Precise Determination of Stable Strontium Isotopic Compositions by MC-ICP-MS

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ABSTRACT: The investigation of variations within the non-traditional stable Sr isotope composition in various natural systems has gained a broader interest in recent years. Although significant improvements in the analytical precision for isotopic ratio analysis have been made, the accurate determination of stable Sr isotopic ratios is still a challenge. This study shows the key controlling factors affecting the precise determination of stable Sr isotopic ratios by using Neptune Plus MC-ICP-MS, including matrix effect, internal standard correction and nebulizer fractionation effect. Further, a novel step is presented in the Sr purification by using Sr-spec[®] resin, which increased the recovery rates to > 98.5%. In this work, the mass bias effects between ⁹²Zr/⁹⁰Zr and ⁸⁸Sr/⁸⁶Sr were investigated and compared, and a 3~5-fold improvement in the precision of the determination of ⁸⁸Sr/⁸⁶Sr was obtained compared to that based on only the standard-sample-bracketing technique. Moreover, nebulizer fractionation was illustrated by using an in-house standard solution, Alfa Sr, and the seawater standard, IAPSO. As for the matrix effect, residual Ca in the purified Sr fraction was evaluated and showed insignificant influence. Overall, a feasible, highly-efficient procedure for the stable Sr separation and analysis was developed. The seawater standard, IAPSO, yielded $\delta^{88/86}\text{Sr} = 0.374 \pm 0.028\text{‰}$ (2SD, n = 23), which is in agreement with reported data. The long-term reproducibility for the rock standard materials, BCR-2 and BHVO-2, yielded $\delta^{88/86}\text{Sr} = 0.232 \pm 0.015\text{‰}$ (2SD, n = 10), $\delta^{88/86}\text{Sr} = 0.249 \pm 0.014\text{‰}$ (2SD, n = 7), respectively, and agrees well with published data. The in-house standard solution, Alfa Sr, was produced to check for the long-term reproducibility of the method and yielded a comparable value of $0.113 \pm 0.039\text{‰}$ (2SD, n = 46) over 6 months.

INTRODUCTION

Strontium (Sr) has four natural isotopes (⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr), all of which are stable. As ⁸⁷Sr is the radiogenic product of ⁸⁷Rb by β -decay, which has a half-life of 4.88×10^{10} a, ⁸⁷Sr/⁸⁶Sr vary in the samples according to their age and initial Rb/Sr ratio. Over the past decades, significant advances in thermal ionization mass spectrometry (TIMS) and multi-collector inductively plasma mass spectrometry (MC-ICP-MS) have been made, allowing for high precision ⁸⁷Sr/⁸⁶Sr analyses. All instruments produce mass bias during ⁸⁷Sr/⁸⁶Sr measurements, and natural fractionation is corrected to

the commonly accepted ⁸⁸Sr/⁸⁶Sr ratio of 8.375209.¹ Thus, measuring the ⁸⁷Sr/⁸⁶Sr ratio together with the Rb/Sr ratio has been one of the most successful chronometers and tracers used in the Earth Sciences and beyond.^{2–5} However, the special interest in radiogenic ⁸⁷Sr and the difficulty using TIMS and MC-ICP-MS to get precise mass-dependent variations render the fractionation patterns of stable Sr isotopes (⁸⁸Sr/⁸⁶Sr) rarely studied.

Following recent improvements in MC-ICP-MS, the fractionation of the non-traditional stable Sr isotopes has received increasing attention.^{6–11} Significant stable Sr

fractionation ($^{88}\text{Sr}/^{86}\text{Sr}$) has been observed in various natural systems, for instance, 0.24 to 0.27‰ in Bulk Silicate Earth (BSE) materials^{12,13} and 0.20 to 0.30‰ in modern marine carbonates.¹⁴ Likewise, the ability for stable Sr fractionation has been used to study the weathering processes, climate regulation and biogeochemical cycling.^{8,9,15–17}

