₃ was used to wash the introduction system for at least 4 min to decline the ⁶⁴Zn blank level $<$ 3 mV. The sensitivity on the ⁶⁴Zn ion beam is $\sim$ 25 V/(μ g·g) under low-resolution mode.

1.8 Rubidium Isotope Analysis

Rubidium (Rb) has a stable isotope of ⁸⁵Rb (72.17%) and a radiogenic isotope ⁸⁷Rb (27.83%). ⁸⁷Rb has a long half-life of 4.92×10^{10} years, making it broadly considered a stable isotope. Rubidium isotope compositions are reported as the $\delta^{87/85}\text{Rb}$ relative to SRM 984. The purification of Rb is through a three-column procedure including two cation resin columns and one Sr-Spec resin column (Hu et al., 2021). A 30 mL microcolumn (0.64 cm ID $\times$ 7.1 cm bed height, Savillex) containing 2 mL AG50W-X12 (Bio-Rad, 200–400 mesh) resin was used in the first two-column procedure. The resin was rinsed with 6 N HCl and Milli-Q water alternately three times before loading onto the column. After loading, the resin was washed with 12 mL 4 N HNO₃ and 0.5 N HF, and then with 2 mL H₂O. 5 mL of 1.5 N HCl was used for the condition of the column. Then 1 mL solution containing $\sim$ 1 mg Rb was loaded onto the column. Matrix elements were eluted off by a 5 mL mixture of 1.5 N HCl + 0.5 N HF, followed by

16 mL 1.5 N HCl. Then 11 mL 1.5 N HCl was rinsed to collect the Rb cut. Two 1 mL solutions before and after the Rb cut were collected and measured to check the Rb yield. The cation-exchange column was repeated twice to ensure the separation of Rb from most matrix elements. After these procedures, a small proportion of K remains in the Rb cut. The purified sample was evaporated to dryness in preparation for the third column procedure.

The third Sr-spec resin column used a 15 mL Teflon microcolumn containing 0.5 mL Eichrom Sr-spec resin. 3 mL 3 N HNO₃ and 3 mL Milli-Q water were used to rinse the resin. 3 mL 3 N HNO₃ was used for column condition. Then, the sample dissolving in 0.25 mL 3 N HNO₃ was loaded onto the column. Rb was collected with 1.5 mL of 3 N HNO₃. The purified Rb is evaporated to dryness and redissolved in 2% HNO₃ in preparation for analysis. The whole procedure blank is $<$ 1 ng, which is negligible relative to the amount of loaded Rb ($\sim$ 1 μ g). The overall yield for Rb through the three-column procedure is higher than 99%.

Rubidium isotope analysis was conducted under low-resolution mode with H skimmer and Jet sample cones. L2, C, and H1 Faraday cups were set to collect ⁸⁵Rb, ⁸⁷Rb, and ⁸⁸Sr, respectively. The isobaric interference of ⁸⁷Sr on ⁸⁷Rb was checked by the ⁸⁸Sr signal. Generally, the signal of ⁸⁸Sr was $<$ 1 mV after purification, and thus ⁸⁷Sr has little effect on the measurement of ⁸⁷Rb. A constant ⁸⁷Sr/⁸⁸Sr of 0.085 was used to calibrate the interference of ⁸⁷Sr on ⁸⁷Rb. Using “wet” plasma with a quartz dual cyclonic Scott spray chamber produces a sensitivity of ⁸⁵Rb ion beam of $\sim$ 45 V/(μ g·g). An analysis block includes sixty cycles of data and the integration time is 8.389 seconds per cycle. Instrumental biases were corrected by the SSB method, and the analysis of one sample includes at least three times repeated measurements. The sample introduction system was cleaned using 5% HNO₃ and 2% HNO₃ alternately between measurements.

1.9 Strontium Isotope Analysis

Strontium (Sr) has four stable isotopes: ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr, and ⁸⁸Sr with abundances of 0.56%, 9.86%, 7.00%, and 82.58%, respectively. Based on the β decay of ⁸⁷Rb to ⁸⁷Sr, the Rb-Sr isotope system has been widely used to reveal the age and source of the geological bodies. In conventional radiogenic Sr isotope analysis, the ⁸⁶Sr/⁸⁸Sr of geological samples is considered unvaried and anchored to be 0.119 4 (Nier, 1938). With the advancement of isotope analytical techniques, the mass-dependent Sr isotope fractionation is documented in natural samples, and the stable Sr isotope compositions of geological samples are reported as the δ -notation relative to SRM 987.

The purification procedure of Sr follows the method developed by Chen et al. (2022). 2 mL of AG50W-X12 resin (Bio-Rad, 200–400 mesh) was used for the purification of Sr (Sun et al., 2022; Nan et al., 2015). The first column used a microcolumn (0.6 cm ID $\times$ 9 cm bed height, Nanjing Binzhenghong Instrument). The resin

was first rinsed with an 8 mL mixture of 4 N HNO₃ + 0.5 N HF and then washed with 2 mL Milli-Q water. 5 mL 2.5 N HCl was used for the condition of the column. 1 mL sample solution in 2.5 N HCl which contains 1.5–2 µg Sr was loaded on the column. Most matrix elements (e.g., Na, Fe, Ti, Mg, Mn, Al, K, Rb, and Ca) were eluted off by 27 mL of 2.5 N HCl. 11 mL of 4 N HCl was subsequently used to collect the Sr cut. Matrix elements such as Lu, Er, Yb, and Hf remain in the Sr cut and will be further separated in the second column. The Sr yield during the column procedure was examined by collecting two 1 mL eluents before and after the Sr cut.

The second column used a polypropylene column (0.8 cm ID × 2.0 cm bed height, Bio-Rad) containing 0.75 mL AG50W-X12 resin. The resin was first rinsed with a mixture of 4 N HNO₃ + 0.5 N HF and then by Milli-Q water. 3 mL 2 N HNO₃ was used for column condition. The sample obtained from the first column was evaporated to dryness and then redissolved in 1 mL 2 N HNO₃ and loaded onto the second column. 7 mL 2 N HNO₃ was used to separate the matrix elements. The Sr cut was subsequently collected with 13 mL 2 N HNO₃. After dryness, the sample solution was re-dissolved in 2% HNO₃ and diluted to 150–200 ng/g for isotope analyses. The overall yield of the column procedure is generally higher than 99%. The whole procedure blank is lower than 100 pg, which is negligible relative to the loaded Sr (1.5–2 mg).

