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Calculation methods for direct internal mass fractionation correction of spiked isotopic ratios from multi-collector mass spectrometric measurements

Zhu-yin Chu*, Yue-heng Yang, Guo Jinghui, Guang-sheng Qiao

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

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ABSTRACT

It is difficult to do internal mass fractionation corrections for isotope dilution analysis by thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), especially for MC-ICP-MS. In this study, calculation methods for direct internal fractionation correction of spiked isotope analysis by TIMS or MC-ICP-MS cycle by cycle for elements having at least two internal reference isotopic ratios are presented. For TIMS, direct internal mass fractionation correction calculation methods, based on both power and exponential laws, are derived; whereas for MC-ICP-MS, due to larger mass fractionation effects, only exponential law is considered. These calculation strategies can be applied for both static and multi-dynamic measurements. For multi-dynamic measurements, the isotope fractionation effect, gain and cup efficiency effects of different collectors, as well as ion beam fluctuation effects are all simultaneously eliminated. The calculation methods were verified by Sr isotopic analyses of spiked NBS987 standard solutions by TIMS and Hf isotopic analyses of spiked geological reference materials by MC-ICP-MS. In addition, precise and accurate calibrations of isotopic ratios of the spikes, based on the calculation methods, are discussed.

1. Introduction

Isotope fractionation is a ubiquitous phenomenon for isotopic analysis using thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Correction for mass fractionation of isotopes in thermal or plasma ionization mass spectrometry of un-spiked (natural) elements is normally achieved by normalizing to one accepted constant isotopic ratio, such as $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.1194$ for Sr isotopic analysis, $^{146}\mathrm{Nd}/^{144}\mathrm{Nd} = 0.7219$ for Nd isotopic analysis, and $^{179}\mathrm{Hf}/^{177}\mathrm{Hf} = 0.7325$ for Hf isotopic analysis. However, there exists no isotopic ratio for direct normalization of spike-normal mixtures because isotopic abundances in the mixture have been altered by the addition of spike. For geochemical research, the measured isotopic ratios of spike-sample mixtures must be corrected for mass fractionation in order to obtain accurate isotopic ratios and isotope dilution calculations. Because of the difficulty of mass fractionation correction for isotope dilution analysis (especially for MC-ICP-MS due to its larger mass fractionation effect), currently, some geochemical laboratories divide the sample solution into two aliquots: one used for isotope dilution determination of elemental concentrations; another one used for accurate and precise isotopic determination.

Various approaches have been used to correct for isotope fractionation of spike-normal mixtures. In the case where fractionation is linearly dependent on mass, algebraic solutions can be derived [1]. Alternatively, an iterative method can be applied to solve for fractionation. In the iterative method, mass fractionation correction is achieved by normalizing to the one accepted ratio in the natural element after subtracting iteratively or algebraically a small spike contribution to it. The iterative cycle is repeated until the calculated fractionation factors and concentrations converge.

For MC-ICP-MS analysis, isotopic fractionation can also be corrected by external normalization method: for example, Pb, Cu, Rb, Lu and Os isotopic ratios have been normalized to Tl, Zn, Zr, Yb and Ir, respectively [2–9]. However, it is becoming increasingly apparent, particularly with highly precise instruments, that mass fractionation factors for different elements are not identical [5,6,9]. One way to overcome this problem is to establish a correlation between the fractionation factors of the element of interest and the doped element [5,6,9]. For example, Yin et al. [6] demonstrated that the correlation between Ir and Os fractionation factors could be used to successfully correct spike-normal mixtures for mass fractionation. It must be noted, however, that their empirical correlation was established by time-consuming, high precision measurements of Ir–Os mixtures by MC-ICP-MS at the beginning of each analytical session. Even with this method, as Wu et al. [9] reported, it is possible that the relationship of mass fractionation factors for different elements may change with measurement time.

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* Corresponding author. Tel.: +86 10 82998586; fax: +86 10 62010846.
E-mail address: zhychu@mail.igcas.ac.cn (Z.-y. Chu).

