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Precise determination of triple Sr isotopes (δ^{87}Sr and δ^{88}Sr) using MC-ICP-MS

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A B S T R A C T

The non-traditional stable strontium (Sr) isotopes have received increasing attention recently as new geochemical tracers for studying Sr isotopic fractionation and source identification. This has been attributed to the advancement in multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), allows to determine precisely and simultaneously of the triple Sr isotopes. In this study, we applied a modified empirical external normalization (EEN) MC-ICPMS procedure for mass bias correction in Sr isotopic measurement using ^{92}Zr/^{90}Zr. High-purity Zr Standard was spiked into sample solutions and the degree of fractionation was calculated off-line using an exponential law. The long-term external reproducibility for NIST SRM 987 δ^{87}Sr and δ^{88}Sr was better than 0.040‰ and 0.018‰ (2SD), respectively. The IAPSO standard seawater was used as a secondary standard to validate the analytical protocol and the absolute ratios measured were 0.709161 ± 0.000018 for ^{87}Sr/^{86}Sr, 0.177 ± 0.021‰ for δ^{87}Sr, and 0.370 ± 0.026‰ for δ^{88}Sr (2SD, $n = 7$). These values are in good agreement with the literature data analyzed by thermal ionization mass spectrometry (TIMS) double spike technique. Rock standards, BHVO-2, BCR-2 and AGV-2 were also analyzed to validate the robustness of the methodology and showed identical results with literature data. Compared to previous ^{91}Zr/^{90}Zr correction, we obtained improved results based on ^{92}Zr/^{90}Zr, probably due to similar mass difference between ^{92}Zr/^{90}Zr and measured Sr isotopes. The new analytical protocol presented in this study not only improves the analytical precision but also increases sample efficiency by omitting the use of the standard-sample bracketing (SSB) procedure.

1. Introduction

Strontium (Sr) has four natural occurring stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, where ^{87}Sr is a radiogenic product of Rubinium-87 (^{87}Rb) through beta decay (half-life = 48.8 Ga [1]). Representing time-integrated Rb/Sr ratios of the sources, the ^{87}Sr/^{86}Sr ratios of the weathering products, dissolved loads and suspension particles in rivers, have been used for provenance identification [2–4]. Silicate minerals in igneous and sedimentary rocks are generally characterized by ^{87}Sr/^{86}Sr ratios of <0.706 and >0.710, respectively. In contrast, the ^{87}Sr/^{86}Sr ratios of carbonates were in equilibrium with that of coexisting seawater, ranging from 0.707 to 0.709 in geological past [1]. Since chemical weathering of silicate minerals is thought to provide the feedback for moderating the long-term global climate, the differences in the ^{87}Sr/^{86}Sr ratios of source rocks/minerals make the ^{87}Sr/^{86}Sr ratios of the weathering products useful for estimating the relative contributions from a variety of sources. Changes in fluxes of continental weathering during the glacial–interglacial cycles in Quaternary (a ~100 ky periodicity in past few million years) have been reported to cause significant imbalance of oceanic Sr budgets [5]. However, the non-steady-state weathering of Sr cycles is dynamic and difficult to quantify by radiogenic Sr isotopes alone. The interpretation of past changes in the marine Sr budgets by the use of radiogenic Sr isotopes has faced a three-fold challenge: (1) the main difficulty due to the similar ^{87}Sr/^{86}Sr values in marine carbonates, the major oceanic Sr sink [1], and seawater (2) inability to constrain past weathering intensity and (3) co-occurrence of silicate and carbonate Sr-bearing minerals, containing high ^{87}Sr/^{86}Sr due to their high Rb/Sr in source rocks [3,6]. Further, the preferential release of Sr from mineral phases that is more susceptible to weathering during the incongruent weathering reactions may complicate the interpretation and raised uncertainties for assessing contribution from silicate and carbonate rocks [7]. Consequently, the Sr budgets in weathering products cannot be evaluated un-ambiguously and hamper the attempt to delineate the relationships between paleo-climate and exogenic weathering processes.

Fractionation of Sr stable isotopes (δ^{88}Sr) has attracted attention recently due to the technical development using MC-ICP-MS for Sr isotopic measurements [8–10]. The ^{88}Sr/^{86}Sr ratio in unknown

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samples are normalized to the international certified reference materials (iCRMs), NIST SRM 987, in this study where δ^{88}Sr is defined as Eq. (1):

$$\delta^{88}\text{Sr} = \left[\frac{(^{88}\text{Sr}/^{86}\text{Sr})_{\text{sample}}}{(^{88}\text{Sr}/^{86}\text{Sr})_{\text{NIST 987}}} - 1\right] \times 1000\,(‰) \qquad (1)$$

Significant Sr isotopic fractionation has been observed in nature specimens. For instance, ∼ +0.27‰ in bulk silicate earth materials [11], ∼ +0.38‰ in IAPSO standard seawater [12] and +0.20–0.30‰ in modern marine carbonates [9,12]. For a complete evaluation of marine Sr budgets, fluxes in all related sources and sinks should be taken into consideration. The application of stable Sr isotopes coupled with radiogenic Sr isotopic system offers an opportunity to delineate the abovementioned challenges and to better constrain the oceanic Sr budgets. Various degree of δ^{88}Sr fractionation may have experienced between seawater and marine carbonates, this allows to study Sr sources or sinks simultaneously [8]. An improved δ^{88}Sr measurement technique is critical for the new applications.

