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An optimized protocol for high precision measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ using a Neptune Plus multi-collector inductively coupled plasma mass spectrometer: evaluation of different cone combinations for Sr isotope determination†

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Measuring $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with MC-ICP-MS is a straightforward technique due to its fast sample introduction. However, excellent accuracy and precision cannot be easily achieved unless careful optimization of plasma running conditions and evaluation of instrumental mass bias are conducted. Here, we developed an optimized protocol for measuring $^{87}\text{Sr}/^{86}\text{Sr}$ ratios using a modified cone arrangement (H skimmer cone + Jet sample cone) by carefully examining the effects of plasma working conditions on the performance of Sr isotope analysis with a Neptune Plus™ MC-ICP-MS. The modified cone arrangement significantly enhanced the Sr signal sensitivities by a factor of 2, compared to the standard cone arrangement (H skimmer cone + standard sample cone). For both cone arrangements, the mass bias of Sr isotopes fits the standard exponential law under optimal conditions. However, at non-optimum sample gas flow rates, the corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios deviated from the reference value, and thus non-linear mass bias was observed. Such mass bias could not be corrected using the standard exponential law. This observation cautioned researchers analyzing Sr ratios at optimized sample gas flow rates when using MC-ICP-MS. With further evaluation of the sample concentration, integration time and interference element correction, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio analysis with high accuracy and precision was achieved. Excellent results of the reference materials were obtained using the optimized protocol. Compared to the classical TIMS technique, our method is comparable in precision ($\sim 8 \times 10^{-6}$, 2SE) but much faster in operation (14 minutes per analysis), and therefore is a technical advance in Sr isotope geochemistry.

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1. Introduction

Strontium (Sr) has four naturally occurring isotopes, ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . Its isotope ratios, such as $^{87}\text{Sr}/^{86}\text{Sr}$, have been widely used as a robust tracer to solve a variety of scientific problems in earth and planetary sciences.¹ Precise measurement of Sr isotope ratios is fundamental but challenging. Thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) are the two available techniques for the precise determination of Sr isotope ratios.^{2,3} TIMS can yield excellent accuracy and precision ($< 1 \times 10^{-5}$ for $^{87}\text{Sr}/^{86}\text{Sr}$, 2SE), but it is cumbersome. In addition to chemical separation of Sr, time-consuming filament preparation and a degassing process are needed prior to isotope analysis using TIMS.⁴ For MC-ICP-MS,

purified Sr solutions are directly introduced into plasma, and thus its sample introduction is obviously faster. Although MC-ICP-MS is time-saving, excellent accuracy and precision cannot be easily achieved unless careful optimization of plasma running conditions and evaluation of instrumental mass bias are carried out.³ The internal precision of $^{87}\text{Sr}/^{86}\text{Sr}$ is normally $> 1 \times 10^{-5}$ during MC-ICP-MS measurement using the manufacturer's recommended conditions (200 ppb Sr content, the standard cone configuration).⁵⁻⁸

The precision of $^{87}\text{Sr}/^{86}\text{Sr}$ may be improved at higher Sr signal intensities. Measuring solutions with high Sr concentrations could improve Sr signal intensity, but tends to increase the time of washing between samples. Alternatively, high Sr signal sensitivity can be achieved by the use of the new generation Neptune Plus™ MC-ICP-MS (Thermo Electron Corp, Bremen, Germany). By combining modified skimmer and sample cone geometries with an enhanced interface pumping configuration, the Neptune Plus™ MC-ICP-MS has largely enhanced the ion sampling efficiency and overall signal sensitivity.⁹⁻¹² While the modified cones result in high signal

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Table 1 Optimal instrumental operating conditions

| | H skimmer cone + Jet sample cone | H skimmer cone + standard sample cone |
|--------------------|--|--|
| RF power | 1200 W | 1200 W |
| Guard electrode | On | On |
| Cool gas | 15 L min ⁻¹ Ar | 15 L min ⁻¹ Ar |
| Auxiliary gas | 0.80 L min ⁻¹ Ar | 0.90 L min ⁻¹ Ar |
| Sample gas | 0.75–1.0 L min ⁻¹ Ar | 0.70–1.0 L min ⁻¹ Ar |
| Z-Position | –1.25 mm | –1.25 mm |
| Extraction voltage | –2000 V | –2000 V |
| Focus | –680 V | –640 V |
| Shape | 220 V | 212 V |
| Source offset | 22 V | 22 V |
| Zoom focus | 6.5–7.5 V | 4.5–5.5 V |
| Zoom dispersion | –15 V | –15 V |
| Nebulizer | PFA microflow nebulizer (52 μL min ⁻¹) | |
| Uptake mode | Self-aspiration | |
| Sensitivity | 60–70 V ppm ⁻¹ | 30–40 V ppm ⁻¹ ⁸⁸ Sr |

sensitivity, their additional effects on the instrumental mass bias need to be evaluated.

The instrumental mass bias is element dependent. Transmission of elements was found to increase linearly with the atomic weight (especially for those above mass 40) and increasing transmission could reduce instrumental mass bias.¹³ Instrumental transmission has kept improving in recent years (*e.g.* new cone design); however, inaccuracy in isotope ratio measurements also presents. For some elements (*e.g.* Nd, Hf, W, and Hg),^{10,14–16} the use of modified cones has been shown to cause non-linear mass dependent fractionation (which cannot be corrected using the standard exponential law), and former studies ascribed this to a variety of reasons such as the cone material, cone geometry, chemical properties of the element and plasma running conditions.¹⁰ To date, however, the use of modified cones for Sr isotope measurement has remained very rare, and their effects on the instrumental mass bias must be evaluated before using modified cones for Sr isotope analysis.