Strontium isotope compositions were measured under low-resolution mode with an ESI PFA microflow nebulizer (aspiration rate of ~50 mL/min), a sample introduction system using a quartz dual cyclonic spray chamber and an H skimmer and a Jet sample cone. The sensitivity for the ⁸⁸Sr ion beam was 0.1 V/(ng·g). In order to eliminate cross-contamination if any, the sample introduction system was washed alternately by 5% HNO₃ and 2% HNO₃. L2, C, H1, and H2 Faraday cups were set to collect ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr, and ⁸⁸Sr, respectively. Notably, trace Kr in Ar carrier gas may cause interferences on Sr isotopes (⁸⁴Kr on ⁸⁴Sr and ⁸⁶Kr on ⁸⁶Sr) and ⁸⁷Rb in the sample solution would influence the measurement of ⁸⁷Sr. Therefore, L3 and L1 cups were set to monitor ⁸³Kr and ⁸⁵Rb, respectively to correct the influence of ⁸⁴Kr, ⁸⁶Kr, and ⁸⁷Rb on ⁸⁴Sr, ⁸⁶Sr, and ⁸⁷Sr, respectively. The double spike technique is applied to correct the instrument shift. First, an unspiked measurement was conducted to obtain the ⁸⁷Sr/⁸⁶Sr ratio and then a spiked measurement was applied to obtain $\delta^{88/86}\text{Sr}$. When measuring ⁸⁷Sr/⁸⁶Sr, the conventional approach is applied using ⁸⁶Sr/⁸⁸Sr = 0.119 4 to correct the instrument bias on ⁸⁷Sr/⁸⁶Sr based on exponential law. An ⁸⁴Sr-⁸⁷Sr double spike solution (⁸⁴Sr = 52.1%, ⁸⁶Sr = 2.7%, ⁸⁷Sr = 32.4%, and ⁸⁸Sr = 12.8%) is applied to correct the instrumental shift on $\delta^{88/86}\text{Sr}$. A double spike solution was added into the solution to achieve $\text{Sr}_{\text{DS}}/\text{Sr}_{\text{sample}} \sim 0.7$ before measurement. Finally, combining the obtained ⁸⁷Sr/⁸⁶Sr in unspiked measurements, the $\delta^{88/86}\text{Sr}$ is calculated through the algebraic approach described in Rudge et al. (2009). Spiked SRM 987 was routinely measured to monitor the systematic offset between

each analytical session. 5% HNO₃ with 0.1% HF was used to wash the sample introduction system before each measurement session to avoid potential memory effects.

1.10 Silver Isotope Analysis

Silver (Ag) has two stable isotopes: ¹⁰⁷Ag (51.839%) and ¹⁰⁹Ag (48.161%) and the isotope compositions of geological samples are reported as $\delta^{109}\text{Ag} (\text{‰}) = [({}^{109}\text{Ag}/{}^{107}\text{Ag})_{\text{sample}}/({}^{109}\text{Ag}/{}^{107}\text{Ag})_{\text{SRM 978a}} - 1] \times 1\,000$. A four-column procedure for Ag isotope analysis was recently developed by Fang et al. (2024), which is modified from the methods described in Schönbächler et al. (2007) and Luo et al. (2010). The first column used 2 mL AG1-X8 (Bio-Rad, 200–400 mesh) resin with a microcolumn (0.6 cm ID × 7 cm bed height, Nanjing Binzhenghong Instrument). The resin was washed with 30 mL of 9 N HCl and 5 mL of Milli-Q water, alternately. The aliquot of a fully dissolved sample containing 10 ng Ag was re-dissolved in 1 mL 0.5 N HCl + 0.001% H₂O₂. Most matrix elements were removed by a 26 mL mixture of 0.5 N HCl + 0.001% H₂O₂. Then, Zn and Cd were eluted off by a 10 mL mixture of 0.05 N HCl + 0.001% H₂O₂ and 10 mL 0.001 N HCl, respectively. Finally, Ag was collected by eluting 30 mL of 1 N HNO₃. The anion column was conducted twice to ensure complete separation. After dryness, the obtained Ag elution was redissolved in 1 mL 0.5 N HNO₃ in preparation for the second column procedure.

The second column used 2 mL AG 50W-X8 cation resin (Bio-Rad, 200–400 mesh). 30 mL of 6 N HCl was used to rinse the resin and then conditioned by 10 mL 0.5 N HNO₃. After sample loading, matrix elements were removed using 40 mL 0.5 N HNO₃ and pure Ag solution was obtained by rinsing with 24 mL 0.5 N HNO₃. After dryness, the Ag aliquot was redissolved in 1 mL of 2% HNO₃. Two 1 mL solutions before and after the Ag cut were collected to check Ag yield. The yield for Ag of the two-column procedure is higher than 95%.

Measurements of Ag on MC-ICP-MS were conducted under dry plasma condition, with an H skimmer, and a Jet sample cone. Faraday cups L3, L2, L1, C, H1, H2, H3, and H4 were set to collect ¹⁰⁴Pd, ¹⁰⁵Pd, ¹⁰⁶Pd, ¹⁰⁷Ag, ¹⁰⁸Pd, ¹⁰⁹Ag, ¹¹⁰Pd and ¹¹¹Cd, respectively. The Cd interferences on ¹⁰⁶Pd, ¹⁰⁸Pd, and ¹¹⁰Pd were corrected by the signal of ¹¹¹Cd. The instrumental shift was corrected by combining the SSB method and the Pd internal mass bias correction method. Before analysis, the Pd standard (NIST 3138) was added to the bracketing standard and the sample with an appropriate ratio, producing an equivalent signal between ¹⁰⁷Ag and ¹⁰⁸Pd. The sensitivity of ¹⁰⁷Ag and ¹⁰⁸Pd signals were ~0.1 V/ng/g under 50 µL/min uptake rate.

1.11 Cadmium Isotope Analysis

Cadmium (Cd) has eight stable isotopes: ¹⁰⁶Cd, ¹⁰⁸Cd, ¹¹⁰Cd, ¹¹¹Cd, ¹¹²Cd, ¹¹³Cd, ¹¹⁴Cd, and ¹¹⁶Cd, with abundances of 1.25%, 0.89%, 12.47%, 12.80%, 24.11%, 12.23%, 28.74%, and 7.52%. Cadmium isotope compositions are

reported as $\delta^{114/110}\text{Cd}$ relative to SRM 3108. The analytical method of Cd isotope at MSIGL was established by Liu et al. (2020). Briefly, a micro-column (0.64 cm ID $\times$ 6.3 cm bed height, Savillex) containing 2 mL AG1-X8 resin (Bio-Rad, 100–200 mesh) was used for the purification of Cd. After loading, the resin was washed with 10 mL 2 N HNO_3 and 10 mL Milli-Q water and then was conditioned with 5 mL 6 N HCl. A 2 mL sample solution was loaded onto the column. Matrix elements Na, Mg, Ca, Al, Ti, and Zr were removed by washing with 4 mL 6 N HCl. Then, Fe, Ga, Pd, Mo, Ag, and In were eluted off by 25 mL of 0.3 N HCl. Sn and Zn were then eluted off with a 30 mL mixture of 0.5 N HNO_3 + 0.1 N HBr. Finally, Cd is collected with 10 mL 2 N HNO_3 . After drying, the sample was re-dissolved in 2% HNO_3 in preparation for measurements. The total procedural blank is < 75 pg, which is insignificant relative to the loaded Cd.