The biggest challenges for highly accurate and precise isotopic determinations with MC-ICP-MS are the mass discrimination effects. Differences of instrumental discrimination in MC-ICP-MS cause the measured isotope ratio to deviate from the actual ratio. Preferential transportation of heavier isotopes from the ion source to the detectors (Faraday cups) results in up to 10% deviations in the isotopic ratios for elements with mass numbers less than 10, about 1–5% for mass numbers in the range of 20–120.¹⁸ To overcome this disadvantage, three strategies have been reported previously for high precision $^{88}\text{Sr}/^{86}\text{Sr}$ measurement. The ^{87}Sr – ^{84}Sr double-spike thermal ionization mass spectrometry method (DS-TIMS) can provide high precision $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ results with external precisions around 0.01‰.¹⁹ However, the double spike method is very complicated and the ^{87}Sr – ^{84}Sr double spike is still not available in the majority of laboratories. The standard-sample-bracketing (SSB) method is also reported to directly obtain the correct $^{88}\text{Sr}/^{86}\text{Sr}$ ratio.^{6,11,20} Nevertheless, it is well known that the signal shift varies with time because of the dynamic nature of the drift in absolute isotope ratios measured by MC-ICP-MS. Although this drift in the MC-ICP-MS can be reduced to comparable levels by careful implementation,^{6,11,13,20} it is not convenient for practical analysis since the time-drift of MC-ICP-MS is inevitable, necessitating an alternative approach to within-run fractionation mass bias correction. Therefore, an effective protocol, involving internal correction of mass bias to overcome this shortcoming, was applied by adopting Zr and using the $^{91}\text{Zr}/^{90}\text{Zr}$ or $^{92}\text{Zr}/^{90}\text{Zr}$ ratios.^{13,21–23} In spite of its benefit, doping Zr to the analytes is challenged by concern about the potential impact on the results. For instance, it has been reported that different elements can isotopically fractionate differently in MC-ICP-MS, such as Pb and Tl.²⁴ Based on these reasons, the benefit of doping samples and standard solutions with Zr for mass bias drift correction was extensively debated in the literature. Ma *et al.*²⁰ considered it unfavorable, whereas, other studies found it more reliable than a simple sample-standard-bracketing approach.^{21,22} Therefore, the effect of Zr added to the Sr solution needs to be studied further.

Another major trouble encountered in attempting to determine stable Sr isotopic components is the potential interferences on mass spectrometric measurements of the Sr isotopes that come from the presence of isobaric and polyatomic interferences.^{25–31} Typically, the ^{86}Sr ion beam was corrected for isobaric interferences from ^{86}Kr due to Kr contamination of the argon gas. ^{87}Sr was corrected for ^{87}Rb by

simultaneous measurement of the ^{85}Rb signal and using the natural isotopic composition of Rb ($^{87}\text{Rb}/^{85}\text{Rb}=0.385750$).^{7,27} Potential polyatomic species in the Sr mass region from the matrices, such as $^{46}\text{Ca}^{40}\text{Ar}$, $^{43}\text{Ca}^{44}\text{Ca}$, and $^{44}\text{Ca}_2$, can have interferences on the ^{86}Sr , ^{87}Sr , and ^{88}Sr signals, respectively, and cause the measured isotopic ratios to significantly deviate from the true value.^{26,28,32,33} High matrices were also found to induce mass bias effects on MC-ICP-MS^{32,34} and also reduce instrument sensitivity and stability.³² However, detailed studies for these effects on high precision $^{88}\text{Sr}/^{86}\text{Sr}$ measurement are not sufficient, and it is necessary to assess those matrix effects, because it is difficult to remove matrices completely during the chemical separating procedure with heterogeneous samples.

Studies related to the elemental fractionation during vaporization in the ICP have been reported starting in 1981. Thompson *et al.*³⁵ reported that incomplete vaporization of large particles in the ICP was a significant source for elemental fractionation. In 1992, Hobbs and Olesik observed large fluctuations in the ICP-MS signal on the microsecond time scale and related them to incomplete vaporization of particles in the plasma.³⁶ Olesik's group obtained further insight into signal and ion cloud formation in the ICP by time-resolved mass spectrometry and optical emission spectroscopy.^{37,38} In the following decades, effects of the aerosol with different particle sizes inside the ion source^{39–41} and the related ionization mechanism^{40,42} have been critically reviewed in a number of publications. Similarly, the impact of the particle diameter on cloud formation and particle distribution have also been widely investigated.^{43–47} As found in solution analysis with ICP-MS and MC-ICP-MS, particle sizes are significantly affected by the nebulizer, and the influence of the nebulizer is necessary to be fully understood, especially for acquiring high precision and accurate isotopic ratios. Although the aerosol properties and other effects related to the nebulizer have been examined in previous studies,^{48,49} research about nebulizer effects on the precision and accuracy of isotopic ratios has rarely been reported.

Apart from fractionations imparted by mass spectrometry, an additional challenge is the Sr recovery during sample processing. Numerous studies have revealed that separation procedures cause mass-dependent isotopic fractionation of the analytes when the SSB method was used.^{50–52} Preferential elution of heavier Sr isotopes was observed during the extraction chromatography in previous studies, which showed that at least 95% Sr recovery was estimated to minimize isotope fractionation below analytical uncertainty.⁷ Therefore, a simple, feasible separation scheme is essential in order to achieve ~100% Sr recovery.