Here, we developed an optimized protocol for measuring ⁸⁷Sr/⁸⁶Sr ratios using the modified cone arrangement (H skimmer cone + Jet sample cone) with a Neptune Plus™ MC-ICP-MS. We showed that the use of a modified cone arrangement could improve the Sr signal sensitivities by a factor of 2, compared to the commonly used standard cone arrangement (H skimmer cone + standard sample cone). Non-linear instrumental mass bias was observed for both cone arrangements;

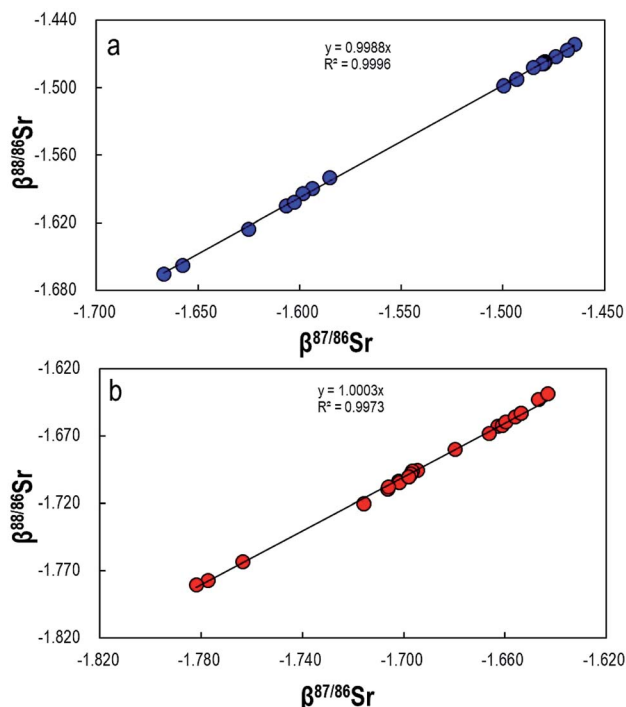


Fig. 1 $\beta^{88}\text{Sr}/^{86}\text{Sr}$ versus $\beta^{87}\text{Sr}/^{86}\text{Sr}$ for NBS 987 standard solutions (200 ng mL⁻¹ Sr) for the (a) modified cone arrangement and (b) standard cone arrangement.

however, it can be corrected at optimized sample gas flow rates. Based on careful chromatographic separation, optimization of instrumental working conditions and instrumental mass bias correction, high precision measurement of ⁸⁷Sr/⁸⁶Sr ratios (2SE < 1 × 10⁻⁵) was achieved.

2. Experimental methods

2.1 Reagents

The acids (HNO₃, HCl and HF) used here were of ultra-pure grade and purified twice by using a Savillex DST-1000 sub-boiling distillation system. 18.2 MΩ cm water (Milli-Q® Integral system) was used to prepare the solutions. NBS 987 standard solutions were purchased from the National Institute of Standards and Technology (NIST) and diluted to 200 ng mL⁻¹ in 2% nitric acid (v/v) for daily use. Plasma standard solution solutions, 13872 Rb (1000 μg mL⁻¹), 13877 Er (1000 μg mL⁻¹) and 13819 Yb (1000 μg mL⁻¹) were purchased from Alfa Aesar company, and used in the interference correction tests.

Table 2 Cup configuration and interfering elements during Sr-isotope analysis

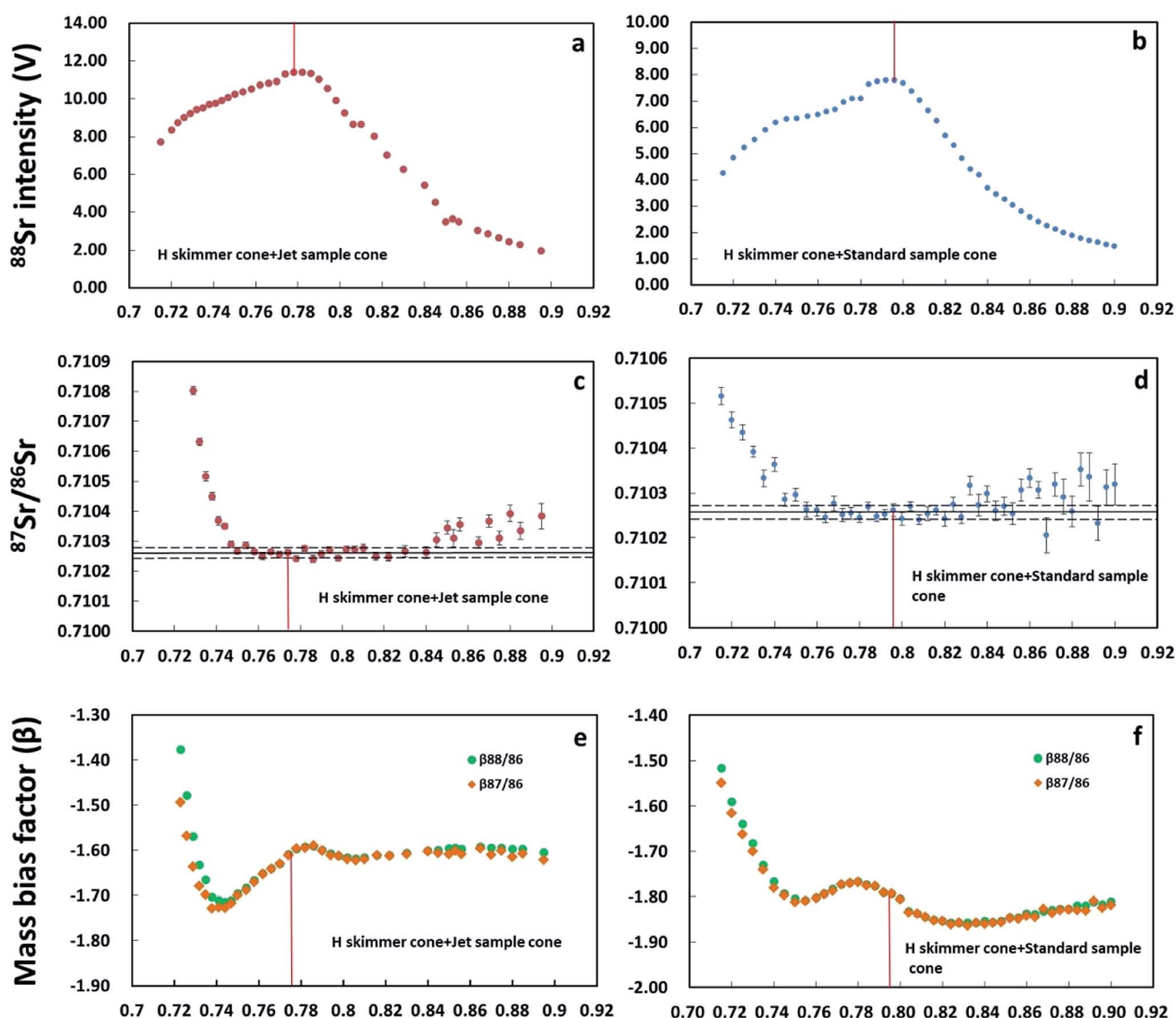
| | L4 | L3 | L2 | L1 | C | H1 | H2 | H3 |
|----------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Mass | 83 | 83.5 | 84 | 85 | 86 | 86.5 | 87 | 88 |
| Isotope of interest | ⁸³ Kr ⁺ | ¹⁶⁷ Er ²⁺ | ⁸⁴ Sr ⁺ | ⁸⁵ Rb ⁺ | ⁸⁶ Sr ⁺ | ¹⁷³ Yb ²⁺ | ⁸⁷ Rb ⁺ | ⁸⁸ Sr ⁺ |
| Interfering isotopes | ¹⁶⁶ Er ²⁺ | | ⁸⁴ Kr ⁺ | ¹⁷⁰ Er ²⁺ | ⁸⁶ Kr ⁺ | | | |
| | | | ¹⁶⁸ Er ²⁺ | ¹⁷⁰ Yb ²⁺ | | | ¹⁷⁴ Yb ²⁺ | ¹⁷⁶ Yb ²⁺ |
| | | | ¹⁶⁸ Yb ²⁺ | | ¹⁷² Yb ²⁺ | | | |

