

Correction of mass fractionation for isotope dilution analysis by MC-ICP-MS

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Isotope dilution analysis can provide precise elemental concentration and isotopic composition data in a single measurement run. However, mass fractionation correction in isotope dilution analysis can be challenging. This study presents two iterative calculation methods, based on isotopic ratios and abundances, for isotope dilution analysis of elements with at least two internal reference isotopic ratios. The strontium isotope system was used to show the details of the calculations. For convenience, a MATLAB program was created based on these calculation methods. Replicate analyses of three reference materials demonstrate that the obtained Rb and Sr concentrations and ⁸⁷Sr/⁸⁶Sr isotopic ratios are in good agreement with previously published values. In addition, two mineral Rb-Sr isochronal ages, which agree with accepted zircon U-Pb ages, demonstrate the validity of the methods presented in this study.

Keywords: isotopic dilution, mass fractionation, MATLAB, MC-ICP-MS, isochronal age

INTRODUCTION

The isotope dilution method is thought to provide the most precise quantitative determination of trace element concentrations (Zou, 2007). In this method, an artificially enriched isotopic spike is mixed with samples, and the concentration of the element of interest is calculated from the isotopic composition of the mixture measured by mass spectrometry. Compared to other methods, two advantages of the isotope dilution method make it remarkable. 1) It can correct instrumental mass fractionation during measurement, as well as the fractionation that occurs during chemical processing, which means the chemical recovery yield does not need to reach 100%. 2) It provides both concentration and isotopic composition data of the element of interest in one measurement. Because the elemental concentration measurement is derived from its isotopic composition, the isotopic composition of a sample must be determined first. Mass fractionation of isotopes is an inevitable phenomenon in mass spectrometry. For unspiked measurement, mass fractionation is corrected for by normalizing isotopic ratios to an accepted constant isotopic ratio, such as ⁸⁸Sr/⁸⁶Sr = 8.735209 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 for strontium and neodymium, respectively. However, for spiked measurement with the isotope dilution method, there is no canonical isotopic ratio to use for mass fractionation correction because of the

addition of the spike (e.g., Chu *et al.*, 2011; Cheong *et al.*, 2014). In previous studies, researchers deduced algebraic solutions by assuming the linear fractionation law (e.g., Boelrijk, 1968; Hofmann, 1971; Qiao, 1988), or applied an iterative method to solve for mass fractionation (e.g., Lu *et al.*, 2007). Although Chu *et al.* (2011) deduced algebraic solutions with the exponential law, their calculations require using the power law to estimate the mass bias factor, which may introduce error into the final results (equation (10) of Chu *et al.* (2011)). In this study, we investigate two iterative methods for isotope dilution analysis with at least two internal reference isotopic ratios (e.g., Sr, Nd, Hf and Os). The strontium isotope system was selected as an example to demonstrate the detailed deduction process with three different mass fractionation laws (the linear, power and exponential laws). A MATLAB program was created based on the algorithm to correct mass fractionation for isotope dilution data. Finally, the Rb and Sr concentrations and Sr isotopic compositions of several geological rock standards were measured, and two Rb-Sr isochrons were constructed to test the program.

CALCULATION METHODOLOGY

The following two iterative methods are based on isotopic ratios and isotopic abundances, respectively. Sr has four stable, naturally occurring isotopes: ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr. Of these, ⁸⁴Sr, ⁸⁶Sr, and ⁸⁸Sr are invariant isotopes, whereas ⁸⁷Sr is derived from the radioactive decay of ⁸⁷Rb through β^- emission.

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Using isotopic ratios

Exponential law For the Sr isotope system, according to the isotope dilution principle (Albarède and Beard, 2004), the following relationship exists:

$$Ratio_{Mix}^{84/86} = \lambda \cdot Ratio_{Spike}^{84/86} + (1 - \lambda) \cdot Ratio_{Sam}^{84/86} \quad (1)$$

where $Ratio_{Sam}^{84/86}$, $Ratio_{Spike}^{84/86}$ and $Ratio_{Mix}^{84/86}$ represent the $^{84}\text{Sr}/^{86}\text{Sr}$ ratios of the sample, spike and mixture, respectively, and λ is the atomic proportion of the isotope ^{86}Sr in a mixture contributed by the spike. Assuming that the isotopic mass fractionation obeys the exponential law, we obtain the following equation:

$$Ratio_{Mix}^{84/86} = Ratio_{Measure}^{84/86} \cdot \left(\frac{M_{84}}{M_{86}} \right)^\beta \quad (2)$$

where β is the fractionation factor, $Ratio_{Measure}^{84/86}$ is the measured $^{84}\text{Sr}/^{86}\text{Sr}$ ratio without mass fractionation correction, and M_{84} and M_{86} refer to the masses of the isotopes ^{84}Sr and ^{86}Sr respectively. Substituting Eq. (2) into Eq. (1) results in:

$$Ratio_{Measure}^{84/86} \cdot \left(\frac{M_{84}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{84/86} - (1 - \lambda) \cdot Ratio_{Sam}^{84/86} = 0. \quad (3)$$

With similar deduction, we obtain similar equations for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$:

$$Ratio_{Measure}^{87/86} \cdot \left(\frac{M_{87}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{87/86} - (1 - \lambda) \cdot Ratio_{Sam}^{87/86} = 0 \quad (4)$$

$$Ratio_{Measure}^{88/86} \cdot \left(\frac{M_{88}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{88/86} - (1 - \lambda) \cdot Ratio_{Sam}^{88/86} = 0 \quad (5)$$

where $Ratio_{Measure}^{87/86}$ and $Ratio_{Measure}^{88/86}$ are the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ ratios, respectively, without mass fractionation correction, and M_{87} and M_{88} refer to the masses of the isotopes ^{87}Sr and ^{88}Sr respectively. In Eqs. (3) and (5), all variables but β and λ are known or measured through mass spectrometry. By combining these two equations, we can determine the values of λ and β .

The Newton-Raphson iterative method is then used to solve these equations. Equations (3) and (5) become the

following functions:

$$F_1(\beta, \lambda) = Ratio_{Measure}^{84/86} \cdot \left(\frac{M_{84}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{84/86} - (1 - \lambda) \cdot Ratio_{Sam}^{84/86}, \quad (6)$$

$$F_2(\beta, \lambda) = Ratio_{Measure}^{88/86} \cdot \left(\frac{M_{88}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{88/86} - (1 - \lambda) \cdot Ratio_{Sam}^{88/86}. \quad (7)$$

The derivatives of F_i with respect to β and λ are

$$\frac{\partial F_1}{\partial \beta} = Ratio_{Measure}^{84/86} \cdot \left(\frac{M_{84}}{M_{86}} \right)^\beta \cdot \ln \left(\frac{M_{84}}{M_{86}} \right) \quad (8)$$

$$\frac{\partial F_1}{\partial \lambda} = -Ratio_{Spike}^{84/86} + Ratio_{Sam}^{84/86} \quad (9)$$

$$\frac{\partial F_2}{\partial \beta} = Ratio_{Measure}^{88/86} \cdot \left(\frac{M_{88}}{M_{86}} \right)^\beta \cdot \ln \left(\frac{M_{88}}{M_{86}} \right) \quad (10)$$

$$\frac{\partial F_2}{\partial \lambda} = -Ratio_{Spike}^{88/86} + Ratio_{Sam}^{88/86}. \quad (11)$$

To start the iterative calculation, an initial set of β and λ are assumed (β_1 and λ_1). By substituting β_1 and λ_1 into Eqs. (6)–(11), we obtain $F_1(\beta, \lambda)_1$, $F_2(\beta, \lambda)_1$, $(\partial F_1/\partial \beta)_1$, $(\partial F_1/\partial \lambda)_1$, $(\partial F_2/\partial \beta)_1$ and $(\partial F_2/\partial \lambda)_1$. The new set of β and λ are derived using the following calculation:

$$\begin{vmatrix} \beta_2 \\ \lambda_2 \end{vmatrix} = \begin{vmatrix} \beta_1 \\ \lambda_1 \end{vmatrix} - \begin{vmatrix} \left(\frac{\partial F_1}{\partial \beta} \right)_1 & \left(\frac{\partial F_1}{\partial \lambda} \right)_1 \\ \left(\frac{\partial F_2}{\partial \beta} \right)_1 & \left(\frac{\partial F_2}{\partial \lambda} \right)_1 \end{vmatrix}^{-1} \begin{vmatrix} F_1(\beta, \lambda)_1 \\ F_2(\beta, \lambda)_1 \end{vmatrix}. \quad (12)$$