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Based on the approach of Boelrijk [10], Qiao [11] presented a calculation method to directly correct for mass fractionation of spiked Sr and Nd isotopes using linear law. Based on the approach of Hofmann [1], Roddick et al. [12] developed a method to accurately calibrate the isotopic compositions of an Nd tracer (spike). Wendt and Haase [13] described a procedure to directly correct spiked ratios from dynamic multi-collection TIMS measurements based on power law. Lee et al. [14] presented a calculation method for highly accurate MC-ICP-MS determination of isotopic compositions and elemental concentrations for isotope dilution analysis using internal normalization based on linear, power, and exponential laws; however, for power and exponential law, the mathematics is complicated. Gopalan [15] reported that two internal reference isotopic ratios of an element permit direct and exact power law correction for mass fractionation of its isotopically spiked ratios from dynamic multi-collector TIMS measurements. Cavazzini [16] developed a method that true isotopic ratios can be obtained without any assumption about the isotopic composition itself for any element at least having three isotopes, if isotope fractionation of the element follows a linear law in TIMS. Lapen et al. [17] presented a complex method for robust correction of instrumentally produced mass-fractionation of both spiked and un-spiked samples that can be applied to MC-ICP-MS isotopic analysis of Hf as well as Nd, Sr, Os, etc. Lu et al. [18] reported an iterative calculation method for simultaneous determination of the Hf concentration and ^{176}Hf/^{177}Hf ratio by MC-ICP-MS with ^{179}Hf spike, which gave similar analytical results to those without spike.

In this study, calculation methods for direct fractionation correction of spiked isotope analysis by TIMS or MC-ICP-MS cycle by cycle for elements having at least two internal reference isotopic ratios are presented. For TIMS, direct internal mass fractionation correction calculation methods, based on both power and exponential laws, are demonstrated via spiked Sr isotopic analysis. For MC-ICP-MS, due to the typically much larger isotope fractionation effects of this type of instrument, only the exponential law is applied; a calculation method for spiked Hf isotopic analysis is derived as an example. The calculation strategies can be applied for both static and multi-dynamic measurements. For multi-dynamic mode, the isotope fractionation effect, gain and cup efficiency effects of different collectors, as well as ion beam fluctuation effects are eliminated. The methods were verified by measurement of spiked Sr NBS987 standard solutions by TIMS and spiked geological Hf reference materials by MC-ICP-MS. In addition, precise and accurate calibrations of isotopic ratios of the spikes, based on the calculation methods, are discussed.

2. Methods

2.1. Calculation method for TIMS

2.1.1. Spiked isotopic measurement by TIMS with static mode

2.1.1.1. Power law. This method is exemplified by spiked Sr isotopic analysis. Strontium isotopes are collected with five collectors, as shown in Table 1, where mass 85 is measured to monitor the ^{87}Rb interference on ^{87}Sr. The baselines are measured at half-mass positions and all the measured ion beam intensities are baseline-corrected.

Because the mass fractionation effect is at a magnitude of ~0.1%/*amu* for TIMS, the power law [e.g., 13,15] could be used for mass fractionation correction. If the gain and cup efficiency effects for different Faraday cups are ignored and the power law is applied, the following equations are obtained for each measurement cycle:

Table 1
Cup configuration for Sr isotopic measurement by TIMS with static mode.

Collectors	1	2	3	4	5
Isotopes	^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot (1+\alpha)^{-2} \quad (1)$$

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot (1+\alpha)^{2} \quad (2)$$

where subscript *mix* means the isotopic ratio of the spike-normal mixture; subscript *m* means the measured value; subscript *n* means the normalized value; α means the isotope fractionation factor according to the power law (the same below).

Combining Eqs. (1) and (2), we get:

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \quad (3)$$

According to the isotope dilution equation [10,11,15], we get:

$$\frac{(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N - [(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n}{[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n - (^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S} = \frac{(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_N - [(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n}{[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n - (^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_S} \quad (4)$$

where $(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N$ and $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_N$ are the isotopic ratios of Natural Sr, and they are 0.0565 and 8.37521, respectively; $(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S$ and $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_S$ are the isotopic ratios of the Sr spike, and they were precisely pre-determined.

Eq. (4) can be reformulated to the following equation:

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = A \cdot \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n + B \quad (5)$$

where

$$A = \frac{(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_N - (^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_S}{(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N - (^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S}$$

$$B = \frac{(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N \cdot (^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_S - (^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_N \cdot (^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S}{(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N - (^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S}$$

Combining Eqs. (3) and (5), the normalized mixed isotopic ratios, $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ and $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$, for each measurement cycle, are obtained (two equations, two unknowns). Then, the fractionation factor for each measurement cycle, α, is calculated using Eq. (2). $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for each measurement cycle, is then obtained with the following equation:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot (1+\alpha) \quad (6)$$

where $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_m$ is the ^{87}Rb interference-, baseline-corrected measured value.

The contribution of spike on sample ^{87}Sr/^{86}Sr is subtracted using the following equation [10,14]:

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_n = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n + \left\{\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n - \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_S\right\} \cdot D \quad (7)$$

where

$$D = \frac{(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_N - [(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n}{[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n - (^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_S}$$

Table 2
Sr isotopic measurement by TIMS with five collectors using dynamic mode.