International rock standards were purchased from the United States Geological Survey.

2.2 Sample pretreatment

All the chemical procedures were performed in the class-1000 ultra-clean laboratory at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (SKLOG-IGCAS). Five standard reference materials, BCR-2 (basalt), BHVO-2 (basalt), GSP-2 (Andesite), AGV-2 (granodiorite) and RGM-2 (rhyolite), were digested using the method reported previously.^{17,18} Briefly, about 100 mg of the

sample was added into a PTFE beaker. Then, 0.3 mL HClO₄ was added to eliminate organic materials, and 1 mL HNO₃ and 2 mL HF were added. The beakers were coated with stainless steel, then the sealed bombs were heated to 190 °C in an oven for 3 days, until the solids were completely dissolved. Soon after, the beakers were screwed open, and heated on a hot plate at 180 °C for about 2 hours to evaporate residual HClO₄. The samples were then treated using 1 mL 6N HCl 2 to 3 times, and re-dissolved in 1.3 mL 2.5N HCl prior to chromatographic purification. Chromatographic work was based on a study by Yang *et al.*⁵ Briefly, a quartz column (*ca.* 100 mm × 5 mm) filled with



Sample gas flow rate (L/Min)

Fig. 2 ⁸⁸Sr intensity for the SRM 987 standard solution (200 ng mL⁻¹ Sr) measured at different sample gas flow rates for the (a) modified cone arrangement and (b) standard cone arrangement. ⁸⁷Sr/⁸⁶Sr ratios for the SRM 987 standard solution measured at different sample gas flow rates for the (c) modified cone arrangement and (d) standard cone arrangement (errors represent 2SE). Relationship between β⁸⁸Sr/⁸⁶Sr and β⁸⁷Sr/⁸⁶Sr for the (e) modified cone arrangement and (f) standard cone arrangement. The vertical solid line represents the optimum sample gas flow rate. Solid and dashed horizontal lines represent the certified value and uncertainty (2SD) of ⁸⁷Sr/⁸⁶Sr (0.710258 ± 0.000013), respectively.

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2 mL AG50W-X12 resin was applied in the chemical separation. After being pre-conditioned with 25 mL of 6 M HCl and then 2 mL of 2.5 M HCl, the supernatant solution was loaded onto the column. The resin was rinsed with 2 mL of 2.5 M HCl and 8 mL of 5 M HCl, and then the Sr fraction was eluted using 3 mL of 5 M HCl. After chemical separation, the Sr solutions were dried on a hot plate and eventually re-dissolved with 2 mL 2% (v/v) HNO₃ prior to isotope analysis.

2.3 Mass spectrometry

Sr isotope ratios were measured by using a Neptune Plus™ MC-ICP-MS at SKLODGI-CAS. Gain calibration of the Faraday cups was daily performed. 200 ng mL⁻¹ NBS987 was prepared in 2% HNO₃ (v/v), and was used for instrumental tuning. The instrumental inlet system, ion sources and zoom optics were tuned carefully to guarantee steady signals (e.g. 0.3–0.6% for RSD of beam intensity), high intensities (e.g. ~12 V or higher for ⁸⁸Sr, Jet/H cone combination) and good peak shape (it has a wide platform and is symmetric). The major instrumental parameters are summarized in Table 1. Sample solutions were introduced through a PFA micro-flow nebulizer (50 μL min⁻¹) connected to a double-Scott spray chamber (“wet” plasma mode). Instrumental blank correction was performed before each sample introduction. Sample solutions were self-aspirated for 60 s to guarantee stable signal intensities before data acquisition. The protocol involved the acquisition of 60 cycles (6 blocks × 10 cycles) with an 8 s or 4 s integration time per cycle. The total volume of the sample used for each measurement was about 450 μL. Between samples, the introduction system was rinsed with 2% HNO₃ for about 5 minutes.

2.4 Interference and mass bias correction

Kr, Rb and doubly charged Er and Yb are the major interfering elements during Sr isotope analysis. Kr usually exists in the Ar gas supply and air in the sample introduction system. ⁸³Kr was monitored to correct the interference of ⁸⁴Kr and ⁸⁶Kr on ⁸⁴Sr and ⁸⁶Sr, using natural Kr isotope ratios. ⁸⁵Rb was monitored to correct the interference of ⁸⁷Rb on ⁸⁷Sr. Residual Er and Yb were usually found in solutions after column separation, due to their similar elution curves to Sr. The doubly charged Er and Yb partly interfere with Kr, Sr and Rb due to the close mass to charge ratios. ¹⁶⁶Er²⁺ interferes with ⁸³Kr⁺, ¹⁷⁰Er²⁺ and ¹⁷⁰Yb²⁺ interfere with ⁸⁵Rb⁺, ¹⁶⁸Er²⁺, ¹⁷²Yb²⁺, ¹⁷⁴Yb²⁺, ¹⁷⁶Yb²⁺ overlap with ⁸⁴Sr⁺, ⁸⁶Sr⁺, ⁸⁷Sr⁺, ⁸⁸Sr⁺ masses by about 0.05 amu (atomic mass unit), respectively. Er and Yb were corrected by monitoring ¹⁶⁷Er²⁺ and ¹⁷³Yb²⁺ using Cup L3 (83.5 amu) and H1 (86.5 amu), respectively. All the isotopes of interest were aligned to the related cups completely by setting the center cup at mass ⁸⁶Sr⁺ (85.909 amu). Cup configurations are shown in Table 2.