The goal of the present research is to characterize comprehensively the key factors affecting stable Sr composition analysis, using a MC-ICP-MS (Neptune plus), as a

function of the effect of matrix elements, influence of varying Zr concentrations, isobaric and polyatomic interferences, nebulizer effect, and Sr recovery during the separation procedure. In this study, we systematically investigated the effects of three different nebulizers, two of which have been running for three months and one is brand new, using the same solution successively, to assess the performance of MC-ICP-MS for the stable Sr isotope analysis.

EXPERIMENTAL

Instrumentation. Sr isotopic ratios were obtained on a double focusing MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Marine Geology, Tongji University, Shanghai, P.R. China. The Faraday collector configuration of the mass spectrometer was composed of an array from L4 to H3 to monitor $^{83}\text{Kr}^+$, $^{84}\text{Sr}^+$, $^{85}\text{Rb}^+$, $^{86}\text{Sr}^+$, $^{87}\text{Sr}^+$, $^{88}\text{Sr}^+$, $^{90}\text{Zr}^+$, and $^{92}\text{Zr}^+$ (Table 1). The element concentrations of the eluted fractions were analyzed using an Agilent 7900 quadrupole ICP-MS instrument (Agilent Technologies, Tokyo, Japan). A summary of MC-ICP-MS instrumental and data acquisition parameters is presented in Table 1.

In this study, zirconium, mixed with solutions of NBS SRM 987 and samples, was used for mass bias correction²¹. According to the conventional power index calibration method, the fractionation factors f_{Zr} , f_{Sr} of Zr and Sr isotopes in MS analysis can be obtained from standards with known isotopic ratios:

$$f_{\text{Zr}} = \ln \left(\frac{(^{92}\text{Zr}/^{90}\text{Zr})_{\text{true}}}{(^{92}\text{Zr}/^{90}\text{Zr})_{\text{measure}}} \right) / \ln \left(\frac{\text{Mass}^{92}\text{Zr}}{\text{Mass}^{90}\text{Zr}} \right) \quad (1)$$

$$f_{\text{Sr}} = \ln \left(\frac{(^{88}\text{Sr}/^{86}\text{Sr})_{\text{true}}}{(^{88}\text{Sr}/^{86}\text{Sr})_{\text{measure}}} \right) / \ln \left(\frac{\text{Mass}^{88}\text{Sr}}{\text{Mass}^{86}\text{Sr}} \right) \quad (2)$$

If there is a simple linear relationship with the certain coefficient ‘a’ between the fractionation factors of Zr and Sr, then

$$f_{\text{Sr}} = a \times f_{\text{Zr}} \quad (3)$$

Based on f_{Zr} , the Sr isotopic ratio in the sample can be calculated as follows:

$$\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{true}} = \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{measure}} \times \left(\frac{\text{Mass}^{88}\text{Sr}}{\text{Mass}^{86}\text{Sr}} \right)^{a \times f_{\text{Zr}}} \quad (4)$$

The correction between $\ln(^{88}\text{Sr}/^{86}\text{Sr})_{\text{measure}}$ and $\ln(^{92}\text{Zr}/^{90}\text{Zr})_{\text{measure}}$ can be determined as follows:

$$\ln \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{measure}} = 0.97076 \times a \times \ln \left(\frac{^{92}\text{Zr}}{^{90}\text{Zr}} \right)_{\text{measure}} + \left(\ln \left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{true}} - 0.97076 \times a \times \ln \left(\frac{^{92}\text{Zr}}{^{90}\text{Zr}} \right)_{\text{true}} \right) \quad (5)$$

where a is calculated from the slope S of the data points of $\ln(^{88}\text{Sr}/^{86}\text{Sr})_{\text{measure}}$ vs $\ln(^{92}\text{Zr}/^{90}\text{Zr})_{\text{measure}}$ (Fig. 4)

$$S = 0.97076 \times a \quad (6)$$

Reagents. Ultrapure water (18.2 MΩ-cm) was acquired using a Milli-Q Element system (Millipore Corporation, USA) and used throughout this work. All AR grade acids, including hydrochloric acid, nitric acid and hydrofluoric acid, were further purified twice using a DTS-1000 acid purification system (Saville, USA). A stock solution of $1 \mu\text{g mL}^{-1}$ Sr was gravimetrically prepared to monitor the instrument’s long-term stability using an in-house Sr stock solution (Alfa Aesar Chemicals). The $\delta^{88/86}\text{Sr}$ values were calculated using the international standard NIST SRM 987 (National Institute of Standards and Technology, USA). The $\delta^{88/86}\text{Sr}$ values are expressed in per mil (‰) and reported in the common δ -notation as listed below:

$$\delta^{88/86}\text{Sr} = \left(\frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{sample}}}{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{standard}}} - 1 \right) \times 1000$$

We used a Sr-spec[®] resin (particle diameter: 50-100 μm , Eichrom) for our Sr separation procedure. Rock powders of certified reference materials (CRMs), BCR-2 (basalt) and BHVO-2 (basalt), were obtained from the United States Geological Survey (USGS), and the standard seawater IAPSO was employed during the experiments.