Cadmium isotopes were measured using a Jet sample and X skimmer cone under a low-resolution mode with an Aridus III desolvator. The sensitivity of ^{114}Cd is ~ 300 V/($\mu\text{g}\cdot\text{g}$), and the concentration of Cd running solutions was in the range of 10–50 ng/g. ^{111}Cd – ^{113}Cd double spike technique was applied to correct the instrument shift. Single spike ^{111}Cd (97.21%) and ^{113}Cd (93.35%) purchased from ISOFLEX were mixed to produce a double spike solution with $^{111}\text{Cd} : ^{113}\text{Cd} \approx 1.032$. The double spike solution was mixed with the purified sample according to spike/sample ratios in a range from 0.02 to 3.0. L3, L1, C, H1, H2, H3 and H4 Faraday cups were set to measure ^{105}Pd , ^{110}Cd , ^{111}Cd , ^{113}Cd , ^{114}Cd , ^{115}In , and ^{119}Sn , respectively. The isobaric effect of Pd, In, Sn on Cd was corrected according to the signal of ^{105}Pd , ^{115}In , and ^{119}Sn . The interferences of Pd and In were also monitored by measuring the signals of ^{105}Pd and ^{115}In via mass jumping. One measurement consists of thirty cycles with an integration time of 4.194 seconds per cycle. After each measurement, the introduction system was washed with 2% HNO_3 for 2 min until the ^{114}Cd signal was < 3 mV.

1.12 Barium Isotope Analysis

Barium (Ba) has seven stable isotopes, ^{130}Ba , ^{132}Ba , ^{134}Ba , ^{135}Ba , ^{136}Ba , ^{137}Ba , and ^{138}Ba , with abundances of 0.105 8%, 0.101 2%, 2.417%, 6.592%, 7.853%, 11.232%, and 71.699%, respectively. Its isotope compositions were expressed as $\delta^{138/134}\text{Ba}$ relative to SRM 3104a. The Ba isotope analytical method at the MSIGL was first developed by Nan et al. (2015) with the SSB method and further optimized by Zeng et al. (2019) with double-spike techniques.

The purification of Ba used a Savillex micro-column (0.6 cm ID $\times$ 6.2 cm bed height, Nanjing Binzhenghong Instrument) with AG50W-X12 (Bio-Rad, 200–400 mesh) resin. The resin was first washed with an 8 mL mixture of 4 N HNO_3 + 0.5 N HF, then with 2 mL Milli-Q water, 5 mL 6 N HCl, and 2 mL Milli-Q water in sequence. Subsequently, the resin was conditioned with 3 mL 3 N HCl. A fully dissolved aliquot containing ~ 2 μg Ba in 1 mL 3 N HCl was loaded onto the column. Matrix elements were

removed by 28 mL 3 N HCl. Subsequently, Ba was collected with 16 mL 3 N HNO_3 . Two 1 mL solutions before and after the Ba cut were collected to check the Ba leakage during purification. This column procedure was conducted twice to achieve complete separation of Ba from other elements. The collected Ba cut was evaporated to dryness and re-dissolved into 2% HNO_3 with a concentration of 100 ng/g. The yield of full procedure chemistry is > 99%. The total procedure blank was < 5 ng, which is negligible relative to loading Ba (2 μg).

Barium isotope compositions were measured using an Aridus III desolvator (CETAC) equipped with a 50 $\mu\text{L}/\text{min}$ PFA MicroFlow Teflon nebulizer on MC-ICP-MS. The mass-dependent bias caused by the instrument was corrected by the ^{135}Ba – ^{136}Ba double spike technique combining the SSB method. The ^{135}Ba – ^{136}Ba double spike solution was added to the collected pure Ba solution, producing a mixture with a $^{135}\text{Ba}/^{134}\text{Ba}$ ratio between 20–35 (more details can be found in Tian et al., 2019). SRM 3104a was used as the bracketing standard. Measurements were conducted under low-resolution mode with a sample and X skimmer cones. L4, L2, L1, C, H1, H2, and H3 Faraday cups were set to collect ^{131}Xe , ^{134}Ba , ^{135}Ba , ^{136}Ba , ^{137}Ba , ^{138}Ba , and ^{140}Ce , respectively. The sensitivity on the ^{137}Ba ion beam was ~ 70 V/($\mu\text{g}\cdot\text{g}$). ^{131}Xe and ^{140}Ce was measured to monitor the interference of ^{136}Xe on ^{136}Ba , ^{134}Xe on ^{134}Ba , and ^{136}Ce on ^{136}Ba . The introduction system was washed with 5% HNO_3 for > 50 s and 2% HNO_3 for < 80 s between measurements, until the ^{137}Ba blank level < 3 mV.

1.13 Uranium Isotope Analysis

The purification procedure of U at the MSIGL follows the method established by Weyer et al. (2008) and has been described in Sheng et al. (2024). Briefly, the purification is carried out using a polypropylene column (0.8 cm ID $\times$ 1.6 cm bed height, Bio-Rad) containing 0.8 mL UTEVA resin. Before loading, 0.05 N HCl and Milli-Q water were alternately used to rinse the resin. The resin was then rinsed with 10 mL 0.05 N HCl and was conditioned by 2.4 mL 3 N HNO_3 . A 5 mL sample solution containing 500 ng U in 3 N HNO_3 was loaded onto the column. Most matrix elements were eluted off by rinsing with 16 mL 3 N HNO_3 . Then the resin was rinsed with 2.4 mL 10 N HCl. Thorium was eluted off by an 8 mL mixture of 5 N HCl + 0.05 N oxalic acid and 2.4 mL 5 N HCl. Then, U was eluted off by 10 mL 0.05 N HCl. The collected U cut was re-dissolved in 2% HNO_3 in preparation for measurements. The whole procedural blank is < 0.1 ng, which is much smaller than the loaded 500 ng U.

Uranium isotopes were measured with an Aridus III desolvating nebulizer with an X skimmer and a Jet sample cone. Uranium isotope data are expressed as $\delta^{238/235}\text{U}$, $^{238}\text{U}/^{235}\text{U}$ of samples relative to an in-house standard USTC-U in per mille deviation. ^{232}Th , ^{233}U , ^{235}U , ^{236}U and ^{238}U were measured simultaneously on L2, L1, C, H1 and H3 Faraday cups, respectively. The ^{233}U – ^{236}U double-spike technique was applied to calibrate the instrumental

shift. The purified samples were dissolved in 2% HNO_3 with a U concentration of 25 ng/g and then added to the double spike solution. One measurement consists of 50 cycles with an integration time of 4.194 s per cycle. The introduction system was washed with 5% HNO_3 for 120 s and then 2% HNO_3 for 80 s between each measurement until the ^{238}U signal < 10 mV.