The data correction method was based on a study by Yang *et al.*,⁵ and a brief description is given below. The interference from doubly charged Er and Yb was primarily corrected due to their influences on both elements of interest and other interfering elements. Pure 13877 Er and 13819 Yb solutions of 10 μg mL⁻¹ were analyzed to obtain the measured Er and Yb ratios (e.g. ¹⁶⁶Er²⁺/¹⁶⁷Er²⁺, ¹⁶⁸Yb²⁺/¹⁷³Yb²⁺) at the beginning of an

analytical session. These ratios and the intensities of ¹⁶⁷Er²⁺ and ¹⁷³Yb²⁺ were used in the interference correction of Er and Yb. The interference of ⁸⁴Kr and ⁸⁶Kr on ⁸⁴Sr and ⁸⁶Sr was then corrected by monitoring ⁸³Kr⁺ and using natural Kr isotope ratios (⁸³Kr/⁸⁴Kr = 0.20175, ⁸³Kr/⁸⁶Kr = 0.66474).¹⁹ The

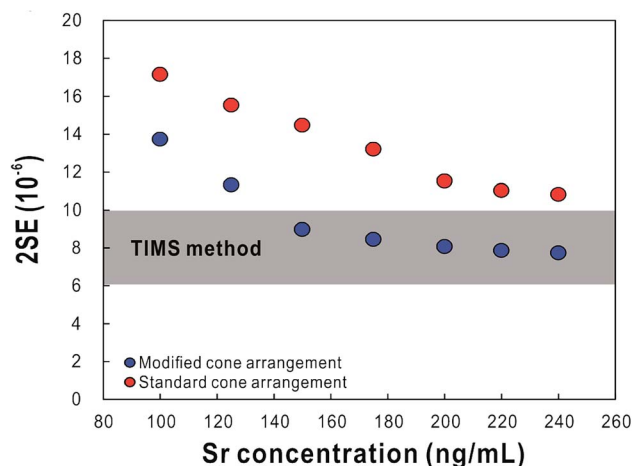


Fig. 3 2SE of ⁸⁷Sr/⁸⁶Sr for the NBS 987 standard solution with different Sr concentrations using the modified cone arrangement and standard cone arrangement. The gray area represents the typical precision of the classical TIMS method.

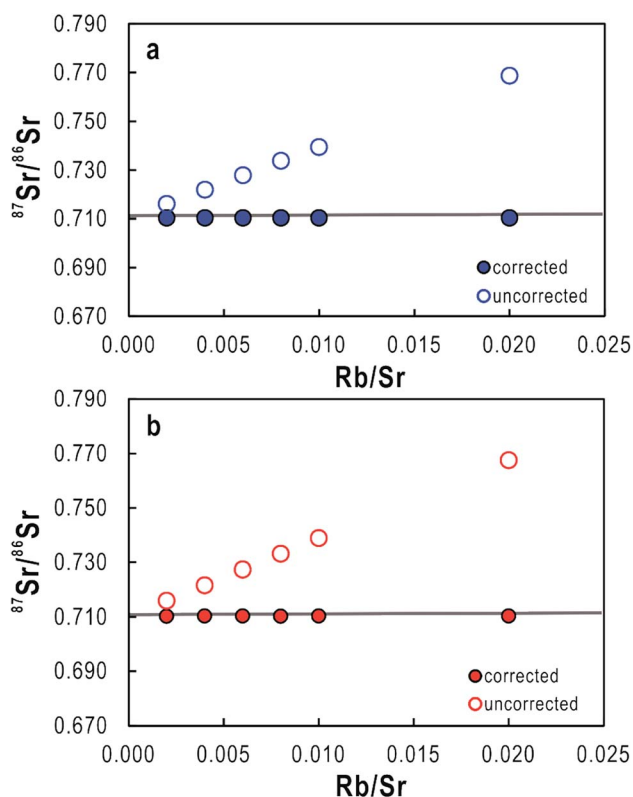


Fig. 4 ⁸⁷Sr/⁸⁶Sr of the NBS 987 standard solutions (200 ng mL⁻¹ Sr) with different Rb/Sr ratios using both the modified cone arrangement (a) and standard cone arrangement (b). Solid horizontal line represents the certified value of ⁸⁷Sr/⁸⁶Sr (0.710258).

interference of ^{87}Rb on ^{87}Sr was corrected using an empirical Rb ratio (see more details in section 3.5),²⁰ assuming Rb and Sr have the same instrumental mass bias. After all the interfering elements were corrected, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was internally normalized to a $^{88}\text{Sr}/^{86}\text{Sr}$ of 8.375209¹⁹ using the exponential law as shown in the following equations.²¹

$$\beta = (R_{\text{ref}}/R_{\text{meas}})/\ln(M_{88}/M_{86}) \quad (1)$$

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{corr}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{meas}} \times (M_{87}/M_{86})^{\beta} \quad (2)$$

where β is the mass bias factor; R_{ref} and R_{meas} are the reference and measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratios of the NBS 987 standard solution, respectively; and M_{88} and M_{86} are the atomic mass units of ^{88}Sr and ^{86}Sr , respectively. Raw data were processed offline and corrected using a self-written Microsoft Excel 2010 program.

3. Results and discussion

3.1 Signal sensitivities

The Sr signal sensitivities were tested using the standard cone arrangement (H skimmer cone + standard sample cone) and modified cone arrangement (H skimmer cone + Jet sample cone), based on the NBS 987 standard solution (200 ng mL⁻¹ Sr in 2% HNO₃). After careful tuning, the standard cone

arrangement resulted in maximum ^{88}Sr sensitivities of 30–40 V per $\mu\text{g mL}^{-1}$ Sr at 50 $\mu\text{L min}^{-1}$ uptake, which was comparable with that of previous results.⁵ The modified cone arrangement resulted in maximum ^{88}Sr sensitivities typically about 60–70 V per $\mu\text{g mL}^{-1}$ Sr at 50 $\mu\text{L min}^{-1}$ uptake, twice higher than that for the standard cone arrangement.