A mono-elemental Zr stock solution ($1000 \mu\text{g mL}^{-1}$, SCP Science, Canada) was used, then diluted and doped into the NIST SRM 987 (Zr/Sr = 2:1) to correct for any mass bias within the instrument. A pure Zr standard solution that has been directly introduced into the plasma was found to have a negligible Sr signal, indicating high purity of the Zr solution.

Table 1. Instrumental parameters of MC-ICP-MS system for Sr isotopic measurement

Instrument	Neptune plus
Radio frequency (W)	1200
Extraction (V)	-2000
Focus (V)	-692
Slit resolution	Low
Measurement mode	Static
Sample gas (argon) flow rate (L min ⁻¹)	1-1.1
Auxiliary gas (argon) flow rate (L min ⁻¹)	0.8
Cones (nickel)	“Sample” + “H”
Idle time (s)	3
Rinsing time (s)	100
Uptake time (s)	50
Acquisition time (s)	180
Running concentrations (ng mL ⁻¹)	200
Faraday cup	L1 ($^{86}\text{Sr}+^{86}\text{Kr}$), L2 (^{85}Rb), L3 ($^{84}\text{Sr}+^{84}\text{Kr}$), L4 (^{83}Kr), C ($^{87}\text{Sr}+^{87}\text{Rb}$), H1 (^{88}Sr), H2 (^{90}Zr), H3 (^{92}Zr)

Sample digestion and column chemistry. Approximately 50 mg of CRM powders were weighed into steel-jacketed acid-washed, high-pressure PTFE bombs. The CRMs were then dissolved in an oven at 190 °C for 24 h using an acid mixture of 1.5 mL conc. HF and 1.5 mL conc. HNO₃. The dissolved CRM solutions were then evaporated to dryness and treated with 2 mL conc. HNO₃. The solution was dried down at approximately 100 °C on a hot plate. Finally, the residues were dissolved with 1 mL of 3M HNO₃ at 100 °C overnight on a hot plate. Clear solutions of all fractions were obtained, and no insoluble fluoride compounds were found in this study.

About 300 mg of Sr-spec[®] resin was loaded into polypropylene columns. All of the columns used in this study were 2 mL standard columns, 7 cm long with a 0.7 mm i.d. and 6 mL reservoir. All samples were dissolved in 1 mL 3M HNO₃ before being loaded onto the prepared column. Any matrix elements were removed by rinsing the resin with 3M HNO₃ and 7M HNO₃. The purified Sr was eluted and collected using 6mL Milli-Q water and 0.2 mL 8M HNO₃. The elution curve of our column chemistry, the total Sr recovery, and procedural blanks produced during Sr separation as well as residual matrix elements (*e.g.* K, Na, Ca, Mg, Ba and Rb) were determined using a quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the State Key Laboratory of Marine Geology, Tongji University Shanghai, P.R. China (see instrumentation chapter below). Table 2 represents the separation procedure.

RESULTS AND DISCUSSION

Sample separation and recovery. For highly accurate MC-ICP-MS analyses, successful separation of the analyte from matrix elements is a crucial pre-requisite for purification, followed by isotope ratio evaluation. This study aims for matrix matching with the adopted standards and isolating the element of interest from potential isobaric and polyatomic interferences. The results for the element elution curves show that all of the major elements, as well as Rb and Zr, were efficiently separated with 3M HNO₃, then 7M HNO₃ was used to eliminate most of Ba. The Rb/Sr ratios obtained by ICP-MS in the final purified Sr analyte solution were below 0.001 after the samples were loaded with Rb/Sr ratios <10 sample. For samples with Rb/Sr >10, repeated purification may be necessary. In addition, the total blank of the whole procedure was less than 0.5 ng, which is <0.1% of the total Sr (600 ng) loaded in our column chemistry. Residual K, Na, Mg, Al and Ba concentrations in the purified Sr solution were negligible. Potential interferences from residual Ca will be discussed in the following section.