2 RESULTS AND DISCUSSION

Long-term $\delta^{26}\text{Mg}$ values of multiple geological references are shown in Table S1 and Figure 1, including IEE, IGG, DTS-2, BHVO-2, BCR-2, BIR-1, W-2, RGM-1, RGM-1, RGM-2, COQ-1, and Jdo-1. Their values reported in the literature are also shown in Table S1 (He et al., 2022; Bao et al., 2020, 2019a, b; An et al., 2014; Choi et al., 2012; Huang et al., 2012; Opfergelt et al., 2012; Wang S J et al., 2012; Bizzarro et al., 2011; Pogge von Strandmann et al., 2011; Bourdon et al., 2010; Teng et al., 2010; Wombacher et al., 2009; Yang et al., 2009; Baker et al., 2005). The number of repeated measurements (N) ranges from 6 to 3 738. The precision represented by the 2SD value ranges from 0.021‰ to 0.065‰. Two pure Mg standards (IEE and IGG) were frequently measured with N of 1 516 and 3 738, respectively. They show consistent 2SD of 0.051‰ to 0.055‰. Three basaltic standards, BHVO-2, BCR-2, and BIR-1 are the most frequently measured geological references with N of 423, 294, and 111,

respectively. They show slightly higher 2SD from 0.056‰ to 0.061‰ than pure Mg standards, which should reflect the trace amount of matrix elements that survived from chemical purification. For standards with $N > 60$, the accuracy is represented by $\pm 2\text{SE}$, and for samples with $N < 60$, $t\text{SE}$ is used for the expression of accuracy. The definitions of 2SE and $t\text{SE}$ have been introduced in our recent paper Wang W Y et al. (2023). Briefly, for samples with a large number of duplicates (> 60), the dataset will follow a normal distribution, and accuracy at a 95% confidence level can be measured by $\pm 2\text{SE}$. For samples with a small number (< 60) of duplicates, the dataset will follow a t -distribution, and the accuracy at a 95% confidence level should be measured by $\pm t\text{SE}$.

Silicon isotope compositions are shown in Table S2 and Figure 2, including pure Si standard USTC-Si and two USGS standards BHVO-2 and AGV-2. N ranges from 126 to 772. Their 2SD values show a range from 0.055‰ to 0.066‰ and the $t\text{SE}/2\text{SE}$ values are from 0.002‰ to 0.006‰. The values of these references measured by previous studies are also shown in Table S2 (Yu et al., 2024; Pringle et al., 2016; Savage et al., 2011; Zambardi and Poitrasson, 2011; Fitoussi et al., 2009).

Long-term $\delta^{51}\text{V}$ values of multiple geological references are shown in Table S3 and Figure 3, including four pure V standard USTC-V, NIST 3165, BDH, and ICP-V as well as six USGS geological standards PCC-1, BCR-

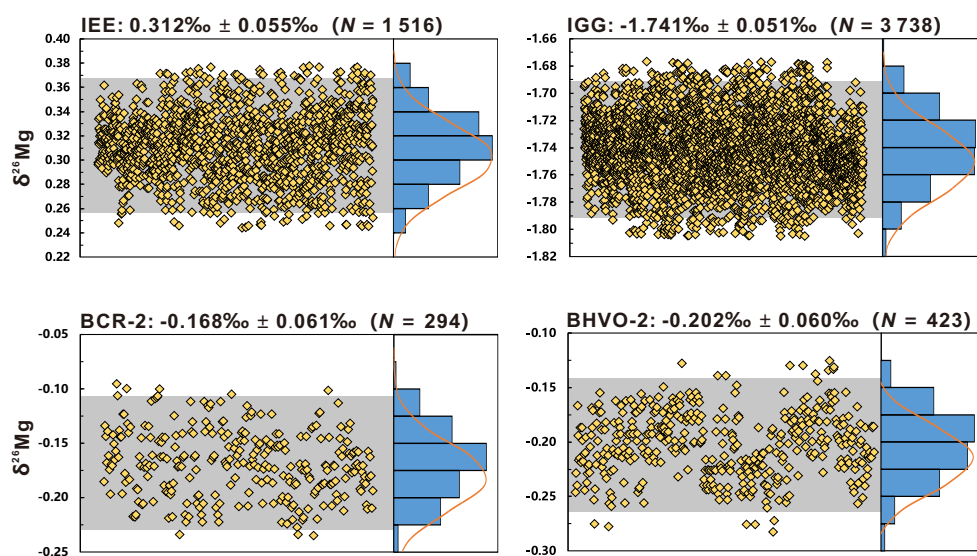


Figure 1. Long-term results for $\delta^{26}\text{Mg}$ of IEE, IGG, BCR-2 and BHVO-2. The right panel of the figure illustrates the normal distribution for each standard.

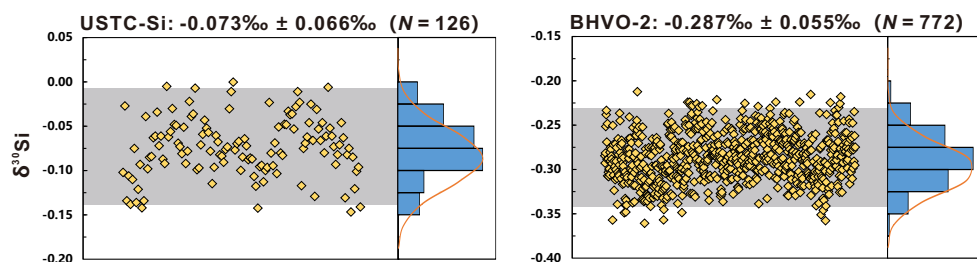


Figure 2. Long-term results for $\delta^{30}\text{Si}$ of USTC-Si and BHVO-2. The right panel of the figure illustrates the normal distribution for each standard.

2, BHVO-2, BIR-1, AGV-2 and GSP-2. N ranges from 12 to 1 429. Their 2SD values fall in a range from 0.063‰ to 0.104‰ and the $tSE/2SE$ values are from 0.002‰ to 0.036‰. The values of these references measured by previous studies are also shown in Table S3 (Stow et al., 2024, 2023; Nielsen et al., 2019, 2011; Qi et al., 2019; Sossi et al., 2018; Prytulak et al., 2017, 2013, 2011;

Schuth et al., 2017; Wu et al., 2016).