Mass discrimination artifacts on MC-ICP-MS can bias the measured isotope ratios from true values significantly. Instrumental discrimination at different masses known as the mass bias effect and matrix-dependent induced interferences on MC-ICP-MS can cause the measured isotope ratios to deviate from the actual values [14]. For instance, preference transport of heavier isotopes from the ion source to the Faraday cups results in up to 10% deviations for elements with mass numbers <10 amu and 1–5% for other heavier elements [15]. Several studies have applied the standard-sample bracketing (SSB) procedure to eliminate the mass bias effect by using two adjacent standards to correct mass bias of samples during MC-ICP-MS determination. However, the SSB method cannot correct completely the short-term drift during measurements [12,16]. Recently an empirical external normalization (EEN) combined with SSB method has been developed to reduce random fluctuation of mass bias [9,10,17,18]. Although ^{91}Zr/^{90}Zr EEN combined with SSB method has been developed for mass bias correction in δ^{88}Sr MC-ICP-MS measurements, mass-dependent isotopic discrimination between ^{91}Zr/^{90}Zr and ^{88}Sr/^{86}Sr are debatable [10]. Utilization of SSB method alone may not be able to obtain accurate and precise ^{87}Sr/^{86}Sr* (^{87}Sr/^{86}Sr without ^{88}Sr/^{86}Sr normalization) and ^{88}Sr/^{86}Sr ratios.

In this study, we present a modified procedure to apply ^{92}Zr/^{90}Zr instead of ^{91}Zr/^{90}Zr for mass bias correction in MC-ICP-MS Sr isotope determinations. The modified EEN technique eliminates significant scattering of the mass bias correction and improves the precision for Sr isotopic determination more than a factor of 1.5 compared with the analytical protocol of Yang et al. [10]. This new procedure allows ^{87}Sr/^{86}Sr, δ^{87}Sr and δ^{88}Sr to be measured simultaneously with high throughput, due to omit of SSB procedure.

2. Experimental

2.1. Materials and reagents

In order to reduce the Sr chemical blank, and eliminate potential interferences in the isotopic measurements, all experiments were conducted inside a class-1000 clean room at the Earth Dynamic System Research Center at National Cheng Kung University. The chemical separation procedures were performed under a class-10 flow bench with constant temperature and moisture control. In addition, HCl and HNO_3 acids purified from GR grade reagents by twice sub-boiling distillation and ∼18.2 ΩM-grade Milli-Q water prepared by Elix 5 system (Millipore, Bedford, MA, USA) were used. An extraction chromatography technique, Sr Spec resin (Eichrom Technologies, Darien, USA), was chosen for separation and purification of Sr from complex sample matrix [19].

Two Sr stock solutions (150 ng g^{-1} in 5% HNO_3 acid) from High-Purity Standards (USA) and NIST SRM 987 (prepared from strontium carbonate powder, NIST, USA) were used as isotopic reference standards and as bracketing standards during Sr isotopic measurements. Four commercial Zr solution standards selected from High-Purity Standards (USA), Fluka (Japan), Merck (Germany) and NIST SRM 3169 (USA) were spiked with 300 ng g^{-1} Zr as calibrators for mass bias correction. A published seawater standard, IAPSO (OSIL), was used for analytical protocol validation and direct comparison with the available literature data. This methodology was applied to measure ^{87}Sr/^{86}Sr, δ^{87}Sr and δ^{88}Sr in three reference materials, two basalt powders, BHVO-2 and BCR-2, and one andesite powder AGV-2 (all of them are obtained from USGS, USA).

2.2. Sample preparation and ion chromatography

A 100 mg of rock powder was dissolved in a HF-HNO_3 mixture (1:2) at 190 °C in a high-pressure bomb for at least 24 h, followed by sequential procedure of evaporating to dryness, dissolution in HCl, and conversion to HNO_3 form. The final step was a 100-fold dilution in ∼2% HNO_3 solution. 450 ng Sr from seawater (IAPSO), dissolved strontium carbonate (NIST SRM 987) and digested rock standards were evaporated on hot plate at 90 °C to dryness and then re-dissolved in 0.5 ml 3 N HNO_3 for column separation. Acid-cleaned polypropylene columns with inner diameter of 5–5.5 mm were loaded with 0.25 ml Eichrom Sr Spec resins (50–100 mesh) to isolate Sr from potential interference elements. Before sample loading, the resin was washed using 3 ml 3 N HNO_3, 3 ml Milli-Q water, and 5 ml 6 N HCl in sequence, and then preconditioned with 1 ml 3 N HNO_3. The sample solution was carefully loaded into the column and then Zr and Rb were removed effectively by the first 3 ml 3 N HNO_3. The Sr fraction was eluted with 4 ml Milli-Q water and collected for MC-ICPMS analyses. These chemical procedures were cross-checked using IAPSO, carbonate matrix multi-elements standard (Ca:Na:Mg:Sr:Zr = 100:2:1:1:1) and BHVO-2 rock matrix standard to evaluate the elution curve under various matrices. These evaluations show identical results and support strongly of our matrix removal ion chromatography. Most of major cations, Na, Mg, Ca and K, Rb and Zr were removed in the first 3 ml of 3 N HNO_3. The Sr yields after ion chromatography were evaluated using HR-ICP-MS (Element 2, Thermo-Fisher Scientific) and showed high reproductivity, close to 100% [20]. In addition, the total procedural blank was less than 100 pg, <0.6% of total Sr used for column chemistry. After ion chromatography, sample solutions were adjusted to a final concentration of 150 ng g^{-1} Sr in 5% HNO_3 and spiked Zr (300 ng g^{-1}). In other words, the total Sr size for isotopic determination is ∼100 ng in this study.