Preferential elution of heavier Sr isotopes was observed during the extraction chromatography. Consequently, >95% Sr recovery was estimated to minimize isotope fractionation

Table 2. Separation scheme of strontium isotopes

Step	Eluent	Volume (mL)
Pre-washing	3 mol/L HNO ₃	6
	MQ	6
	6 mol/L HCl	6
	MQ	6
	3 mol/L HNO ₃	6
	MQ	6
Resin equilibration	3 mol/L HNO ₃	6
Sample loading	Addition (~600 ng Sr)	1
Removal of matrix elements	3 mol/L HNO ₃	1 mL × 4
	7 mol/L HNO ₃	4 mL × 4
	MQ	1 mL × 4
Sr collection	8 mol/L HNO ₃	0.2
	MQ	1 mL × 2

Fig. 1 Element elution curves for Sr purification procedure.

below the analytical uncertainty.⁷ Sr recovery for our extraction chromatography was evaluated by comparing the Sr content prior and after the matrix separation procedure, and the yield was >98.5%. Fig. 1 shows that adding a further step of 0.2 mL 8M HNO₃, followed by 2 mL MQ, can be used to collect ~5% of the remaining Sr since only ~93.5% was obtained in the first 4 mL of MQ water. It is worth noting that 0.2mL of 8M HNO₃ is essential for a nearly complete recovery of Sr, and our study shows that the remaining ~5% Sr was not available when only MQ water was used for elution of Sr from Sr-spec[®]. Moreover, as illustrated in Fig. 1, the elution curves of Zr and Y are overlapping each other exactly, which shows that the Sr-spec[®] resin possesses similar adsorption abilities for Zr and Y.

Isotopic interferences and matrix effect. In all plasma-based mass spectrometers, Kr mainly originates from the impurity of the Ar gas supply. The signal of ⁸³Kr was small and typically <0.1 mV in our measurements, corresponding to ~0.15 mV in ⁸⁶Kr, and accounted for 0.02% in the signal on mass 86. Thus, the Kr isobaric interference on ⁸⁶Sr was minor. The interference of ⁸⁷Rb on ⁸⁷Sr typically arises from any incomplete matrix separation. There is a possibility that the Rb isobaric interference can be significant, particularly in a sample matrix

Fig. 2 Results of 200 ng mL⁻¹ NIST SRM 987 mixed with various amounts of Ca. (a) Each $\delta^{88/86}\text{Sr}$ value represents the average value of three measurements and the error bars for individual data are 2SD, $n = 3$. (b) Each $^{87}\text{Sr}/^{86}\text{Sr}$ data represents the average value of five measurements and the error bars for individual data are 2SD, $n = 5$.

Fig. 3 MC-ICP-MS measured ratios of $\ln(^{88}\text{Sr}/^{86}\text{Sr})$ versus $\ln(^{92}\text{Zr}/^{90}\text{Zr})$.

with high Rb/Sr ratios, which potentially causes the Rb elution curves' tail to overlap with the Sr elution peak. A failure of the isobaric correction in high Rb level samples may be caused by the different mass bias effect on the Rb and Sr isotopic ratios.^{53,54} However, there were no isotopic deviations found in our study, since the Rb/Sr ratio was less than 0.002.

Aside from the isobaric interference issues, matrix elements can form direct polyatomic interferences on the analyte such as $^{46}\text{Ca}^{40}\text{Ar}$ on ^{86}Sr , $^{43}\text{Ca}^{44}\text{Ca}$ on ^{87}Sr , and $^{44}\text{Ca}_2$ on ^{88}Sr . The presence of matrix elements may also change the ion

transmission efficiency and/or ionization efficiency for the analyte, resulting in erroneous mass bias correction by using pure bracketing standards.³⁴ Following Yang *et al.* (2011),⁵⁵ who found that a certain amount of Ca had insignificant influence on Sr isotope analyses obtained in different types of mass spectrometers, we evaluated the performance of our instrument by adding various amounts of a pure Ca stock solution (Alfa Aesar Chemicals) into 200 ng mL⁻¹ NIST SRM 987 solutions (Ca/Sr = 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1). Further, a mono-elemental Ca standard solution that has been directly introduced to the plasma was found to have a negligible Sr signal, indicating the high purity of the solution. The series of NIST SRM 987 solutions doped with different amounts of Ca were measured sequentially. As shown in Fig. 2a, each SRM 987 solution was analyzed 5 times, so three $\delta^{88/86}\text{Sr}$ values were obtained, and each square represents the average value of them. The $^{87}\text{Sr}/^{86}\text{Sr}$ values are shown in Fig. 2b and each triangle represents the average value of five measurements. The results show that there was insignificant influence of Ca on the $\delta^{88/86}\text{Sr}$ values even though the Ca/Sr ratios were as high as 10. In fact, Ca/Sr ratios ≤ 2 were found in our collected Sr fraction after the separation procedure, demonstrating that the residual Ca in the Sr solution is negligible.