Iron isotope compositions of multiple geological standards are shown in Table S4 and Figure 4, including three pure Fe standards UI-Fe, GSB, and USTC-Fe as well as six USGS geological standards BHVO-2, BCR-2, AGV-2, BIR-1, RGM-2 and GSP-2. N ranges from 36 to 2 572. Their 2SD values fall in a narrow range from

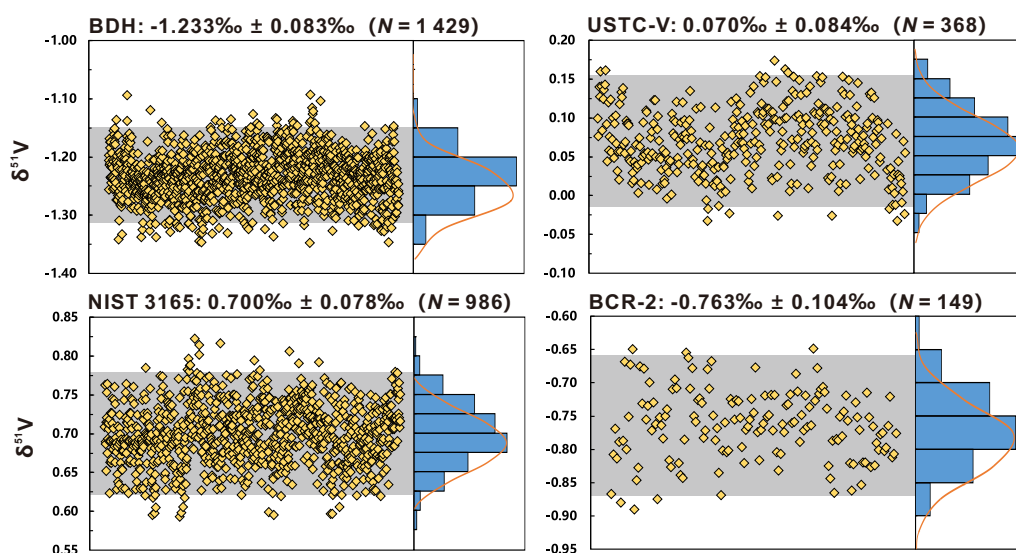


Figure 3. Long-term results for $\delta^{51}\text{V}$ of BDH, USTC-V, NIST 3165 and BCR-2. The right panel of the figure illustrates the normal distribution for each standard.

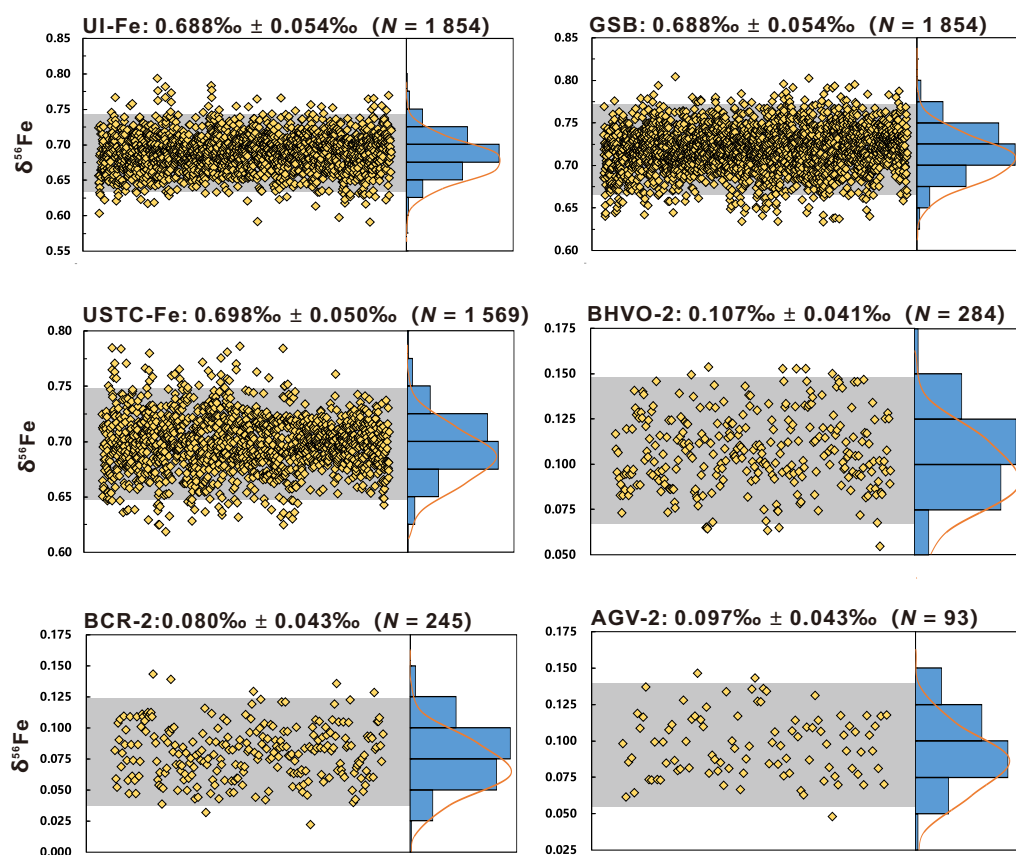


Figure 4. Long-term results for $\delta^{56}\text{Fe}$ of UI-Fe, GSB, USTC-Fe, BHVO-2, BCR-2 and AGV-2. The right panel of the figure illustrates the normal distribution for each standard.

0.040‰ to 0.054‰ and the $tSE/2SE$ values are from 0.001‰ to 0.008‰. The values of these references measured by previous studies are also shown in Table S4 (Chen D D et al., 2023; Liang et al., 2022; Yang et al., 2021; Gong H M et al., 2020; Hu and Teng, 2019; An et al., 2017; Chen X Y et al., 2017; Du et al., 2017; He et

al., 2015; Liu et al., 2014; Wang K et al., 2012; Craddock and Dauphas, 2011; Weyer et al., 2005).

Copper isotope compositions of multiple geological standards are shown in Table S5 and Figure 5, including two pure Cu standard ERM-AE-647 and AAS as well as five USGS geological standards BHVO-2, BIR-1, GSP-1, AGV-1, and W-2a. N ranges from 12 to 1 026. Their 2SD values fall in a narrow range from 0.034‰ to 0.067‰ and the $tSE/2SE$ values are from 0.001‰ to 0.019‰. The values of these references measured by previous studies are also shown in Table S5 (Li and Liu, 2022; Lü and Liu, 2022; Zhang et al., 2022; Guo et al., 2020; Zhu et al., 2019; Huang et al., 2017; Savage et al., 2015; Liu et al., 2014; Moeller et al., 2012).