3.2 Instrumental mass bias

Based on running NBS 987 solutions (200 ng mL⁻¹ Sr), the instrument was tuned to optimize the Sr sensitivity and peak shape, and the instrumental mass bias factors (β) were evaluated for the two cone arrangements, using the exponential law (eqn (1)). As shown in Fig. 1a, the standard cone arrangement followed the exponential law, consistent with previous observations.^{6,20} The H skimmer cone + Jet sample cone also showed no anomalous instrumental mass bias (Fig. 1b), *i.e.*, the β for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ perfectly matched with each other. Thus, under optimal instrumental conditions, the instrumental mass bias for both cone arrangements could be corrected using the standard exponential law.

Additionally, we evaluated the instrumental mass bias under non-optimal instrumental conditions. The sample gas flow rates were adjusted to higher or lower flow rates, which resulted in lower Sr sensitivities, to test whether the standard

Table 3 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of standard reference materials

| Sample name | $^{85}\text{Rb}^+$ [mV] | $^{167}\text{Er}^2$ [mV] | $^{173}\text{Yb}^{2+}$ [mV] | $^{88}\text{Sr}^+$ [V] | $^{87}\text{Sr}/^{86}\text{Sr}$ (2SE) corrected | $^{87}\text{Sr}/^{86}\text{Sr}$ (2SD) Reference value |
|--------------------------|-------------------------|--------------------------|-----------------------------|------------------------|---|---|
| BCR-2 | 0.407 | 0.204 | 0.042 | 12.3 | 0.705012 ± 0.000008 | 0.705019 ± 0.000016 ^a |
| BCR-2 | 0.412 | 0.221 | 0.041 | 13.0 | 0.705026 ± 0.000008 | 0.705003 ± 0.000016 ^b |
| BCR-2 | 0.402 | 0.215 | 0.045 | 12.7 | 0.705016 ± 0.000009 | 0.705015 ^c |
| BCR-2 | 0.419 | 0.219 | 0.037 | 12.5 | 0.705005 ± 0.000008 | |
| Mean (2SD) | | | | | 0.705015 ± 0.000018 (n = 4) | |
| BHVO-2 | 0.212 | 0.197 | 0.052 | 13.3 | 0.703488 ± 0.000008 | 0.703479 ± 0.000020 ^a |
| BHVO-2 | 0.203 | 0.203 | 0.056 | 13.5 | 0.703479 ± 0.000009 | 0.703469 ± 0.000014 ^b |
| BHVO-2 | 0.217 | 0.201 | 0.051 | 12.9 | 0.703491 ± 0.000008 | 0.703487 ^d |
| BHVO-2 | 0.208 | 0.207 | 0.046 | 13.1 | 0.703483 ± 0.000009 | |
| Mean (2SD) | | | | | 0.703485 ± 0.000011 (n = 4) | |
| GSP-2 | 0.412 | 0.301 | 0.035 | 12.5 | 0.765179 ± 0.000008 | 0.765144 ± 0.000075 ^a |
| GSP-2 | 0.405 | 0.307 | 0.031 | 12.8 | 0.765161 ± 0.000009 | 0.765175 ± 0.000013 ^e |
| GSP-2 | 0.417 | 0.297 | 0.037 | 12.3 | 0.765168 ± 0.000009 | 0.765177 ± 0.000013 ^f |
| GSP-2 | 0.411 | 0.300 | 0.032 | 11.8 | 0.765172 ± 0.000008 | |
| Mean (2SD) | | | | | 0.765170 ± 0.000013 (n = 4) | |
| AGV-2 | 0.066 | 0.055 | 0.012 | 13.1 | 0.703977 ± 0.000009 | 0.703981 ± 0.000009 ^a |
| AGV-2 | 0.053 | 0.059 | 0.011 | 13.5 | 0.703989 ± 0.000009 | 0.703988 ± 0.000012 ^e |
| AGV-2 | 0.061 | 0.063 | 0.015 | 13.3 | 0.703992 ± 0.000008 | |
| AGV-2 | 0.052 | 0.053 | 0.017 | 12.8 | 0.703985 ± 0.000009 | |
| Mean (2SD) | | | | | 0.703986 ± 0.000011 (n = 4) | |
| RGM-2 | 0.401 | 0.311 | 0.023 | 13.1 | 0.704225 ± 0.000007 | 0.704210 ± 0.000014 ^a |
| RGM-2 | 0.423 | 0.323 | 0.025 | 13.5 | 0.704221 ± 0.000009 | 0.704227 ± 0.000018 ^e |
| RGM-2 | 0.421 | 0.305 | 0.019 | 13.2 | 0.704201 ± 0.000008 | |
| RGM-2 | 0.412 | 0.313 | 0.022 | 12.8 | 0.704203 ± 0.000009 | |
| Mean (2SD) | | | | | 0.704215 ± 0.000011 (n = 4) | |
| Mean NBS987 (2SD) | | | | | 0.710258 ± 0.000011 (n = 18) | 0.710266 ^g 0.710260 ^h 0.710250 ⁱ |