The new β and λ values are used to repeat the iterative calculation until β and λ converge. By then substituting β and λ into Eq. (4), we obtain the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the sample; that is,

$$Ratio_{Sam}^{87/86} = \frac{Ratio_{Measure}^{87/86} \cdot \left(\frac{M_{87}}{M_{86}} \right)^\beta - \lambda \cdot Ratio_{Spike}^{87/86}}{1 - \lambda}. \quad (13)$$

Power law The power law for mass fractionation of $^{84}\text{Sr}/^{86}\text{Sr}$ can be expressed as:

$$Ratio_{Mix}^{84/86} = Ratio_{Measure}^{84/86} \cdot (1 + \alpha)^{M_{84} - M_{86}} \quad (14)$$

where α is the mass fractionation factor. Substituting Eq. (14) into Eq. (1) results in:

$$\begin{aligned} & Ratio_{Measure}^{84/86} \cdot (1 + \alpha)^{M_{84} - M_{86}} \\ &= \lambda \cdot Ratio_{Spike}^{84/86} + (1 - \lambda) \cdot Ratio_{Sam}^{84/86}. \end{aligned} \quad (15)$$

For $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$, similar equations are deduced:

$$\begin{aligned} & Ratio_{Measure}^{87/86} \cdot (1 + \alpha)^{M_{87} - M_{86}} \\ &= \lambda \cdot Ratio_{Spike}^{87/86} + (1 - \lambda) \cdot Ratio_{Sam}^{87/86} \end{aligned} \quad (16)$$

$$\begin{aligned} & Ratio_{Measure}^{88/86} \cdot (1 + \alpha)^{M_{88} - M_{86}} \\ &= \lambda \cdot Ratio_{Spike}^{88/86} + (1 - \lambda) \cdot Ratio_{Sam}^{88/86}. \end{aligned} \quad (17)$$

Except for α and λ , all variables in Eqs. (15) and (17) are known or measured through mass spectrometry. The Newton-Raphson iterative method is again used to resolve these equations:

$$\begin{aligned} Y_1(\alpha, \lambda) &= Ratio_{Measure}^{84/86} \cdot (1 + \alpha)^{M_{84} - M_{86}} - \lambda \cdot Ratio_{Spike}^{84/86} \\ &\quad - (1 - \lambda) \cdot Ratio_{Sam}^{84/86} \end{aligned} \quad (18)$$

$$\begin{aligned} Y_2(\alpha, \lambda) &= Ratio_{Measure}^{88/86} \cdot (1 + \alpha)^{M_{88} - M_{86}} - \lambda \cdot Ratio_{Spike}^{88/86} \\ &\quad - (1 - \lambda) \cdot Ratio_{Sam}^{88/86}. \end{aligned} \quad (19)$$

The derivatives of Y_i with respect to α and λ are

$$\frac{\partial Y_1}{\partial \alpha} = Ratio_{Measure}^{84/86} \cdot (M_{84} - M_{86}) \cdot (1 + \alpha)^{M_{84} - M_{86} - 1} \quad (20)$$

$$\frac{\partial Y_2}{\partial \alpha} = Ratio_{Measure}^{88/86} \cdot (M_{88} - M_{86}) \cdot (1 + \alpha)^{M_{88} - M_{86} - 1} \quad (21)$$

$$\frac{\partial Y_1}{\partial \lambda} = -Ratio_{Spike}^{84/86} + Ratio_{Sam}^{84/86} \quad (22)$$

$$\frac{\partial Y_2}{\partial \lambda} = -Ratio_{Spike}^{88/86} + Ratio_{Sam}^{88/86}. \quad (23)$$

Like the process described in the previous section, an ini-

tial set of α and λ are assumed (α_1 and λ_1). By substituting the initial values into Eqs. (18)–(23), we obtain $Y_1(\alpha, \lambda)_1$, $Y_2(\alpha, \lambda)_1$, $(\partial Y_1/\partial \alpha)_1$, $(\partial Y_1/\partial \lambda)_1$, $(\partial Y_2/\partial \alpha)_1$ and $(\partial Y_2/\partial \lambda)_1$. The new set of α and λ are derived from the following calculation:

$$\begin{vmatrix} \alpha_2 \\ \lambda_2 \end{vmatrix} = \begin{vmatrix} \alpha_1 \\ \lambda_1 \end{vmatrix} - \begin{vmatrix} \left(\frac{\partial Y_1}{\partial \alpha}\right)_1 & \left(\frac{\partial Y_1}{\partial \lambda}\right)_1 \\ \left(\frac{\partial Y_2}{\partial \alpha}\right)_1 & \left(\frac{\partial Y_2}{\partial \lambda}\right)_1 \end{vmatrix}^{-1} \begin{vmatrix} Y_1(\alpha, \lambda)_1 \\ Y_2(\alpha, \lambda)_1 \end{vmatrix}. \quad (24)$$