Zinc isotope compositions of multiple geological standards are shown in Table S6 and Figure 6, including three pure Zn standards SRM 3702, AAS, and USTC-Zn as well as six USGS geological standards PCC-1, DTS-2, BCR-2, BIR-1, BHVO-2, W-2, AGV-2, NOD-P-1, and G-2. N ranges from 20 to 567. Their 2SD values vary from 0.026‰ to 0.058‰ and the $tSE/2SE$ values are from 0.001‰ to 0.016‰. The values of these references measured by previous studies are also shown in Table S6 (Sun et al., 2023; Wang Z X et al., 2023; Xu et al., 2019; Wang Z Z et al., 2017; Chen et al., 2016; Moeller et al., 2012; Sonke et al., 2008; Toutain et al., 2008; Archer and Vance, 2004).

Long-term $\delta^{87/85}Rb$ values are shown in Table S7 and Figure 7, including two pure Rb standard ICP-Rb and USTC-Rb as well as eight geological standards BHVO-2, BCR-2, AGV-2, GSR-1, GSR-3, G-2, and GSP-2. N ranges from 8 to 559. Their 2SD values fall in a narrow range from 0.044‰ to 0.061‰ and the $tSE/2SE$ values are from 0.002‰ to 0.031‰. The values of these references measured by previous studies are also shown in Table S7 (Wang et al., 2024; Zhang et al., 2023, 2018; Hu et al., 2021; Pringle and Moynier, 2017).

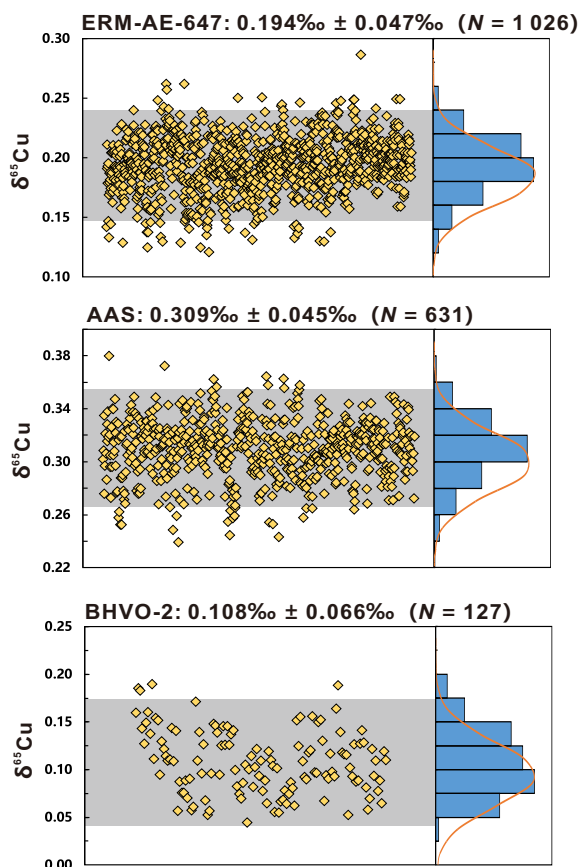


Figure 5. Long-term results for $\delta^{65}Cu$ of AAS, ERM-AE-647 and BHVO-2. The right panel of the figure illustrates the normal distribution for each standard.

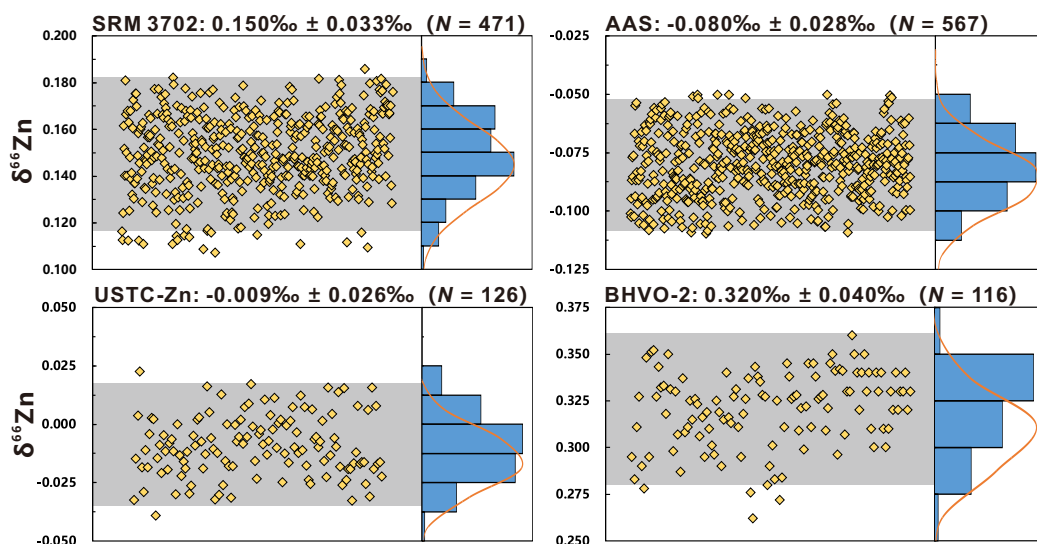


Figure 6. Long-term results for $\delta^{66}Zn$ of SRM 3702, AAS, USTC-Zn and BHVO-2. The right panel of the figure illustrates the normal distribution for each standard.

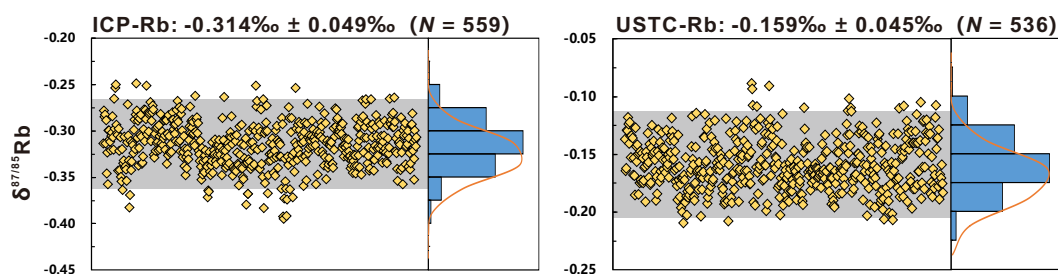


Figure 7. Long-term results for $\delta^{87/85}\text{Rb}$ of ICP-Rb and USTC-Rb. The right panel of the figure illustrates the normal distribution for each standard.