2.3. Instrumentation

Strontium isotopic determinations were conducted using MC-ICP-MS (Neptune, Thermo-Fisher Scientific), which is equipped with 8 movable Faraday cups and one fixed central cup. Previous studies [9,10] used only the ^{91}Zr/^{90}Zr ratio for mass bias correction; here we precisely monitor all three Zr isotopes, ^{90}Zr, ^{91}Zr and ^{92}Zr, and compare the mass bias corrected data using ^{91}Zr/^{90}Zr and ^{92}Zr/^{90}Zr ratios, respectively. ^{86}Sr, ^{87}Sr, ^{88}Sr, ^{90}Zr, ^{91}Zr and ^{92}Zr ion-beams were collected simultaneously in a static mode. In addition, ^{85}Rb and ^{83}Kr were monitored for the correction of ^{87}Rb contribution on ^{87}Sr (^{87}Rb/^{85}Rb = 0.385617) and ^{86}Kr correction on ^{86}Sr (^{83}Kr/^{86}Kr = 0.664740). These isobaric interferences were automatically corrected by the Neptune software using an exponential fractionation law [21]. The amplifier gains were calibrated daily and the detector baselines were measured in each analytical batch. A virtual amplifier technique was used further to eliminate

Table 1
Instrument operating conditions.

Instrument setting	
RF power	1200 W
Guard electrode	On
Plasma Ar gas flow rate	15.0 L min^{-1}
Auxiliary Ar gas flow rate	0.75 L min^{-1}
Ar carrier gas flow rate	1.0–1.03 L min^{-1}
Cones	Sampler: nickel, 1.1 mm/skimmer: nickel, 0.8 mm
Sample uptake rate	100 μL min^{-1}
Extraction voltage	2 kV
Accelerating voltage	10 kV
Focus/dispersion quad	0.20 V/0.00 V
Vacuum ICP/analyzer	$\sim 2 \times 10^{-7}$ mbar/$\sim 2 \times 10^{-9}$ mbar
Cup configuration	L4(^{83}Kr), L2(^{85}Rb), L1(^{86}Sr), C(^{87}Sr), H1(^{88}Sr), H2(^{90}Zr), H3(^{91}Zr) and H4(^{92}Zr)
Mass resolution	Low mass resolution mode (~300)
Data acquisition parameters	
Scan type	Static mode
Cycles/blocks	6 cycles/8 blocks
Sensitivity	45 V ppm^{-1} for ^{88}Sr ion-beam
Integration/idle time	4.194 s/1.000 s
Analyze concentration	Sr: 150 ng g^{-1}/Zr: 300 ng g^{-1} (in 5% nitric acid)
Sample size	~100 ng for Sr

potential amplifier bias. The operating conditions were adjusted to the ^{88}Sr ion-beam at about 6–8 V, never exceeding ~10 V ^{88}Sr ion-beam using the Sr High-Purity Standards solution. The details of instrumental operation parameters are summarized in Table 1. The analytical protocol employed in this study starts with stability and quality control evaluation using 6 sets of NIST SRM 987 standards bracketed by Sr High-Purity Standards before analysis of sample materials.

2.4. Analytical procedures and mass bias correction

To eliminate the mass bias effect in isotopic measurements, a modified EEN method was developed for this study and the flow chart diagram of the experiments is shown in Fig. 1.

A two-step correction procedure was conducted using an exponential fractionation law. In the first section, we used NIST SRM 987 $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$ for mass bias correction to obtain the correct values of $^{91}\mathrm{Zr}/^{90}\mathrm{Zr}$ and $^{92}\mathrm{Zr}/^{90}\mathrm{Zr}$ in the spiked Zr standards:

$$\left(\frac{^{9X}\mathrm{Zr}}{^{90}\mathrm{Zr}}\right)_{\mathrm{corr}} = \left(\frac{^{9X}\mathrm{Zr}}{^{90}\mathrm{Zr}}\right)_{\mathrm{meas}} \times \left[\frac{(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{ref}}}{(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{meas}}}\right]^{[(\ln(M_{9X}/M_{90}))/(\ln(M_{88}/M_{86}))]} \tag{2}$$

where “corr”, “meas” and “ref” represent corrected, measured and reference isotopic ratio, respectively. “M” is the absolute mass for each isotope and “X” is either 1 or 2. The $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{ref}}$ used is the international convention value of 8.375209 (IUPAC, [13]). The corrected mean values of Zr isotopic ratios were used for Sr isotope ratios normalization in the following analytical sequences of NIST SRM 987 and samples.