Furthermore, Fig. 2b illustrates that the obtained $^{87}\text{Sr}/^{86}\text{Sr}$ values show high stability and reliability, *i.e.* 0.710246 ± 11 (2SD, $n = 10$), with satisfactory results of $\delta^{88/86}\text{Sr}$ values, *i.e.* $\delta^{88/86}\text{Sr} = 0.00 \pm 0.02$ (2SD, $n = 10$).

Internal standard-based correction. In this study, $^{92}\text{Zr}/^{90}\text{Zr}$ was used to correct for $^{88}\text{Sr}/^{86}\text{Sr}$ by the exponential law and assuming that the fractionation factor of Zr is the same as that of Sr. To evaluate the fractionation factor between Sr and Zr, the isotopic ratios of Sr and Zr measured in the same analytical cycle in a mixed solution are plotted in Fig. 3. The slope of a linear fit through all data points is 1.0134, and a in Equation (6) in the preceding instrumentation section was calculated to be 1.022, which demonstrates that our assumption is reasonable and in accordance with previous studies.^{13,21–23} This analytical session yielded a constant $f_{\text{Sr}}/f_{\text{Zr}}$ of 1.022, suggesting that the internal standard Zr-correction method is reliable.

Within the same analytical cycle, inserting a into Equation (3), we were able to obtain the fractionation factor for Sr. Inserting Equation (4) obtained the Sr isotopic composition of the samples. Note that differences in instrumental conditions may cause considerable changes in the absolute values of the Sr and Zr isotopic ratios. Therefore, the calculations should only be based on $\ln(^{88}\text{Sr}/^{86}\text{Sr})_{\text{measure}}$ and $\ln(^{92}\text{Zr}/^{90}\text{Zr})_{\text{measure}}$ with data obtained in the same analysis section under identical instrumental analytical conditions.

Moreover, during a daily analytical run, the instrumental mass bias drift typically resulted in the raw $^{88}\text{Sr}/^{86}\text{Sr}$ ratios to

Fig. 4 (a) Temporal evolution of $^{88}\text{Sr}/^{86}\text{Sr}$ (or $^{92}\text{Zr}/^{90}\text{Zr}$ on a matched scale) ratios using a 200 ng mL^{-1} NIST SRM 987 solution during an analytical session of 12 h. Samples were analyzed in a defined standard-sample-bracketing order. This shows clearly the similar $^{92}\text{Zr}/^{90}\text{Zr}$ ratio evolution through time relative to $^{88}\text{Sr}/^{86}\text{Sr}$, indicating that Zr and Sr behaved similarly in the MS. (b) Effects of the Zr mass bias correction on the Sr isotopic ratios. This shows an excellent mass bias correction leading to improved stability of the $^{88}\text{Sr}/^{86}\text{Sr}$ ratios over time.

Fig. 5 Comparison of the precision using the two methods, with or without doping Zr within the same analytical run. The precision of obtained $\delta^{88/86}\text{Sr}$ values is improved 5-fold compared to the “SSB only” technique.

vary with time, almost identical to the trend for raw $^{92}\text{Zr}/^{90}\text{Zr}$ ratios (Fig. 4a). Using the $^{92}\text{Zr}/^{90}\text{Zr}$ ratios clearly allows a reliable mass bias drift correction of the Sr ratios, leading to stable corrected $^{88}\text{Sr}/^{86}\text{Sr}$ ratios through time (Fig. 4b). This is further evidence that the Zr-correction method is necessary and feasible for improving the precision of the $^{88}\text{Sr}/^{86}\text{Sr}$ values.

Furthermore, to compare both methods, the $\delta^{88/86}\text{Sr}$ values were calculated by standard-sample-bracketing using either Zr

mass bias-corrected or raw Sr isotope ratios. The results indicate that the $\delta^{88/86}\text{Sr}$ values obtained by SSB, plus Zr internal standard and by SSB without the internal standard, were consistent within the error range. However, the Zr-doped internal standard plus SSB method resulted in much more stable standard deviation than the method without an internal standard (Fig. 5). According to our data set, using the Zr-corrected ratios usually led to an improvement of the uncertainty by a factor of ~ 3 . This improvement was even up to a factor of 5 within the same analytical cycles when the SSB calculated results were not satisfactory, which showed variations of up to 0.169‰ (2SD) in reproducibility, compared to the 0.032‰ (2SD) with the Zr-doped correction (Fig. 5). Thus, our Zr-doping method reduces the level of instrumental stability required for the analyses, which is very important for applications.