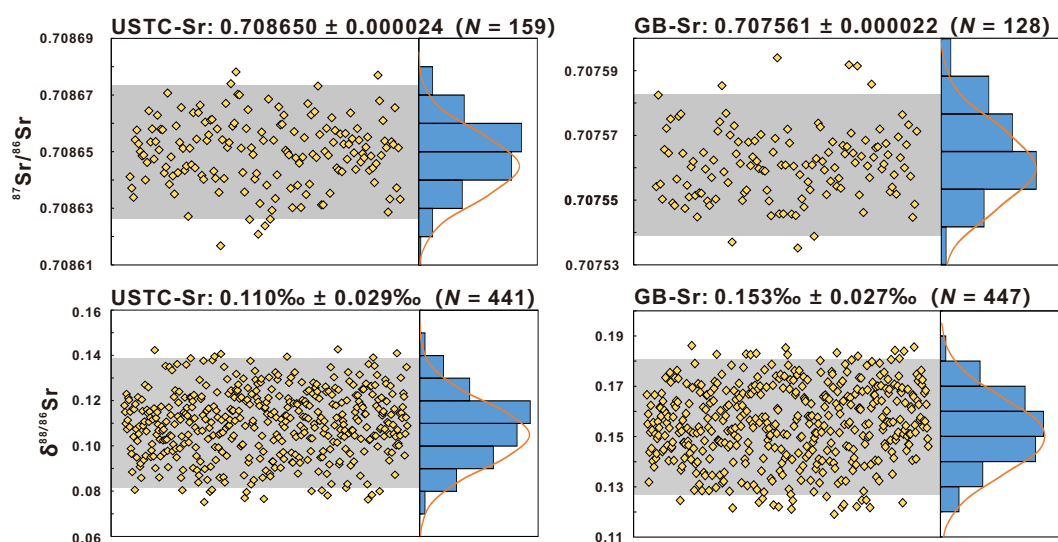


Figure 8. Long-term results for $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{88/86}\text{Sr}$ of USTC-Sr and GB-Sr. The right panel of the figure illustrates the normal distribution for each standard.

Long-term $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{88/86}\text{Sr}$ values of references are shown in Table S8 and Figure 8, including two pure Sr standard USTC-Sr and GB-Sr, SRM 2709a and SRM 2710 as well as six geological standards SRM 2709a, SRM 2710, G-2, AGV-2, BHVO-2 and RGM-1. The 2SD values for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from 0.000 017 to 0.000 044 and the 2SD of $\delta^{88/86}\text{Sr}$ ratios vary from 0.027‰ to 0.033‰. The values of these references measured by previous studies are also shown in Table S8 (Brazier et al., 2020; Klaver et al., 2020; Xu et al., 2020; Andrews et al., 2016; Chao et al., 2015; Pearce et al., 2015; Ma et al., 2013; Charlier et al., 2012; Liu et al., 2012; Moynier et al., 2010).

Silver isotope compositions of multiple geological references are reported in Table S9 and Figure 9, including two pure Ag standards ICP-Ag and USTC-Ag as well as eight USGS geological standards BIR-1, BCR-2, AGV-2, RGM-2, G-2, GSP-2, GSS-13, and NOD-P-1. Their 2SD values fall in a narrow range from 0.020‰ to 0.116‰ and the $t\text{SE}/2\text{SE}$ values are from 0.005‰ to 0.095‰. The values of these references measured by previous studies are also shown in Table S9 (Schönbachler et al., 2010; Woodland et al., 2005).

Long-term $\delta^{114/110}\text{Cd}$ values are listed in Table S10 and Figure 10, including four pure Cd standards Münster Cd, BAM I012 Cd, HPS Cd, and AAS as well as three USGS geological standards SRM 2710, NOD-P-1, and

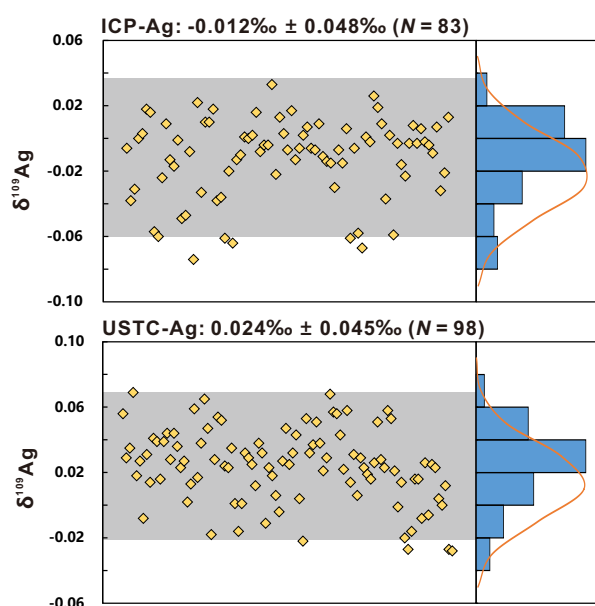


Figure 9. Long-term results for $\delta^{109}\text{Ag}$ of ICP-Ag and USTC-Ag. The right panel of the figure illustrates the normal distribution for each standard.

BIR-1. Their 2SD values fall in a narrow range from 0.041‰ to 0.054‰ and the $t\text{SE}/2\text{SE}$ values are from 0.002‰ to 0.011‰. The values of these references mea-

sured by previous studies are also shown in Table S10 (Devos et al., 2024; Pickard et al., 2022; Borovička et al., 2021; Liu et al., 2020; Tan et al., 2020; Li et al., 2018; Murphy et al., 2016; Pallavicini et al., 2014; Abouchami et al., 2013).

Long-term $\delta^{138/134}\text{Ba}$ are reported in Table S11 and

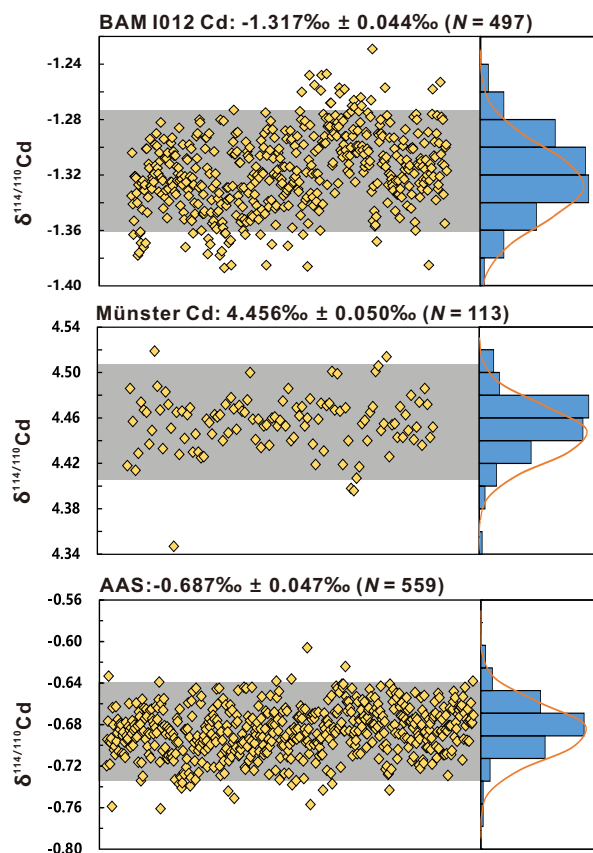


Figure 10. Long-term results for $\delta^{114/110}\text{Cd}$ of BAM I012 Cd, Münster Cd and AAS. The right panel of the figure illustrates the normal distribution for each standard.