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)^{*}_{\mathrm{corr}} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{meas}} \times \left[\frac{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{ref}}}{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{meas}}}\right]^{[(\ln(M_{87}/M_{86}))/(\ln(M_{9X}/M_{90}))]} \tag{3}$$

$$\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{corr}} = \left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{meas}} \times \left[\frac{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{ref}}}{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{meas}}}\right]^{[(\ln(M_{88}/M_{86}))/(\ln(M_{9X}/M_{90}))]} \tag{4}$$

The $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^{*}$ is the ratio without the $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio normalization. The use of NIST SRM 987 was as a reference standard in later analytical sequence to correct for the daily isotopic offset for $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^{*}$ and $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$. The NIST certified reference values is 0.71034 ± 0.00026 and 8.37861 ± 0.00325 for SRM 987 $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^{*}$ and $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$, respectively. However, the reported uncertainties for both ratios were too large for our calibration purpose. We, therefore, decided to use our own $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^{*}$ and the IUPAC $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$ value [13], 0.710245 and 8.375209, respectively. The former ratio was determined by the long-term TIMS (Triton TI, Thermo-Fisher Scientific) measurements in our laboratory, which has an external precision of better than 5 ppm (2SD, $n = 61$) [22]. The deviations of measured $^{88}\mathrm{Sr}/^{86}\mathrm{Sr}$ in unknown samples from NIST SRM 987 are expressed as δ-notation:

$$\delta^{88}\mathrm{Sr} = \left[\frac{(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\text{sample-final}}}{8.375209} - 1\right] \times 1000\ (‰) \tag{5}$$

The $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}^{*}$ ratio obtained using Zr for mass bias correction integrates the effect both from the radiogenic source and the potential isotope fractionation in nature. In order to emphasize the mass dependence isotope fractionation in nature, $\delta^{87}\mathrm{Sr}$ is defined as:

$$\delta^{87}\mathrm{Sr} = \left[\frac{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})^{*}}{0.710245} - 1\right] \times 1000 - \left[\frac{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}}{0.710245} - 1\right] \times 1000\,(‰) \tag{6}$$

where 0.710245 is the TIMS value for NIST SRM 987.

3. Results and discussion

3.1. Evaluation of Sr and Zr isotopic fractionation

We fixed Sr concentration at 150 ng g^{-1} and examined the spiked Zr concentration at 150–300 ng g^{-1} in Sr High-Purity Standards solution, integration time between 2.097 and 4.194 s, over 6 cycles and 8 blocks. Based on repeated measurements of the Sr in-house standard solution, we found that at least >300 ng g^{-1} Zr was needed for precise Zr isotopic determination and 4.194 s as an optimized integration time.

Correlation between the Sr and Zr mass bias of all measured NIST SRM 987 is shown in Fig. 2. The apparent mass dependent isotope fractionation relationships between Sr and Zr, shows slight differences in fractionation between the two elements [10]. Though linear relationship is observed for all plots of $^{8X}\mathrm{Sr}/^{86}\mathrm{Sr}$ vs. $^{9X}\mathrm{Zr}/^{90}\mathrm{Zr}$ in natural log scale, it is clear that the regression line was better in $^{92}\mathrm{Zr}/^{90}\mathrm{Zr}$ than for $^{91}\mathrm{Zr}/^{90}\mathrm{Zr}$. For the present study, we assume the mass bias follows the exponential law that isotopic fractionation factor β_{Sr} equals β_{Zr}. The fractionation factor β is defined as

$$\beta = \frac{\ln(R_{\mathrm{ref}}/R_{\mathrm{meas}})}{\ln(M_1/M_2)} \tag{7}$$

where R_{ref} is the certified isotopic ratio of NIST SRM 987 and Zr standard mentioned above, R_{meas} represents the measured isotopic ratio, and M referring to the absolute mass of selected numerator and denominator isotopes. The relation between β_{Sr} and β_{Zr} of all analyzed NIST SRM 987 measurements in this study shows $\beta(^{8X}\mathrm{Sr}/^{86}\mathrm{Sr})$ and $\beta(^{92}\mathrm{Zr}/^{90}\mathrm{Zr})$ are fitted more closed to the 1:1 correlation line and indicates the more similar mass bias between $^{8X}\mathrm{Sr}/^{86}\mathrm{Sr}$ vs. $^{92}\mathrm{Zr}/^{90}\mathrm{Zr}$,

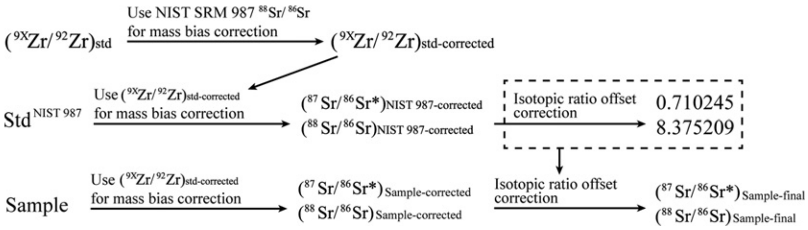

Fig. 1. Flow chart for modified EEN Sr isotope analytic protocol. Within this method, Zr isotope ratio is first calibrated using NIST SRM 987 $^{88}Sr/^{86}Sr$ ratio (assuming the value is 8.375209), and applied to mass bias correction in Sr isotope determinations. Daily isotopic offset driven by plasma-based mass spectrometers is corrected using NIST SRM 987 and fixes the ratio to 0.710245 and 8.375209 in $^{87}Sr/^{86}Sr^{*}$ and $^{88}Sr/^{86}Sr$, respectively. Then apply the extent of isotopic correction in following analytical sequence of samples.