Collectors	1	2	3	4	5
Sequence 1	83	84	85	86	87
Sequence 2	84	85	86	87	88
Sequence 3	85	86	87	88	89

2.1.1.2. Exponential law. The exponential law is normally preferred for isotope fractionation correction for isotope analysis by both TIMS and MC-ICP-MS [19–21]. If the exponential law is considered, the following equations can be obtained:

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left(\frac{m_{84}}{m_{86}}\right)^{\beta} \tag{8}$$

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left(\frac{m_{88}}{m_{86}}\right)^{\beta} \tag{9}$$

i.e.,

$$\begin{aligned}&\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \\ &= \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left(\frac{m_{84}}{m_{86}}\right)^{\beta} \cdot \left(\frac{m_{88}}{m_{86}}\right)^{\beta} \\ &\cong 0.999466^{\beta} \cdot \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m\end{aligned} \tag{10}$$

where m_{84}, m_{86} and m_{88} refer to the masses of isotopes $^{84}\mathrm{Sr}$, $^{86}\mathrm{Sr}$ and $^{88}\mathrm{Sr}$, β refers to the isotope fractionation factor according to exponential law (the same below).

The calculation for exponential law is started with the results obtained based on power law, i.e., we use the $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ obtained according to the power law, as discussed in Section 2.1.1.1, to get an approximate β value for each measurement cycle with Eq. (9). Then, by combining Eqs. (10) and (5), we obtain $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for the exponential law; substituting this new $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ into Eq. (9) again, we obtain the exponential fractionation factor, $\beta 1$. Because the $\beta 1$ value should be very close to the β value, and the small change of the β value only results in a very small change in 0.999466^{β}, substituting $\beta 1$ into Eq. (10) to do iteration calculations is unnecessary.

$[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for each measurement cycle, according to the exponential law, is then obtained using the following equation:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_m \cdot \left(\frac{m_{87}}{m_{86}}\right)^{\beta 1} \tag{11}$$

Finally, the contribution of spike on sample $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ is subtracted using Eq. (7).

The calculation strategies for Sr can be expanded to spiked isotopic analysis of elements having at least three stable isotopes, such as Nd, Os, etc. For example, for spiked Nd isotopes, $^{146}\mathrm{Nd}/^{144}\mathrm{Nd}$ and $^{148}\mathrm{Nd}/^{144}\mathrm{Nd}$ could be used as the two internal reference ratios, with the values of $(^{146}\mathrm{Nd}/^{144}\mathrm{Nd})_N = 0.7219$ and $(^{148}\mathrm{Nd}/^{146}\mathrm{Nd})_N = 0.334642$ [20]; as $^{142}\mathrm{Nd}$ could be subject to isobaric interference from $^{142}\mathrm{Ce}$ due to incomplete chemical separation prior to mass spectrometry, $^{142}\mathrm{Nd}/^{144}\mathrm{Nd}$ should be avoided to be used for the calculations.

2.1.2. Spiked isotope measurement by TIMS with multi-dynamic mode

2.1.2.1. Power law. Strontium isotopes are measured *via* a multi-dynamic mode, as shown in Table 2. One measurement cycle consists of three static measurement sequences. The baselines are measured at half-mass positions before each measurement block and all the measured ion beam intensities are baseline-corrected. Mass 85 is measured in each sequence to monitor the interference of $^{87}\mathrm{Rb}$ on $^{87}\mathrm{Sr}$.

We assume the isotope fractionation factors per *amu* are identical for the different measurement sequences in a dynamic measurement cycle. The assumption is reasonable because the time difference between each measurement sequence in a measurement cycle is very small.

If the power law is applied, the following equations are obtained for each measurement cycle from sequence 1:

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} = \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot (1+\alpha)^2 \cdot \frac{G(2)}{G(4)} \tag{12}$$

from sequence 3:

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m3} = \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot (1+\alpha)^{-2} \cdot \frac{G(4)}{G(2)} \tag{13}$$

where $G(i)$ is the total effect of the gain factor of amplifier and cup efficiency for Faraday cup i; subscript mi means the measured value of sequence i in a measurement cycle; α means the fratcionation factor for power law, and so on. By combining Eqs. (12) and (13), the following equation is obtained:

$$\begin{aligned}&\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \\ &= \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m3}\end{aligned} \tag{14}$$

By combining Eq. (14) and (5), we obtain the $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ and $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ according to the power law for each measurement cycle.