^a Reference value from Weis *et al.* (2006).¹⁷ ^b Reference value from Elburg *et al.* (2005).²⁴ ^c Reference value from Balcaen *et al.* (2005).⁷ ^d Reference value from Raczek *et al.* (2003).²⁵ ^e Reference value from Yang *et al.* (2014).^{5,f} ^f Reference value from Li *et al.* (2012).²⁸ ^g Reference value from Muynck *et al.* (2009).²⁶ ^h Reference value from Ehrlich *et al.* (2001).²⁰ ⁱ Reference value from Monna *et al.* (1998).²⁷

exponential law could still be used for mass bias correction. For both cone arrangements, decreases in Sr signal intensities and large 2SE values of $^{87}\text{Sr}/^{86}\text{Sr}$ were observed at non-optimum sample gas flow rates (Fig. 2a–d). Taking the 2SE values into consideration, the $^{87}\text{Sr}/^{86}\text{Sr}$ of NBS 987 solutions was still deviated from the certified value at non-optimum sample gas flow rates (Fig. 2c and d). More importantly, the deviations could not be corrected using the standard exponential law, suggesting that non-linear mass dependent fractionation occurred. For both cone arrangements, the $\beta^{88}\text{Sr}/^{86}\text{Sr}$ and $\beta^{87}\text{Sr}/^{86}\text{Sr}$ separated from each other at lower or higher sample gas flow rates (Fig. 2e and f). Non-linear mass dependent fractionation has been previously observed during the measurement of many elements using MC-ICP-MS.^{10,14,15} In this study, we demonstrated that non-linear mass dependent fractionation and erroneous determination of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may occur at non-optimum sample gas flow rates. This is consistent with some previous studies,^{10,14,22} which also demonstrated that instrumental mass bias could be affected by sample gas flow rates. However, it should be noted that the non-linear mass dependent fractionation during isotope analysis is quite complicated, and needs further investigation.²³ If we optimize the plasma conditions that could minimize non-linear mass bias to ~ 0 , we could still obtain accurate $^{87}\text{Sr}/^{86}\text{Sr}$ using the standard exponential law. Note that plasma conditions change with time, and we caution researchers monitoring mass bias by measuring NIST987 solutions every 10 samples in an analytical session.

3.3 Optimization of integration time

Based on the NBS 987 solution (200 ng mL⁻¹ Sr), we tested the effect of integration time on the analytical precision of $^{87}\text{Sr}/^{86}\text{Sr}$ using the two cone arrangements. Two protocols of data integration were evaluated: 4 s per cycle \times 60 cycles and 8 s per cycle \times 60 cycles. Compared with the standard cone arrangement, the use of the modified cone arrangement resulted in 26% and 30% decreases in 2SE for the “4 s per cycle \times 60 cycles” and “8 s per cycle \times 60 cycles” protocols, respectively. Compared with the “4 s per cycle \times 60 cycles” protocol, the “8 s per cycle \times 60 cycles” protocol resulted in 19% and 23% decreases in 2SE for the standard cone arrangement and modified cone arrangement, respectively. Longer integration time may result in a higher Sr background. In this study, the “8 s per cycle \times 60 cycles” protocol did not significantly increase the Sr background level, and therefore was chosen as the optimized integration time.

3.4 Optimization of Sr concentration

Based on the “8 s per cycle \times 60 cycles” protocol, we further tested the 2SE of $^{87}\text{Sr}/^{86}\text{Sr}$ for the NBS 987 solution at varying concentrations (100 to 240 ng mL⁻¹ Sr). As shown in Fig. 3, the 2SE of $^{87}\text{Sr}/^{86}\text{Sr}$ for both cone arrangements decreased as the Sr concentrations increased, but the decrease tended to be limited after the Sr concentrations were >200 ng mL⁻¹. At the same Sr concentrations, the modified arrangement showed much smaller 2SE of $^{87}\text{Sr}/^{86}\text{Sr}$, compared to the standard cone arrangement. Considering higher Sr concentrations (>200 ng

mL⁻¹) did not significantly improve the 2SE of $^{87}\text{Sr}/^{86}\text{Sr}$, but resulted in increasing time of washing, we considered 150 to 200 ng mL⁻¹ as the optimized Sr concentrations. At optimized integration time (8 s per cycle \times 60 cycles) and Sr concentrations (150 to 200 ng mL⁻¹), the 2SE of $^{87}\text{Sr}/^{86}\text{Sr}$ for the H skimmer cone + Jet sample cone arrangement was at the same level as the TIMS technique.

3.5 Interfering elements

We evaluated the influence of interfering elements (Kr, Rb, Er, and Yb) during $^{87}\text{Sr}/^{86}\text{Sr}$ measurement. The signal intensities of ^{83}Kr for both cone arrangements were around 0.05 mV on a daily basis. Based on ^{83}Kr intensities, the limited interference of ^{84}Kr and ^{86}Kr on ^{84}Sr and ^{86}Sr was corrected using natural Kr ratios ($^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$, $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$).

By adding different amounts of the 13872 Rb standard to NBS 987 solutions (200 ng mL⁻¹ Sr), we evaluated the interference of Rb on Sr isotopes, using the correction method mentioned in section 2.4. When a reference $^{87}\text{Rb}/^{85}\text{Rb}$ value of 0.385705 (ref. 19) was applied, our method was effective for samples with Rb/Sr < 0.004 and 0.008 for the modified and standard cone arrangement respectively. To improve the effectiveness of Rb correction in our method, we applied an empirical $^{87}\text{Rb}/^{85}\text{Rb}$ value of 0.3860 suggested in a previous study.²⁰ As shown in Fig. 4a and b, when this empirical value

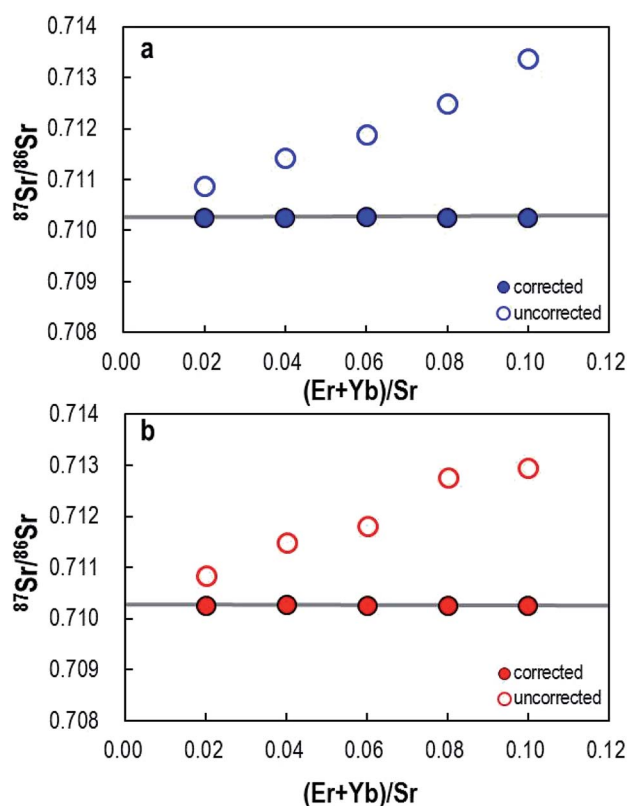


Fig. 5 $^{87}\text{Sr}/^{86}\text{Sr}$ of NBS 987 standard solutions (200 ng mL⁻¹ Sr) with different (Er + Yb)/Sr ratios measured using the modified cone arrangement (a) and standard cone arrangement (b). Solid horizontal lines represent the certified value of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.710258), respectively.

was used, our method accurately corrected the interference of Rb for samples with Rb/Sr ratios up to 0.02, for both cone arrangements. What should be noted is that the empirical $^{87}\text{Rb}/^{85}\text{Rb}$ ratio did not deviate beyond the 2σ of the reference value. Rb was effectively removed after purification, as suggested by the low signal intensities of Rb in Table 3. All the rock standards have Rb/Sr ratios much less than that required by our method. Thus, the interference of Rb could be easily corrected.