$$\beta(^{88}Sr/^{86}Sr) = 0.912 \times \beta(^{92}Zr/^{90}Zr) - 0.160;$$
$$\beta(^{88}Sr/^{86}Sr) = 0.907 \times \beta(^{91}Zr/^{90}Zr) - 0.169;$$
$$\beta(^{87}Sr/^{86}Sr) = 0.930 \times \beta(^{92}Zr/^{90}Zr) - 0.163;$$
$$\beta(^{87}Sr/^{86}Sr) = 0.926 \times \beta(^{91}Zr/^{90}Zr) - 0.170.$$

Critical examination of NIST SRM 987 results (without removed matrix elements) have found that the impurities such as Ca, $^{44}Ca^{40}Ar^{+}$ and $^{48}Ca^{40}Ar^{+}$, can cause a bias and shift values from the mass dependent fractionation line [23]. In our study, no detectable spectral interferences were detected at mass 92 from blank analyses (less than ~0.2 mV at ^{92}Zr signal 2.5 V) and no potential isobaric impurity in High-Purity Standards solution by HR-ICP-MS. The observed improved correlation in Sr isotope ratios and $^{92}Zr/^{90}Zr$ is therefore probably due to the relative small mass differences (ΔM) compared with the $^{91}Zr/^{90}Zr$. A simple calculation using absolute mass values suggests the differences are: $\Delta M_{92-90} \approx 1.00200 \times \Delta M_{88-86}$, $2 \times \Delta M_{91-90} \approx 1.00277 \times \Delta M_{88-86}$, $0.5 \times \Delta M_{92-90} \approx 1.00055 \times \Delta M_{87/86}$, and $\Delta M_{91-90} \approx 1.00132 \times \Delta M_{87-86}$. This calculation agrees with the measured data from MC-ICP-MS and suggests more similar mass dependence fractionation between Sr isotope ratios and $^{92}Zr/^{90}Zr$. Further, using the more abundant isotope ^{92}Zr for mass bias correction results in better analytical precision than using ^{91}Zr when no other interference exists. Applying this analytical protocol, we found that much better precision for $\delta^{88}Sr$ measurements result when $^{92}Zr/^{90}Zr$ is used for mass bias correction (0.027 and 0.018‰ for $^{91}Zr/^{90}Zr$ and $^{92}Zr/^{90}Zr$, respectively, 2SD, $n = 26$, see Fig. 3). There is an available EEN method for $\delta^{88}Sr$ measurement reported by Yang et al. [10] which used $^{91}Zr/^{90}Zr$ coupled with SSB for Sr isotopic mass bias correction. Since the sample size, inlet system, sample uptake rate and operating condition are quite different

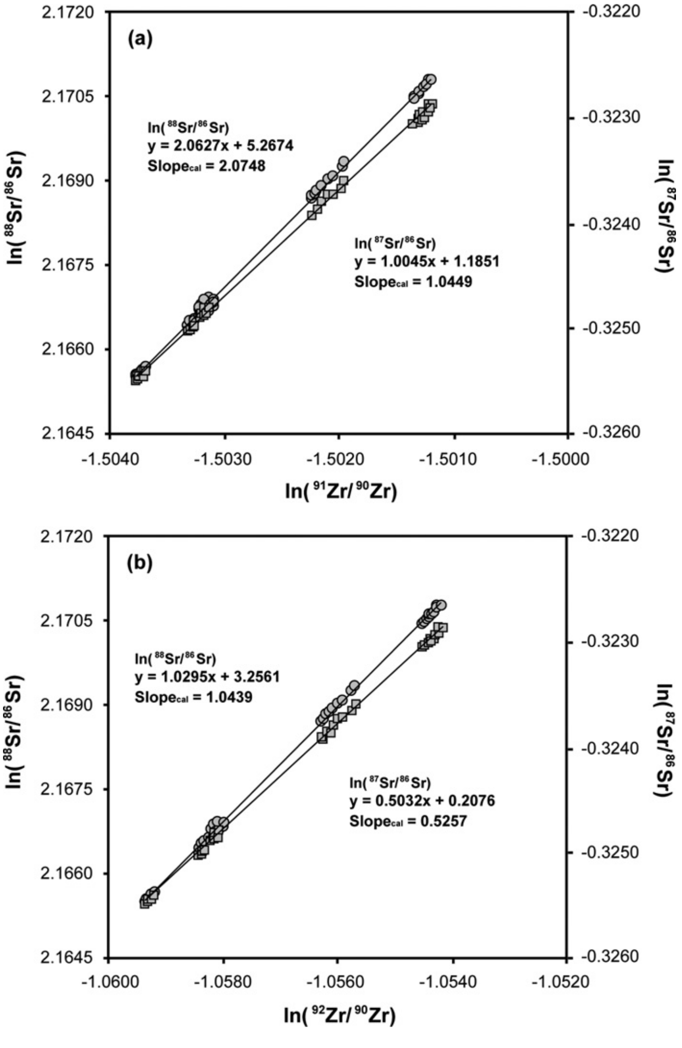

Fig. 2. ln–ln space plot for long-term (six days to over half year) measured $^{8X}Sr/^{86}Sr$ and $^{9X}Zr/^{90}Zr$ ratios. The theoretical regression slopes are calculated based on an exponential law using absolute isotopic mass as slope$_{cal}$ = $[\ln(M_{8X}/M_{86})/\ln(M_{9X}/M_{90})]$. Our data shows a mass-dependence isotopic fractionation between Sr and Zr isotopes and the slope similar with mass-dependence theoretical regression slopes.