Similarly,from sequence 1:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot (1+\alpha)^{-1} \cdot \frac{G(5)}{G(4)} \tag{15}$$

from sequence 2:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m2} = \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_n \cdot (1+\alpha)^{1} \cdot \frac{G(4)}{G(5)} \tag{16}$$

By combining Eqs. (15) and (16), the following equation is obtained:

$$\begin{aligned}&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m2} \\ &= \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_n \\ &= \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n^2 \cdot \left[\left(\frac{^{86}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_n\end{aligned} \tag{17}$$

From this, we obtain a value of $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for a measurement cycle, i.e., $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n1}$:

$$\left[\left(\frac{^{87}Sr}{^{86}Sr}\right)_{mix}\right]_{n1} = \sqrt{\frac{[(^{87}Sr/^{86}Sr)_{mix}]_{m1} \cdot [(^{87}Sr/^{88}Sr)_{mix}]_{m2}}{[(^{86}Sr/^{88}Sr)_{mix}]_n}} \tag{18}$$

Similarly,from sequence 2:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m2} = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_n \cdot (1+\alpha)^{-1} \cdot \frac{G(4)}{G(3)} \tag{19}$$

from sequence 3:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m3} = \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{n} \cdot (1+\alpha)^{1} \cdot \frac{G(3)}{G(4)} \tag{20}$$

By combining Eqs. (19) and (20), the following equation is obtained:

$$\begin{aligned}
&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m2} \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m3} \\
&= \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n} \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{n} \\
&= \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n}^{2} \cdot \left[\left(\frac{^{86}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{n}
\end{aligned} \tag{21}$$

We obtain another value of $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for a measurement cycle, i.e., $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n2}$:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n2} = \sqrt{\frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{m2} \cdot [(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{m3}}{[(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}}} \tag{22}$$

Then,

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n} = \frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n1} + [(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n2}}{2} \tag{23}$$

We get two $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ values from a multi-dynamic measurement cycle. If the average values of the two $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for a measurement run are almost identical (the difference should normally be less than 30 ppm), the results are acceptable; otherwise, this may reflect problems during the measurement process or the power law is not appropriate to characterize the actual fractionation in the ion source.

Similarly, using Eq. (7), the contribution of the spike on $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ of natural sample is subtracted.

It should be noted that, with our calculation strategy, the ion beam fluctuation effect, the cup efficiencies and gain factors of amplifiers for Faraday cups, and isotope fractionation effects are all eliminated simultaneously within a multi-dynamic measurement cycle.

2.1.2.2. Exponential law. If exponential law is considered, for each measurement cycle, we get the following equations from sequence 1:

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} = \frac{\left[\left(^{84}\mathrm{Sr}/^{86}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{84}/m_{86}\right)^{\beta}} \cdot \frac{G(2)}{G(4)} \tag{24}$$

from sequence 3:

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m3} = \frac{\left[\left(^{88}\mathrm{Sr}/^{86}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{88}/m_{86}\right)^{\beta}} \cdot \frac{G(4)}{G(2)} \tag{25}$$

Combining Eqs. (24) and (25), we get:

$$\begin{aligned}
&\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n} \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n} \\
&= \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m3} \cdot \left(\frac{m_{84}}{m_{86}}\right)^{\beta} \cdot \left(\frac{m_{88}}{m_{86}}\right)^{\beta} \\
&\cong 0.999466^{\beta} \cdot \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} \cdot \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m3}
\end{aligned} \tag{26}$$

where β means the isotope fractionation factor according to the exponential law.

Similarly, we use $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$, calculated based on the power law for the dynamic mode, as discussed in Section 2.1.2.1, and the $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{m2}$, to obtain the approximate β value for each measurement cycle using Eq. (9). Then, by combining Eqs. (26) and (5), we obtain $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ and $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ values for each measurement cycle according to the exponential law.

Then,from sequence 1:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} = \frac{\left[\left(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{87}/m_{86}\right)^{\beta}} \cdot \frac{G(5)}{G(4)} \tag{27}$$

from sequence 2:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m2} = \frac{\left[\left(^{87}\mathrm{Sr}/^{88}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{87}/m_{88}\right)^{\beta}} \cdot \frac{G(4)}{G(5)} \tag{28}$$

By combining Eqs. (27) and (28), the following equation is obtained:

$$\begin{aligned}
&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m1} \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m2} \\
&= \frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n} \cdot [(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}}{(m_{87}/m_{86})^{\beta} \cdot (m_{87}/m_{88})^{\beta}} \\
&\cong \frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n}^{2} \cdot [(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}}{1.000165^{\beta}}
\end{aligned} \tag{29}$$

From this equation, we obtain one value of $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for a measurement cycle, i.e., $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n1}$:

$$\begin{aligned}
&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n1} \\
&= \sqrt{\frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{m1} \cdot [(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{m2}}{[(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}} \cdot 1.000165^{\beta}}
\end{aligned} \tag{30}$$

Similarly,from sequence 2:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m2} = \frac{\left[\left(^{87}\mathrm{Sr}/^{86}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{87}/m_{86}\right)^{\beta}} \cdot \frac{G(4)}{G(3)} \tag{31}$$

from sequence 3:

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m3} = \frac{\left[\left(^{87}\mathrm{Sr}/^{88}\mathrm{Sr}\right)_{mix}\right]_{n}}{\left(m_{87}/m_{88}\right)^{\beta}} \cdot \frac{G(3)}{G(4)} \tag{32}$$

By combining Eqs. (31) and (32), the following equation is obtained:

$$\begin{aligned}
&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{m2} \cdot \left[\left(\frac{^{87}\mathrm{Sr}}{^{88}\mathrm{Sr}}\right)_{mix}\right]_{m3} \\
&= \frac{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n} \cdot [(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}}{(m_{87}/m_{86})^{\beta} \cdot (m_{87}/m_{88})^{\beta}} \\
&\cong \frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n}^{2} \cdot [(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}}{1.000165^{\beta}}
\end{aligned} \tag{33}$$

From Eq. (33), we obtain another value of $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_n$ for a measurement cycle, i.e., $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{n2}$:

$$\begin{aligned}
&\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{mix}\right]_{n2} \\
&= \sqrt{\frac{[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_{m2} \cdot [(^{87}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{m3}}{[(^{86}\mathrm{Sr}/^{88}\mathrm{Sr})_{mix}]_{n}} \cdot 1.000165^{\beta}}
\end{aligned} \tag{34}$$

Table 3
Hf isotopic measurement by MC-ICP-MS with nine collectors using static mode.

Collectors	1	2	3	4	5	6	7	8	9
Isotopes	^{173}Yb	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{181}Ta	^{183}W

The following calculations are similar to those for the power law.

2.2. Direct normalization of spiked isotopes by MC-ICP-MS

Calculation method for spiked isotopic analysis by MC-ICP-MS is exemplified by Hf. The calculation method can be expanded to spiked isotopic analysis by MC-ICP-MS of elements having at least three stable isotopes such as Sr, Nd, and Os.

Hafnium isotopes are measured with static mode using nine collectors as shown in Table 3; ^{173}Yb and ^{175}Lu are measured to monitor the isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf; ^{181}Ta and ^{183}W are measured to monitor the isobaric interferences of ^{180}Ta and ^{180}W on ^{180}Hf. Similar to the TIMS methods, the baselines are measured off-peak and all the measured ion beam intensities are baseline-corrected.

For MC-ICP-MS, due to its much larger isotope fractionation effect, the exponential law is normally applied [6,14,22–24]. According to the exponential law, the following equations are obtained:

$$\left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n = \left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{177}}{m_{178}}\right)^{\beta} \qquad (35)$$

$$\left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n = \left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{179}}{m_{178}}\right)^{\beta} \qquad (36)$$

where m_{177}, m_{178} and m_{179} refer to the masses of isotopes ^{177}Hf, ^{178}Hf and ^{179}Hf, β refers to the isotope fractionation factor according to exponential law. Based on the measurement of the Hf solution standard that is interspersed with the samples, we can get the approximate value of β (normally about 2 [23]).

By combining Eqs. (21) and (22), we get:

$$\begin{aligned}&\left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n \cdot \left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n \\ &= \left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{177}}{m_{178}}\right)^{\beta} \cdot \left(\frac{m_{179}}{m_{178}}\right)^{\beta} \\ &\cong 0.999977^{\beta} \cdot \left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_m \qquad (37)\end{aligned}$$

According to the isotope dilution equation [10,11,15], we get:

$$\begin{aligned}&\frac{(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_N - [(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n}{[(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n - (^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_S} \\ &= \frac{(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_N - [(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n}{[(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n - (^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_S} \qquad (38)\end{aligned}$$

where subscript S means the isotopic ratios of Hf spike, and they were precisely pre-determined; $(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_N$ and $(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_N$ are the isotopic ratios of natural Hf, and their values are 0.681560 and 0.499242, based on numerous measurements of JMC475 (normalized to $^{179}\mathrm{Hf}/^{177}\mathrm{Hf} = 0.7325$), respectively.

Similarly, Eq. (38) can be reformulated to the following equation:

$$\left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n = A \cdot \left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_{mix}\right]_n + B \qquad (39)$$

where

$$A = \frac{(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_N - (^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_S}{(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_N - (^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_S}$$

$$B = \frac{(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_N \cdot (^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_S - (^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_N \cdot (^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_S}{(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_N - (^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_S}$$

By combining Eqs. (37) and (39), we obtain $[(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n$ and $[(^{177}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n$ for each measurement cycle (two equations, two unknowns). Substituting the $[(^{179}\mathrm{Hf}/^{178}\mathrm{Hf})_{mix}]_n$ into Eq. (36), we obtain the actual fractionation factor value, $\beta 1$, for a measurement cycle. Because the mass fractionation factor for MC-ICP-MS is stable during a measurement period, the β obtained from the Hf standard measurement should be very close to the $\beta 1$ value; meantime, the small change on β only causes a very small change on the 0.999977^{β}. Consequently, substituting $\beta 1$ into Eq. (37) to do iteration calculation is unnecessary.