Optimum Zr/Sr ratio. To evaluate the effect of Zr on the $\delta^{88/86}\text{Sr}$ values, various amounts of a mono-elemental Zr stock solution were doped into a 200 ng mL^{-1} NIST SRM 987 solution ($\text{Zr}/\text{Sr}=1:1, 1:1.5, 1:2, 1:3$) and analyzed in a typical run under identical instrumental condition. The results show that a significant improvement on the precision of $\delta^{88/86}\text{Sr}$ was obtained within the same analytical run when our Zr-doping correction method was used in comparison to the “SSB only” method. While the SSB method revealed a long-term reproducibility of the $\delta^{88/86}\text{Sr}$ of NIST SRM 987 $> 0.64\%$ (2SD) (Fig. 6, red squares), the precisions in the Zr-doped SSB runs were 0.054‰, 0.039‰, 0.023‰ and 0.030‰ (2SD) when the Zr/Sr was 1:1, 1:1.5, 1:2, 1:3, respectively (Fig. 6a, b, c and d, blue circles). Our best results were acquired when $\text{Zr}/\text{Sr} \geq 1.5$, and the precision of the obtained $\delta^{88/86}\text{Sr}$ values were ~ 3 -fold better than the “SSB only” method in the same measurement, where the Zr/Sr ratio was 2:1 (Fig. 6c). Therefore, the best optimum value of $\text{Zr}/\text{Sr} = 2:1$ was adopted for this study.

Nebulizer fractionation effect. A notable difference of $\delta^{88/86}\text{Sr}$ value was observed when three different $100 \mu\text{L min}^{-1}$ nebulizers (shown as Nebulizer #1, #2 and #3 in Fig. 7) were employed under the optimum instrumental conditions. During a typical run, an in-house standard Alfa Sr solution (without chemical separation) and a standard seawater IAPSO solution (with chemical separation) were introduced into Nebulizer #1, #2 and #3, respectively. The long-term reproducibility of our in-house standard Alfa Sr yielded $\delta^{88/86}\text{Sr}$ of $0.113 \pm 0.039 \%$ (2SD, $n = 46$) over 6 months and the $\delta^{88/86}\text{Sr}$ value of the IAPSO was reported widely.^{6,11,15,19,20,22,23} It is worth noting that Nebulizer #1 and #3 have already been used over 3 months and Nebulizer #2 was used for the first time. When Nebulizer #1 was employed, the $\delta^{88/86}\text{Sr}$ values of the Alfa Sr and IAPSO were -0.163 ± 0.049 (2SD, $n=19$) and 0.133 ± 0.042 (2SD, $n=5$), respectively, which were significantly lower than the long-term repeatability value $0.113 \pm 0.039\%$ (2SD, $n = 46$) and published values, respectively (Fig. 7a).^{6,11,15,19,20,22,23} Instead, Nebulizer #3

Fig. 6 Effect of Zr on $\delta^{88/86}\text{Sr}$ with different amounts of Zr added to 200 ng mL^{-1} NIST SRM 987 solution.

Fig. 7 Fractionation effect on $\delta^{88/86}\text{Sr}$ value with different nebulizers. (a), (c) are results of using the outdated and/or much used nebulizers and (b) is the results of using a new nebulizer.

led to an opposite result and was higher than the normal value, separately (Fig. 7c). But, unlike Nebulizers #1 and #3, when Alfa Sr and IAPSO were introduced into the new Nebulizer #2 (Fig. 7b), the $\delta^{88/86}\text{Sr}$ values were 0.115 ± 0.038 (2SD, $n=17$) and 0.375 ± 0.029 (2SD, $n=4$), which agreed well with the long-term reproducible value of $0.113 \pm 0.039\%$ (2SD, $n=46$) and the reference values.^{6,11,15,19,20,22,23}

This phenomenon may be caused during the sample introduction process, since the experiment was executed under the identical instrumental condition, except with different nebulizers. It is recognized that the factors related to the sample introduction process, such as particle size in the aerosol, aerosol and analyte transport rate, have a notable impact on the signal and the results of the mass spectrometer.^{39–41,48,56} For instance, the study by Fuchs *et al.* shows that the extent of the atomic cloud grows with increasing particle diameter; thus, it takes longer for larger particles to get completely atomized and eventually ionized.⁴⁷ As we known, the nebulizer plays an important role in the generation of aerosol with fine particle size; so in this study, the fractionation effect was observed when outdated and/or much used nebulizers were used during stable Sr analysis. For high precision and accurate data, homogeneous aerosol particles are supposed to be introduced into the plasma; however, an outdated and/or much used nebulizer may produce a complex aerosol with different particle sizes and, therefore, lead to a complex interaction of these particles within the ICP. Besides, droplets and drops on the tip of the outdated and/or much used nebulizer were observed. The droplet was formed and grew bigger gradually until the large drop dripped from the tip while samples were