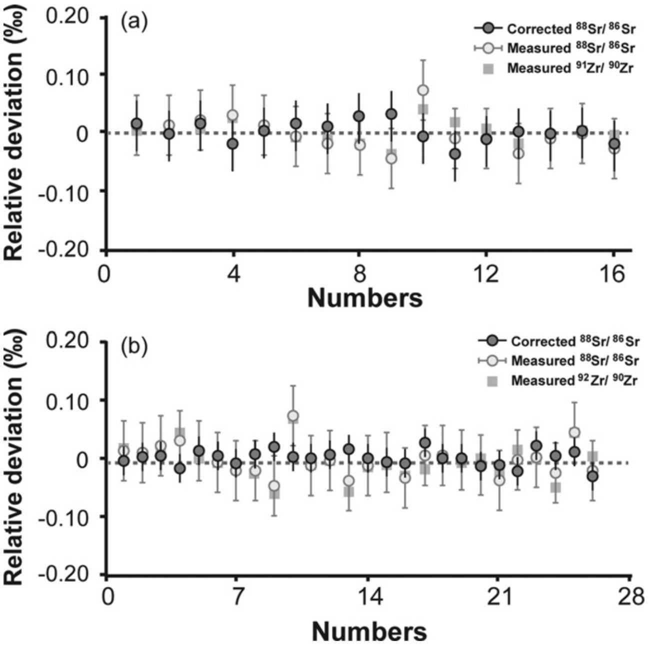

Fig. 3. The correction of mass bias drift using $^{91}Zr/^{90}Zr$ and $^{92}Zr/^{90}Zr$ ratios, respectively. The open and solid points represent the relative deviation of measured and corrected $^{88}Sr/^{86}Sr$ ratios compared to IUPAC value (8.375209 [13]), and the light square represents the measured (a) $^{91}Zr/^{90}Zr$ and (b) $^{92}Zr/^{90}Zr$ ratios. Dash line is the mean value of mass bias corrected $\delta^{88}Sr$.

Table 2
Sr isotope ratios in IAPSO seawater determined by various mass spectrometry techniques.

Reference	Instrument	Method	δ^{88}Sr [a,d]	δ^{87}Sr [d]	^{87}Sr/^{86}Sr [d]	^{87}Sr/^{86}Sr* [b,d]	Isotopic difference [c]
This study	MC-ICP-MS	EEN (^{92}Zr/^{90}Zr)	0.370 ± 0.026	0.177 ± 0.021	0.709161 (18)	0.709286 (14)	126 ± 15 ppm
Krabbenhoft et al. [9]	TIMS	Double spike (^{87}Sr/^{84}Sr)	0.386 ± 0.011		0.709173 (40)	0.709312 (20)	144 ± 20 ppm
Fietzke and Eisenhauer [10]	MC-ICP-MS	SSB	0.381 ± 0.022				
Halicz et al. [11]	MC-ICP-MS	SSB	0.350 ± 0.100				

[a] ^{88}Sr/^{86}Sr ratio is normalized to NIST SRM 987 in this study (^{88}Sr/^{86}Sr ratio for NIST SRM 987 of 8.375209 was used).
[b] ^{87}Sr/^{86}Sr* represents the measured ^{87}Sr/^{86}Sr ratio without ^{88}Sr/^{86}Sr ratio normalization.
[c] The value of Isotopic difference between ^{87}Sr/^{86}Sr and ^{87}Sr/^{86}Sr* ratios.
[d] The analytical errors were expressed as 2 standard deviation.

between Yang's and ours. We tested the two methods using the same data measurements. The precision of our result performed using ^{91}Zr/^{90}Zr mass bias correction without SSB suggests no significant difference compared with that of Yang et al. [10]. However, an approximately 1.5-fold improvement in precision for δ^{88}Sr determination can be obtained using our ^{92}Zr/^{90}Zr mass bias correction protocol. Furthermore, the two EEN δ^{88}Sr precisions show also no discernible difference, no matter if SSB procedures applied or not. This supports that the ^{92}Zr/^{90}Zr is more robust for Sr isotopic mass bias correction to correct most mass discrimination fluctuation. Consequently, we adopted this strategy to use ^{92}Zr/^{90}Zr for mass bias correction of δ^{87}Sr and δ^{88}Sr measurements and no SSB procedure is necessary in this study.

3.2. Different Zr standards for mass bias correction

Four different commercial available Zr standards, including High-Purity Standards (USA), Fluka (Japan), Merck (Germany) and NIST SRM 3169 (USA), were spiked with NIST SRM 987 to carefully examine their Zr isotopic compositions. We assumed that ^{88}Sr/^{86}Sr is 8.375209 for NIST SRM 987 and this ratio was used for mass bias correction during Zr isotope determination. The adjacent two NIST SRM 3169 measurements were used as the bracketing standards. The measured ^{9X}Zr/^{90}Zr ratio in the other standards deviated from NIST SRM 3169 were expressed as ε^{9X}Zr:

$$\varepsilon^{9X}\mathrm{Zr} = \left[\frac{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\text{Zr-standard}}}{(^{9X}\mathrm{Zr}/^{90}\mathrm{Zr})_{\text{average NIST 3169}}} - 1\right] \times 10000 \tag{8}$$