The $[(^{176}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_n$, $[(^{179}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_n$ and $[(^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_n$ for a measurement cycle are then obtained using the following equations:

$$\left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n = \left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{176}}{m_{177}}\right)^{\beta 1} \qquad (40)$$

$$\left[\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n = \left[\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{179}}{m_{177}}\right)^{\beta 1} \qquad (41)$$

$$\left[\left(\frac{^{180}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n = \left[\left(\frac{^{180}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_m \cdot \left(\frac{m_{180}}{m_{177}}\right)^{\beta 1} \qquad (42)$$

The small contribution of the spike on the sample is subtracted using the following equations [10,11,15]:

$$\begin{aligned}\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_n &= \left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n \\ &\quad + \left\{\left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n - \left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_S\right]\right\} \cdot D \qquad (43)\end{aligned}$$

$$\begin{aligned}\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_n &= \left[\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n \\ &\quad + \left\{\left[\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_{mix}\right]_n - \left[\left(\frac{^{179}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_S\right]\right\} \cdot D \qquad (44)\end{aligned}$$

where

$$D = \frac{(^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_N - [(^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_n}{[(^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_n - (^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_S}$$

where a $(^{180}\mathrm{Hf}/^{177}\mathrm{Hf})_N$ value of 1.88676 is used.

From the result of Eq. (44), we can test the reliability of the mass fractionation correction method. If the final mean $(^{179}\mathrm{Hf}/^{177}\mathrm{Hf})_n$ value for a measurement run is very close to 0.7325 (the difference should normally be smaller than 50 ppm), the result may be judged to be acceptable. Otherwise, the results may reflect problems during the measurement process or the exponential law is not completely appropriate to characterize the actual fractionation in MC-ICP-MS for the sample analyzed as Vance and Thirlwall [22] and Lapen et al. [17] argued.

If the multi-dynamic method is used, the calculation method can also be derived using method similar to Sr isotope analyses by TIMS, except that we start the calculation directly with the β value, obtained according to the measurement of the Hf standard.

Table 4
Calculated results for spike Sr isotope analyses by TIMS[a].

Analysis No.	$[(^{84}Sr/^{86}Sr)_{mix}]_n$			$(^{87}Sr/^{86}Sr)_n$			
	This study		Normal	This study		Normal	2 SE (ppm)
	Power	Exp		Power	Exp		
Sr-mix-1	0.097379	0.097379	0.097379	0.710237	0.710235	0.710235	12
Sr-mix-2	0.169758	0.169749	0.169750	0.710246	0.710252	0.710256	20
Sr-mix-3	0.777539	0.777415	0.777491	0.710240	0.710257	0.710320	12
Sr-mix-4	1.47150	1.47112	1.47155	0.710186	0.710211	0.710408	15
Sr-mix-5	2.27022	2.26986	2.27049	0.710254	0.710270	0.710460	15
Sr-mix-6	3.29723	3.29631	3.29867	0.710199	0.710224	0.710711	18
Ref. Value					0.71024 [25]		

[a] Power and Exp mean that the mass fractionation was corrected using power law and exponential law, respectively; Normal means that the mass fractionation was corrected using the normal method (see text for details).

3. Applications and examples

3.1. Sr static measurements by TIMS

Because the ^{84}Sr abundance of available commercial Sr spike is mostly about 80% at current, the Sr spike contains relative high amounts of ^{86}Sr, ^{87}Sr and ^{88}Sr. Therefore, although only a little amount of Sr spike should be added to the sample to obtain an appropriated ^{84}Sr/^{86}Sr mixed ratio due to the very low (about 0.56%) abundance of ^{84}Sr in natural Sr, ^{87}Sr/^{86}Sr and ^{86}Sr/^{88}Sr could still be significantly altered by the added Sr spike. Consequently, it is very important to use an appropriate method to correct the mass fractionation for spiked Sr isotope analysis.

In this study, NBS987 Sr standard solutions spiked with different amounts of ^{84}Sr spike (containing about ~80% of ^{84}Sr), were analyzed by an Isoprobe-T mass spectrometer equipped with nine Faraday cups with static mode using the cup configuration as shown in Table 1, to test our calculation method. The measurement consisted of 6 blocks with 20 cycles per block. The integration time per cycle is 8 s. The baseline was measured at half mass positions prior to each block with an integration time of 15 s.