Different amounts of 13877 Er and 13819 Yb standards were added to NBS 987 solutions ($200 \text{ ng mL}^{-1} \text{ Sr}$), to address the influence of doubly charged Er and Yb on Sr analysis, using the correction method mentioned in section 2.4. For the modified and standard cone arrangement, our correction was effective in samples with $(\text{Er} + \text{Yb})/\text{Sr}$ up to 0.10, as illustrated in Fig. 5a and b respectively. As shown in Table 3, significantly low $(\text{Er} + \text{Yb})/\text{Sr}$ ratios of <0.006 were confirmed for rock standards after

purification. These ratios were far below the requirement suggested by our experiment. Thus the interference of Er and Yb could be easily corrected for samples after purification.

3.6 $^{87}\text{Sr}/^{86}\text{Sr}$ of certified reference materials

Using our optimized protocol (integration time: 8 s per cycle \times 60 cycles; Sr concentration: 200 ng mL^{-1}), standard reference materials (BCR-2, BHVO-2, GSP-2, AGV-2 and RGM-2) were measured based on the modified cone arrangement. As shown in Table 3 and Fig. 6, the results of these reference materials well agreed with those of previous studies.^{5,7,17,20,24–28} The precision of our method ($2\text{SE}: 8 \times 10^{-6}$ for $^{87}\text{Sr}/^{86}\text{Sr}$) was comparable with that of the classical TIMS technique but better than that of previous methods based on MC-ICP-MS.^{5–8} With 8 min data acquisition (8 s integration \times 60 cycles), 5 min wash out and 1 min for solution uptake/stabilization, a typical

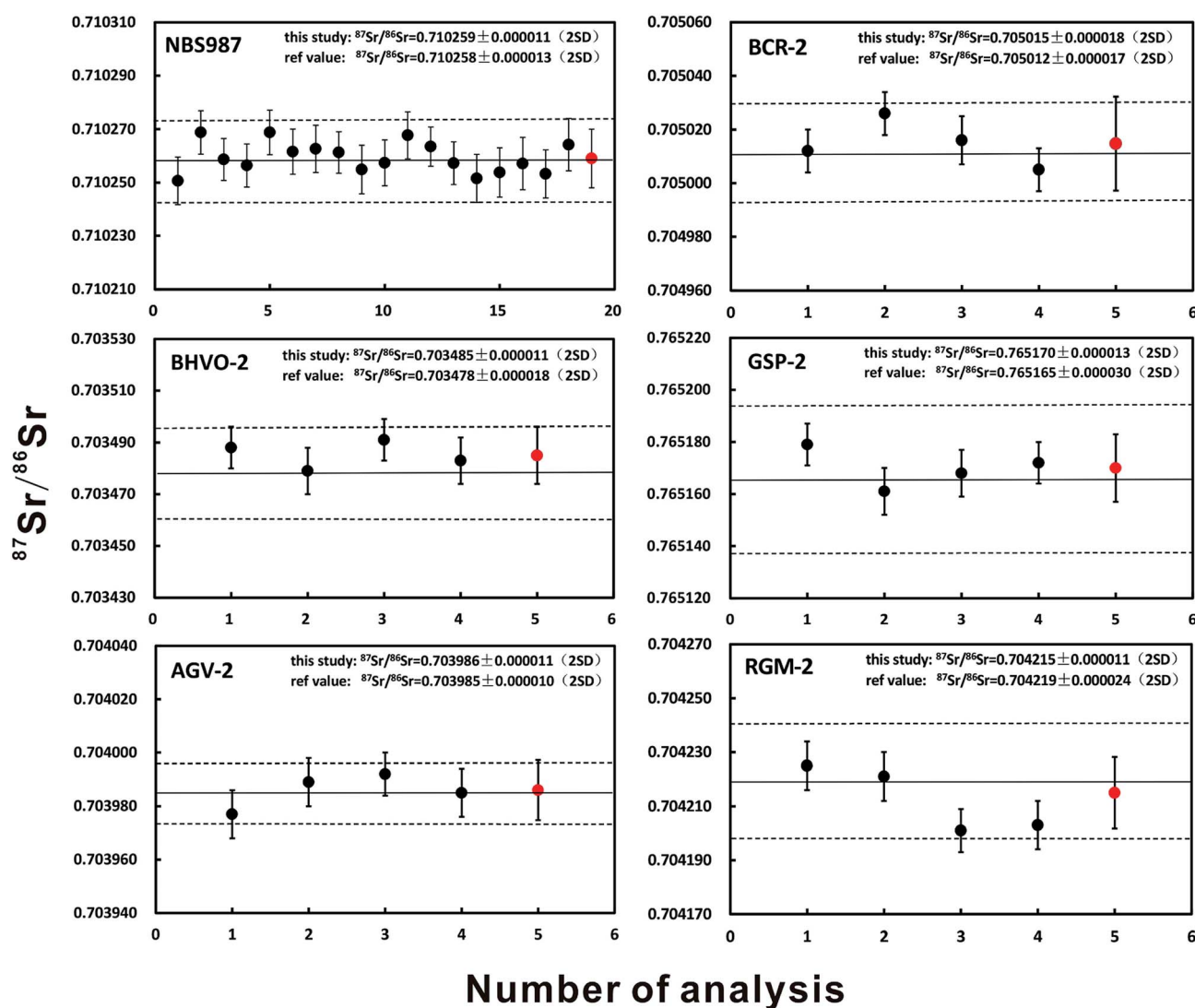


Fig. 6 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the standard reference materials measured by our modified method. Solid and dashed horizontal lines represent the certified value and uncertainty (2SD) of $^{87}\text{Sr}/^{86}\text{Sr}$, respectively. Black circles represent the measured $^{87}\text{Sr}/^{86}\text{Sr}$ of an individual test (errors represent 2SE). Red circles represent the average $^{87}\text{Sr}/^{86}\text{Sr}$ of all the tests in this study (errors represent 2SD).

analysis using our method took about 14 minutes, which was much faster than the TIMS technique (1 hour per analysis).