Table 3. $\delta^{88/86}\text{Sr}$ of the selected standard references

Sample	This Study (‰)	Reference value (‰)	^b n	Instrument	Calculation Method
BHVO-2	0.249±0.014 (n=7)	0.24±0.24 ¹³	5	Neptune	doping Zr (using ⁹⁰ Zr/ ⁹¹ Zr)
		0.248±0.014 ²²	4	Neptune	doping Zr (using ⁹² Zr/ ⁹⁰ Zr)
		0.25±0.02 ²⁰	3	Neptune	SSB
		0.24±0.09 ¹³	6	Neptune	doping Zr (using ⁹⁰ Zr/ ⁹¹ Zr ratio)
BCR-2	0.232±0.015 (n=10)	0.28±0.17 ¹³	6	Neptune	SSB
		0.284±0.075 ²²	4	Neptune	doping Zr (using ⁹² Zr/ ⁹⁰ Zr)
		0.22±0.02 ²⁰	2	Neptune	SSB
		0.381±0.010 ⁶	5	Axiom VG Element	SSB
		0.35±0.10 ¹¹	15	Nu	SSB
IAPSO	0.374±0.028 (n=23)	^a 0.386±0.005 ¹⁹	10	TIMS	Double spike (⁸⁷ Sr- ⁸⁴ Sr)
		0.370±0.026 ²²	5	Neptune	doping Zr (using ⁹² Zr/ ⁹⁰ Zr)
		^a 0.402±0.004 ²⁰	23	Neptune	SSB
		0.38±0.04 ²³	20	Neptune	doping Zr (using ⁹² Zr/ ⁹⁰ Zr)
		0.396±0.020 ¹⁵	54	TIMS	Double spike (⁸⁷ Sr- ⁸⁴ Sr)

^a Errors are expressed as 2SE and all other errors are expressed as 2SD.

^b n represents the repeated times.

introduced into the outdated and/or much used nebulizer. However, the uniform micro-diameter spray droplets were sprayed into the plasma immediately and there were no visible droplets on the tip of the nebulizer when a new one was used. This may also be the reason that different $\delta^{88/86}\text{Sr}$ values were produced when the outdated and/or much used and new nebulizers were used, separately.

Accurate and precise determination of $\delta^{88/86}\text{Sr}$ values in natural materials. In this study, the Zr internal standard plus SSB calibration method was used to determine the $\delta^{88/86}\text{Sr}$ values of BHVO-2, BCR-2 and IAPSO for which reference values exist in the literature. The results in Table 3 show that the $\delta^{88/86}\text{Sr}$ values for BHVO-2, BCR-2 and IAPSO obtained by our method agree well with the reported values. 6,11,13,15,19,20,22,23 This indicates that the complete analytical procedure, from the sample digestion method to the type of spectrometer (including the sample introduction), does not induce any significant bias in the fractionation factors between Sr and Zr. In addition, an in-house mono-elemental Sr reference sample Alfa, which was not chemically treated, was adopted to check the long-term stability of the instrument, and yielded the comparable result of 0.113± 0.039‰ (2SD, n = 46).

CONCLUSIONS

Our study shows that multiple factors, including varyingly doped Zr concentrations, matrix element effects, isobaric and polyatomic interferences, nebulizer effect, as well as Sr recovery during the separation procedure, can impact the

analytical results. Compared with the $\delta^{88/86}\text{Sr}$ values obtained by the SSB method without Zr-correction, the proposed Zr-correction approach features stable and reliable accuracy and a 3~5-fold improvement in precision. The $\delta^{88/86}\text{Sr}$ results show high tolerance for matrix elements, and Ca does not cause measurable isotopic shift with Ca/Sr ratios up to 10. We also found that nebulizer property could notably affect the accuracy and precision of $\delta^{88/86}\text{Sr}$. Further, a useful improvement for the Sr recovery rate was developed during the chemical separation process and the recovery was over 98.5%. Certified rock reference materials were dissolved by acid digestion, Sr was purified with Sr-spec[®] ion exchange resin, and the best reproducibility was obtained using the ⁹²Zr/⁹⁰Zr correction approach, which results in the precise measurements of $\delta^{88/86}\text{Sr}$ in silicate rocks and seawater. The new understanding of critical considerations could provide more information for following an efficient and feasible protocol in the precise determination of stable Sr isotopes.

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Notes

The authors declare no competing financial interest.

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