The measured results calculated with our method are shown in Table 4. The calculated results using the normal method, i.e., subtraction of the contribution of the spike on natural ^{86}Sr/^{88}Sr according to the measured ^{84}Sr/^{86}Sr directly first, then the corrected ^{86}Sr/^{88}Sr was used to calculate the mass fractionation factor using $^{86}Sr/^{88}Sr = 0.1194$ as a reference value, are also listed in Table 4 for comparison. It could be concluded that the results of our method are better than that calculated using the normal method, especially for the over-spiked samples. The results calculated using the power law are almost identical to those calculated using the exponential law.

3.2. Hf static measurements by MC-ICP-MS

Several geological reference materials spiked with ^{180}Hf spike (^{180}Hf, ~97.8%) were digested and chemically treated as outlined by Yang et al. [24], and measured by a Thermo Neptune MC-ICP-MS using the cup configuration as shown in Table 3. One run of Hf isotope analyses for standard solution and actual sample consisted of a 60 s off-peak baseline measurement and 90 cycles of sample signal collection, which are divided into 9 blocks so as to complete the 9 rotations of the amplifiers connected to the Faraday cups, in order to eliminate amplifier gain errors between different amplifiers [26]. The integration time of signal per cycle was set at a value of 4 s.

Because ^{180}Hf is the most abundant natural isotope of Hf, a relatively large amount of ^{180}Hf spike must be added into the sample solution to obtain an appropriate ^{180}Hf/^{177}Hf mixed ratio. Therefore, although the isotopic abundance of ^{180}Hf in commercial ^{180}Hf spike is very high (~97.8%), and isotopic abundances of ^{176}Hf, ^{177}Hf, ^{178}Hf and ^{179}Hf in the spike are very low, ^{176}Hf/^{177}Hf and ^{179}Hf/^{177}Hf isotopic ratios could be significantly altered by the relatively large amount of the added ^{180}Hf spike. Furthermore, the mass bias for MC-ICP-MS is about one order of magnitude greater than that of TIMS. Consequently, it is especially difficult to obtain accurate mass fractionation-corrected isotope ratios for spiked Hf analyses.

Table 5
Calculated results for spiked Hf isotope analyses by MC-ICP-MS.

Sample	$(180/177)_n$	$(176/177)_n$ (±2 SE)	Ref. values
1 GSR-3	2.89289	0.282998 ± 04	0.282984 ± 03 (2 SE) [27]
2 GSR-3	4.91468	0.282984 ± 06	
3 BHVO-2	3.13991	0.283102 ± 04	0.283098 ± 03 (2 SE) [27]
4 BHVO-2	3.97444	0.283102 ± 03	0.283105 ± 11 (2 SD) [28]
5 W-2	3.48951	0.282748 ± 05	0.282721 ± 05 (2 SE) [27]
6 W-2	4.65427	0.282727 ± 07	0.282745 ± 10 (2 SE) [29]
7 BCR-2	3.41340	0.282879 ± 07	0.282887 ± 07 (2 SE) [29]
8 BCR-2	4.16580	0.282885 ± 04	0.282876 ± 06 (2 SE) [30]
9 BIR-1	2.70674	0.283239 ± 11	0.283250 ± 06 (2 SE) [29]
10 BIR-1	5.10107	0.283266 ± 11	0.283252 ± 10 (2 SE) [30]

Measured results of isotopic compositions for the geological reference materials calculated with our method are listed in Table 5. It is found that our results agreed with the reported values within analytical error. It could be concluded that, our calculation method for spiked Hf isotopic analyses by MC-ICP-MS is reliable.

4. Precise measurements of isotopic compositions of Sr and Hf spikes

Any error in the isotopic composition of tracers used in isotope dilution analysis propagates to an error in the determination of sample isotopic composition as a result of the subtraction of tracer contribution from the sample-tracer mixture data. The main error in the tracer composition is due to mass fractionation, which cannot be easily corrected in the absence of an internal reference ratio. Normally, external correction methods are used to correct mass fractionation for measurements of the isotopes of spike [e.g., 20], however, the accuracy of external correction method is typically worse than that of internal correction methods. For this reason isotopic results from spiked analyses rarely have accuracy and precision comparable to un-spiked analyses, even if samples could be optimally spiked to minimize propagation of error in the spike composition to unknown sample compositions.

For TIMS, because the mass fractionation effect is normally at a magnitude of ~0.1%/amu, power law could normally be applied. Since two internal reference ratios in a normal standard can directly correct isotopic data of its mixture with a tracer according to the power law, they can in principle facilitate accurate and precise determination of the tracer composition. As an example, for measurement of isotopic ratios of a Sr spike by TIMS, if power law is considered, the following equations are obtained:

$$\left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_n = \left[\left(\frac{^{84}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_m \cdot (1+\alpha)^{-2} \tag{45}$$

$$\left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_n = \left[\left(\frac{^{88}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_m \cdot (1+\alpha)^{2} \tag{46}$$

$$\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_n = \left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_s\right]_m \cdot (1+\alpha) \tag{47}$$

where subscript s means isotopic ratio of the spike, n means normalized isotopic ratio, and m means the measured value (the same below).