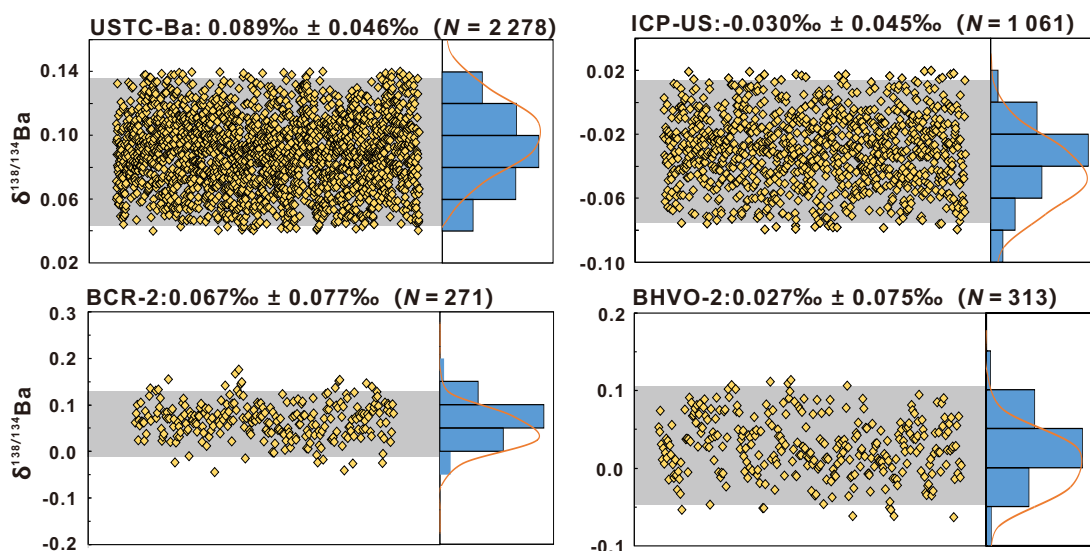


Figure 11. Long-term results for $\delta^{138/134}\text{Ba}$ of USTC-Ba, ICP-US, BCR-2 and BHVO-2. The right panel of the figure illustrates the normal distribution for each standard.

Figure 11, including two pure Ba standard USTC-Ba and ICP-US as well as six geological references BHVO-2, JB-2, BCR-2, JA-2, JCP-1, and SGR. Their 2SD values vary from 0.045‰ to 0.079‰ and the $t\text{SE}/2\text{SE}$ values are from 0.001‰ to 0.022‰. The values of these references measured by previous studies are also shown in Table S11 (Gong Y Z et al., 2020; Li et al., 2020; Liu et al., 2019; Zeng et al., 2019; Nan et al., 2018, 2015; Horner et al., 2015; Miyazaki et al., 2014).

Long-term $\delta^{238}\text{U}$ are shown in Table S12 and Figure 12, including two pure U standard ICP-U as well as two USGS geological standards BCR-2 and G-2. Their 2SD values fall in a range from 0.057‰ to 0.064‰ and the $t\text{SE}/2\text{SE}$ values are from 0.007‰ to 0.014‰. The values of these references measured by previous studies are also shown in Table S12 (Tissot et al., 2015; Weyer et al., 2008).

3 CONCLUSION

We review the stable isotope analytical methods at the MSI GL on Mg, Si, V, Fe, Cu, Zn, Rb, Sr, Ag, Cd, Ba, and U isotopes. The long-term results of inter-laboratory standards and international geological standards since 2013 are compiled. The 2SD of standards are better than 0.065‰ for $\delta^{26}\text{Mg}$ (with maximum of N , $N_{\text{max}} = 3\,738$), 0.055‰ for $\delta^{30}\text{Si}$ ($N_{\text{max}} = 772$), 0.083‰ for $\delta^{51}\text{V}$ ($N_{\text{max}} = 1\,429$), 0.054‰ for $\delta^{56}\text{Fe}$ ($N_{\text{max}} = 1\,429$), 0.066‰ for $\delta^{65}\text{Cu}$ ($N_{\text{max}} = 1\,026$), 0.058‰ for $\delta^{66}\text{Zn}$ ($N_{\text{max}} = 567$), 0.064‰ for $\delta^{87/85}\text{Rb}$ ($N_{\text{max}} = 559$), 0.000 044 for $\delta^{87}\text{Sr}/^{86}\text{Sr}$ ($N_{\text{max}} = 559$), 0.033‰ for $\delta^{88/86}\text{Sr}$ ($N_{\text{max}} = 447$), 0.116‰ for $\delta^{109}\text{Ag}$ ($N_{\text{max}} = 98$), 0.054‰ for $\delta^{114/110}\text{Cd}$ ($N_{\text{max}} = 559$), 0.079‰ for $\delta^{138/134}\text{Ba}$ ($N_{\text{max}} = 2\,278$), and 0.061‰ for $\delta^{238}\text{U}$ ($N_{\text{max}} = 68$). Our long-term results can provide a benchmark for calibration, method validation, quality control, and quality assurance for future non-traditional stable isotope studies.

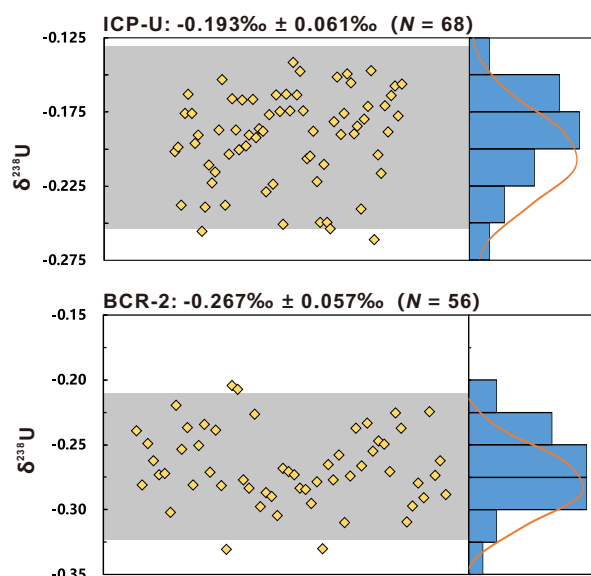


Figure 12. Long-term results for $\delta^{238}\text{U}$ of ICP-U and BCR-2. The right panel of the figure illustrates the normal distribution for each standard.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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