The long-term external precision of ε^{91}Zr and ε^{92}Zr in our laboratory is 0.17 and 0.20 ε (2SD, $n = 16$), respectively. In comparison with NIST SRM 3169, the mean ε^{91}Zr in High-Purity Standards, Fluka, and Merck were −0.63, −0.10, and −0.34, and the mean ε^{92}Zr were −1.24, −0.25, and −0.71, respectively ($n = 5$). Our results show that the Zr isotopic compositions of High-Purity Standards and Merck were significantly different from that of NIST SRM 3169. Since the Zr isotopic heterogeneity is proved in various reference materials on the planet [24], a proper Zr isotopic certification is important for different selection of standards using the EEN approach. In this study, the Zr standards will be spiked into samples after the procedure of ion chromatography, thus the purity of the spiked standards is critical. No detectable element of any matrix or isobaric interferences was found in the Zr standard solutions, instead of small impurities of nickel (Ni), iron (Fe), cadmium (Cd), silver (Ag) and hafnium (Hf). To eliminate any potential interference from these impurities, High-Purity Zr Standard was selected as the standard solution for mass bias correction and for precise Sr isotope determinations in this study.

3.3. Daily offset correction

In order to circumvent the mass bias effect in MC-ICP-MS measurements, we applied EEN approach for long-term and daily instrumental drift correction. However, the space charge effect on MC-ICP-MS will also bias the measured Sr isotope ratios compared with TIMS measurements [23]. The mass bias together with the space charge effect resulted in the small difference between β_{Sr} and β_{Zr}. Consequently shifts in ^{87}Sr/^{86}Sr* and ^{88}Sr/^{86}Sr ratios differ from the certified values by +112 and +384 ppm (0.710245 and 8.375209 certified by TIMS). To resolve this problem, an iCRM is recommended for correcting the daily offset in isotope ratios.

The analytical reproducibility of the absolute Sr isotope abundance determinations was evaluated by repeated analyses of NIST SRM 987. The initial analytical set of NIST SRM 987 each day was used as the reference for the correction of daily isotopic offset. The average value of NIST SRM 987 for ^{87}Sr/^{86}Sr* and ^{88}Sr/^{86}Sr is 0.710254 ± 0.000030 and 8.375380 ± 0.000296 (2SD, $n = 34$, Fig. 4). All the results obtained using our analytical protocol agreed with the recommended values of

Table 3
Sr isotopic composition of geochemical samples.

Materials	δ^{88}Sr [a,d]	δ^{87}Sr [d]	^{87}Sr/^{86}Sr [d]	^{87}Sr/^{86}Sr* [b,d]	Isotopic difference [c]	n
Igneous rock (basalt)						
BHVO-2	0.248 ± 0.014	0.108 ± 0.018	0.703471 (21)	0.703560 (20)	89 ± 13 ppm	4
	0.24 ± 0.24 [f]		0.703479 (20) [e]			
BCR-2	0.284 ± 0.075	0.126 ± 0.039	0.705040 (43)	0.705130 (66)	89 ± 28 ppm	4
	0.24 ± 0.09 [f]		0.705013 (10) [e]			
Igneous rock (andesite)						
AGV-2	0.270 ± 0.038	0.146 ± 0.020	0.703965 (34)	0.704071 (38)	106 ± 15 ppm	4
Seawater						
IAPSO	0.370 ± 0.026	0.177 ± 0.021	0.709169 (29)	0.709295 (41)	126 ± 17 ppm	5

[a] ^{88}Sr/^{86}Sr ratio is normalized to NIST SRM 987 in this study (^{88}Sr/^{86}Sr ratio in NIST SRM 987 of 8.375209 was selected).
[b] ^{87}Sr/^{86}Sr* represents the measured ^{87}Sr/^{86}Sr ratio without ^{88}Sr/^{86}Sr ratio normalization.
[c] The value of Isotopic difference between ^{87}Sr/^{86}Sr and ^{87}Sr/^{86}Sr* ratios.
[d] The analytical errors were expressed as 2 standard deviation.
[e] Data from Weis et al. [26]. Measured ratio is performed by TIMS and normalized to NIST SRM 987 ^{87}Sr/^{86}Sr = 0.710248.
[f] Data from Moynier et al. [11]. Analytical bias corrected using ^{90}Zr/^{91}Zr ratio.

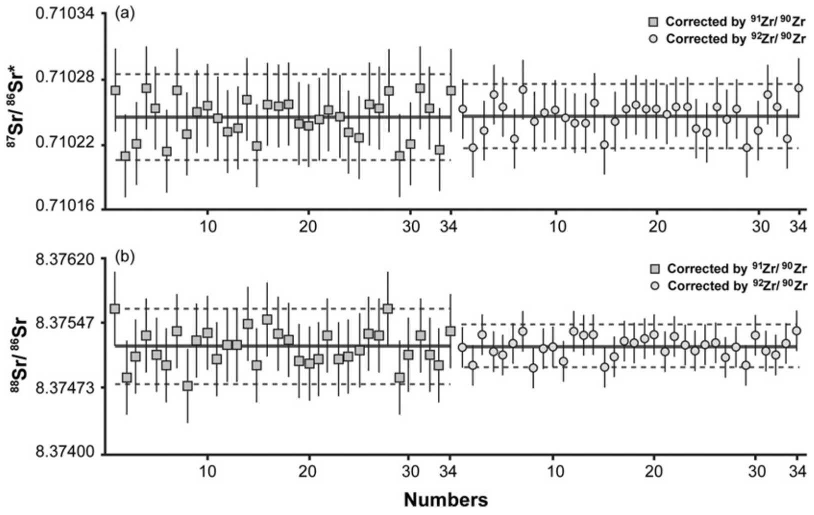

Fig. 4. Long-term measurements of NIST SRM 987 using the proposed analytical procedures (a) ^{87}Sr/^{86}Sr* and (b) ^{88}Sr/^{86}Sr ratios. For each High-Purity Standard Zr was doped, ^{91}Zr/^{90}Zr and ^{92}Zr/^{90}Zr ratios were choice to correct the mass bias effect in Sr isotope determinations, respectively. The errors marked in the figure represent 2 standard deviation (n = 34, 2SD). Solid lines are the mean values in NIST SRM 987 and dash lines are the confidence intervals.