It is possible to begin with a mass fractionated isotopic composition of a Sr tracer and measure the apparent $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_m$, $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_m$ and $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{mix}]_m$ ratios for its mixture with a normal Sr standard. According to Eqs. (45)–(47), if $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_s]_n$ increases by a factor of 1.001, $[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_s]_n$ should decrease by a factor of 1.001, and $[(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_s]_n$ should decrease by a factor of SQRT(1.001). Substituting incrementally and systematically adjusted values of the tracer composition of $[(^{84}\mathrm{Sr}/^{86}\mathrm{Sr})_s]_n$, using Eqs. (45)–(47) and (3)–(7), one can quickly compute a tracer composition that yields the spike corrected standard ratios $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_n$ closest to their known values (0.71024 in the case of SRM 987 Sr standard). This can be checked with the results from other mixtures of the standard and tracer.

For MC-ICP-MS, as an example, if isotopic ratios of a ^{180}Hf spike are measured and, the exponential law is applied, the following equations are obtained:

$$\left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_s\right]_n = \left[\left(\frac{^{177}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_s\right]_m \cdot \left(\frac{m_{177}}{m_{178}}\right)^{\beta} \tag{48}$$

$$\left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_s\right]_n = \left[\left(\frac{^{179}\mathrm{Hf}}{^{178}\mathrm{Hf}}\right)_s\right]_m \cdot \left(\frac{m_{179}}{m_{178}}\right)^{\beta} \tag{49}$$

$$\left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_s\right]_n = \left[\left(\frac{^{176}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_s\right]_m \cdot \left(\frac{m_{176}}{m_{177}}\right)^{\beta} \tag{50}$$

$$\left[\left(\frac{^{180}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_s\right]_n = \left[\left(\frac{^{180}\mathrm{Hf}}{^{177}\mathrm{Hf}}\right)_s\right]_m \cdot \left(\frac{m_{180}}{m_{177}}\right)^{\beta} \tag{51}$$

Similarly, one could start with a mass fractionated isotopic composition of a Hf tracer and measure the apparent $[(^{176}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_m$, $[(^{178}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_m$, $[(^{179}\mathrm{Hf}/^{177}\mathrm{Hf})_{mix}]_m$ and $[(^{180}\mathrm{Hf}/^{179}\mathrm{Hf})_{mix}]_m$ ratios for the mixture with a normal Hf standard. Normally, we use the β value obtained from the measurement of the Hf solution standard that is interspersed with the spikes to start the calculation. Then, substituting incrementally and systematically adjusted the values of β in Eqs. (48)–(51) to change the values of $[(^{177}\mathrm{Hf}/^{178}\mathrm{Sr})_s]_n$, $[(^{179}\mathrm{Hf}/^{178}\mathrm{Sr})_s]_n$, $[(^{176}\mathrm{Hf}/^{177}\mathrm{Sr})_s]_n$ and $[(^{177}\mathrm{Hf}/^{178}\mathrm{Sr})_s]_n$, using Eqs. (37)–(45), we can quickly compute a tracer composition that yields spike corrected standard ratios $(^{179}\mathrm{Hf}/^{177}\mathrm{Hf})_n$ and $(^{176}\mathrm{Hf}/^{177}\mathrm{Hf})_n$ closest to their known values (0.7325 and 0.282158, respectively in the case of Hf JMC475 standard). This can also be checked with the results from other mixtures of the standard and tracer.

5. Conclusions

Calculation methods for direct mass fractionation correction of spiked isotope analyses by TIMS or MC-ICP-MS cycle by cycle for elements having at least three stable isotopes such as Sr, Nd, Hf, Os are presented. For TIMS, direct mass fractionation correction calculation methods, using both power and exponential laws, are derived; whereas for MC-ICP-MS, due to larger mass fractionation effects, only the exponential law is considered. Calculation methods for both static and dynamic mode are given. For dynamic mode, the fractionation effects, gain effects of the different amplifiers, the ion beam fluctuation effects, and the cup efficiency effects are all eliminated. The calculation methods were verified by measurement of spiked Sr NBS987 standard solutions by TIMS with static mode, and spiked Hf geological reference materials by MC-ICP-MS; both gave satisfactory results. Finally, strategies for precise and accurate calibration of isotopic compositions of isotope tracers (spikes), based on the calculation methods, are presented.

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