4. Conclusions

The optimized protocol for high precision measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios using a Neptune Plus™ MC-ICP-MS with a modified cone arrangement (H skimmer cone + Jet sample cone) was established. We demonstrated that with complete chromatographic separation to remove the interfering elements (Rb, Er and Yb), careful instrumental optimization (especially sample gas flow rates) and mass bias correction, the use of the modified cone arrangement enabled the excellent accuracy and precision of $^{87}\text{Sr}/^{86}\text{Sr}$ that were comparable with those of the classical TIMS technique. However, we cautioned that failure to do the above may lead to erroneous results. Considering the straightforward and time-saving character of MC-ICP-MS, our study is an advance in Sr isotope geochemistry.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 G. Faure and J. L. Powell, *Strontium Isotope Geology*, Springer Science & Business Media, 2012.
- 2 R. Avanzinelli, E. Boari, S. Conticelli, L. Francalanci, L. Guarnieri, G. Perini, C. M. Petrone, S. Tommasini and M. Ulivi, *Period. Mineral.*, 2005, **75**, 147–166.
- 3 L. Yang, *Mass Spectrom. Rev.*, 2009, **28**, 990–1011.
- 4 G. Faure and T. M. Mensing, *Isotopes: Principles and Applications*, Wiley-Blackwell, 2005.
- 5 Y.-H. Yang, F.-Y. Wu, L.-W. Xie, Z.-Y. Chu and J.-H. Yang, *Spectrochim. Acta, Part B*, 2014, **97**, 118–123.
- 6 T. Waight, J. Baker and D. Peate, *Int. J. Mass Spectrom.*, 2002, **221**, 229–244.
- 7 L. Balcaen, I. De Schrijver, L. Moens and F. Vanhaecke, *Int. J. Mass Spectrom.*, 2005, **242**, 251–255.
- 8 A. J. Wall, R. C. Capo, B. W. Stewart, T. T. Phan, J. C. Jain, J. A. Hakala and G. D. Guthrie, *J. Anal. At. Spectrom.*, 2013, **28**, 1338–1344.
- 9 A. Makishima and E. Nakamura, *J. Anal. At. Spectrom.*, 2010, **25**, 1712–1716.
- 10 Z. Hu, Y. Liu, S. Gao, W. Liu, W. Zhang, X. Tong, L. Lin, K. Zong, M. Li and H. Chen, *J. Anal. At. Spectrom.*, 2012, **27**, 1391–1399.
- 11 N. Lloyd, A. Trinquier and C. Bouman, *AGU Fall Meeting Abstracts*, 2013.
- 12 M. He, Z. Jin, H. Lu, L. Deng and C. Luo, *Int. J. Mass Spectrom.*, 2016, **408**, 33–37.
- 13 F. Albarède, E. Albalat and P. Télouk, *J. Anal. At. Spectrom.*, 2015, **30**, 1736–1742.
- 14 L. Xu, Z. Hu, W. Zhang, L. Yang, Y. Liu, S. Gao, T. Luo and S. Hu, *J. Anal. At. Spectrom.*, 2015, **30**, 232–244.
- 15 N. Shirai and M. Humayun, *J. Anal. At. Spectrom.*, 2011, **26**, 1414–1420.
- 16 R. Yin, D. P. Krabbenhoft, B. A. Bergquist, W. Zheng, R. F. Lepak and J. P. Hurley, *J. Anal. At. Spectrom.*, 2016, **31**, 2060–2068.
- 17 D. Weis, B. Kieffer, C. Maerschalk, J. Barling, J. de Jong, G. A. Williams, D. Hanano, W. Pretorius, N. Mattielli and J. S. Scoates, *Geochem., Geophys., Geosyst.*, 2006, **7**.
- 18 Z. C. Hu and L. Qi, *15.5-Sample Digestion Methods, Treatise on Geochemistry*, Elsevier, Oxford, 2nd edn, 2014, pp. 87–109.
- 19 K. Rosman and P. Taylor, *Pure Appl. Chem.*, 1998, **70**, 217–235.
- 20 S. Ehrlich, I. Gavrieli, L.-B. Dor and L. Halicz, *J. Anal. At. Spectrom.*, 2001, **16**, 1389–1392.
- 21 W. Russell, D. Papanastassiou and T. Tombrello, *Geochim. Cosmochim. Acta*, 1978, **42**, 1075–1090.
- 22 H. Andrén, I. Rodushkin, A. Stenberg, D. Malinovsky and D. C. Baxter, *J. Anal. At. Spectrom.*, 2004, **19**, 1217–1224.
- 23 L. Yang, S. Tong, L. Zhou, Z. Hu, Z. Mester and J. Meija, *J. Anal. At. Spectrom.*, 2018, **33**, 1849–1861.
- 24 M. Elburg, P. Vroon, B. van der Wagt and A. Tchalikian, *Chem. Geol.*, 2005, **223**, 196–207.
- 25 I. Raczek, K. P. Jochum and A. W. Hofmann, *Geostand. NewsL.*, 2003, **27**, 173–179.
- 26 D. De Muynck, G. Huelga-Suarez, L. Van Heghe, P. Degryse and F. Vanhaecke, *J. Anal. At. Spectrom.*, 2009, **24**, 1498–1510.
- 27 F. Monna, J.-L. Loizeau, B. Thomas, C. Guéguen and P.-Y. Favarger, *Spectrochim. Acta, Part B*, 1998, **53**, 1317–1333.
- 28 C.-F. Li, X.-H. Li, Q.-L. Li, J.-H. Guo, X.-H. Li and Y.-H. Yang, *Anal. Chim. Acta*, 2012, **727**, 54–60.