0.71034 ± 0.00026 and 8.37861 ± 0.00325 for ^{87}Sr/^{86}Sr* and ^{88}Sr/^{86}Sr.

3.4. Validation of analytical protocol

An IAPSO solution containing 150 ng g^{-1} Sr and spiked with 300 ng g^{-1} High-Purity Standards Zr was used to validate the proposed analytical protocol. The Sr isotope composition results of 0.709161 ± 0.000018, 0.177 ± 0.021‰, and 0.370 ± 0.026‰ (2SD, n = 7) were obtained for IAPSO ^{87}Sr/^{86}Sr, δ^{87}Sr and δ^{88}Sr [12,25] (Table 2). A significant isotopic difference of ^{87}Sr/^{86}Sr and ^{87}Sr/^{86}Sr* in IAPSO standard was observed corresponding to a value of 126 ± 15 ppm that agrees previously reported value of 144 ± 20 ppm analyzed by DS-TIMS [25] (Table 2). Since ^{87}Sr/^{86}Sr ratio is determined based on constant ^{88}Sr/^{86}Sr ratio of 8.375209 (0‰ in δ^{88}Sr), the difference between ^{87}Sr/^{86}Sr and ^{87}Sr/^{86}Sr* can be used to interpret approximately +0.37‰ variation in δ^{88}Sr. We further used IAPSO to evaluate our modified EEN approach in comparison with EEN method combined with SSB by Yang et al. [10], used ^{91}Zr/^{90}Zr for mass bias correction. The results showed no detectable difference between the two approaches and suggest that ^{92}Zr/^{90}Zr ratio can be used to correct the in-time mass bias fluctuation. Consequently, SSB is not required in our analytical protocol, which increases the analytical efficiency for more than 2 times, and sample size (~100 ng for Sr) was reduced 2-folds compared with Yang et al. [10] (at least 200 ng, see Table 1).

We applied the modified analytical protocol for Sr isotope determination to three igneous rock standards. The δ^{88}Sr values obtained from basalt samples (BHVO-2 and BCR-2) and andesite sample (AGV-2) were identical and fall in a range between +0.24‰ and +0.28‰, the difference is within the analytical error (for details see Table 3). These values are within the range of previous literature values for the following igneous rock materials (JB-1a, JA-2, G2, AGV-1 and S2, +0.26 ± 0.03‰, +0.25 ± 0.01‰, +0.31 ± 0.09‰, +0.28 ± 0.03‰, and +0.28 ± 0.08‰ in δ^{88}Sr, respectively [9,11]). The δ^{88}Sr ~+0.27‰ agrees with the Bulk Silicate Earth (BSE) related to NIST SRM 987 [11]. The ^{87}Sr/^{86}Sr value of BHVO-2, BCR-2 and AGV-2 are 0.703471 ± 0.000021, 0.705040 ± 0.000043, and 0.703965 ± 0.000034, consistent with available literature data [26] (see Table 3). About 95 ppm isotopic difference between ^{87}Sr/^{86}Sr and ^{87}Sr/^{86}Sr* ratios can be explained by ~+0.27‰ in δ^{88}Sr, indicating our analytical protocol provides excellent efficiency and reliable Sr isotope measurements.

4. Conclusion

A highly precise and accurate MC-ICP-MS method with EEN technique has been established for Sr isotopic abundance determination. In contrast with previous studies, we used ^{92}Zr/^{90}Zr to correct for the short-term drift and the mass bias effects during Sr isotope measurements. Due to the tight correlation between Sr isotope and ^{92}Zr/^{90}Zr, this new method provides a useful correction of random mass bias fluctuation and achieves a 2-fold improvement in precision of δ^{88}Sr compared with ^{91}Zr/^{90}Zr correction. The long-term reproducibility of Sr isotope performed using NIST SRM 987 is 0.710254 ± 0.000030 and 8.375380 ± 0.000296 (2SD, n = 34, over half-year) for ^{87}Sr/^{86}Sr* and ^{88}Sr/^{86}Sr, respectively. IAPSO standard seawater was used for analytical protocol validation and suggests absolute isotope ratio of 0.709161 ± 0.000018, 0.177 ± 0.021‰ and 0.370 ± 0.026‰ (2SD, n = 7) for ^{87}Sr/^{86}Sr, δ^{87}Sr and δ^{88}Sr, all in good agreement with previous studies. Three igneous rock standards, BHVO-2, BCR-2 and AVG-2, were analyzed and obtained Sr isotopic compositions, which are consistent with available literature data. These cross-calibration results support that our new analytical protocol can provide a reliable and effective method for high precision determination of triple Sr isotopes in natural specimens.

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