The new α and λ values are used to repeat the iterative calculation until α and λ converge. By then substituting α and λ into Eq. (16), we obtain the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the sample as follows:

$$Ratio_{Sam}^{87/86} = \frac{Ratio_{Measure}^{87/86} \cdot (1 + \alpha)^{M_{87} - M_{86}} - \lambda \cdot Ratio_{Spike}^{87/86}}{1 - \lambda}. \quad (25)$$

Linear law If the mass fractionation that occurs during measurement obeys the linear law, the following equation can be applied:

$$Ratio_{Mix}^{84/86} = Ratio_{Measure}^{84/86} \cdot (1 + \Delta \cdot (M_{84} - M_{86})) \quad (26)$$

where Δ is the mass fractionation factor. Combining Eq. (26) with Eq. (1) gives

$$\begin{aligned} & Ratio_{Measure}^{84/86} \cdot (1 + \Delta \cdot (M_{84} - M_{86})) \\ &= \lambda \cdot Ratio_{Spike}^{84/86} + (1 - \lambda) \cdot Ratio_{Sam}^{84/86}. \end{aligned} \quad (27)$$

For $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$, similar equations are deduced:

$$\begin{aligned} & Ratio_{Measure}^{87/86} \cdot (1 + \Delta \cdot (M_{87} - M_{86})) \\ &= \lambda \cdot Ratio_{Spike}^{87/86} + (1 - \lambda) \cdot Ratio_{Sam}^{87/86} \end{aligned} \quad (28)$$

$$\begin{aligned} & Ratio_{Measure}^{88/86} \cdot (1 + \Delta \cdot (M_{88} - M_{86})) \\ &= \lambda \cdot Ratio_{Spike}^{88/86} + (1 - \lambda) \cdot Ratio_{Sam}^{88/86}. \end{aligned} \quad (29)$$

Using Eqs. (27) and (29), we obtain

$$\Delta = \frac{U \cdot (Ratio_{Measure}^{88/86} - Ratio_{Sam}^{88/86}) + (Ratio_{Sam}^{84/86} - Ratio_{Measure}^{84/86})}{(M_{84} - M_{86}) \cdot Ratio_{Measure}^{84/86} - U \cdot Ratio_{Measure}^{88/86} \cdot (M_{88} - M_{86})} \quad (30)$$

where

$$U = \frac{Ratio_{Spike}^{84/86} - Ratio_{Sam}^{84/86}}{Ratio_{Spike}^{88/86} - Ratio_{Sam}^{88/86}}. \quad (31)$$

By substituting the obtained Δ value into Eq. (27) or (29), we can determine λ . Finally, by adjusting Eq. (28), we obtain the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the sample; that is,

$$Ratio_{Sam}^{87/86} = \frac{Ratio_{Measure}^{84/86} \cdot (1 + \Delta \cdot (M_{87} - M_{86})) - \lambda \cdot Ratio_{Spike}^{87/86}}{1 - \lambda}. \quad (32)$$

Using isotopic abundances

If we use I_{Spike}^{84} , I_{Spike}^{86} , I_{Spike}^{87} and I_{Spike}^{88} , respectively, to represent the isotopic abundances of ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr in the ^{84}Sr spike, and I_{Sam}^{84} , I_{Sam}^{86} , I_{Sam}^{87} and I_{Sam}^{88} , respectively, to represent the isotopic abundances of ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr in a sample, the following relationships apply:

$$I_{Sam}^{84} + I_{Sam}^{86} + I_{Sam}^{87} + I_{Sam}^{88} = 100 \quad (33)$$

$$I_{Sam}^{84} / I_{Sam}^{86} = 0.0565 \quad (34)$$

$$I_{Sam}^{88} / I_{Sam}^{86} = 8.375209. \quad (35)$$

By combining Eqs. (33)–(35) we obtain:

$$I_{Sam}^{84} = (100 - I_{Sam}^{87}) / 166.932903 \quad (36)$$

$$I_{Sam}^{86} = (100 - I_{Sam}^{87}) / 9.431709 \quad (37)$$

$$I_{Sam}^{88} = (100 - I_{Sam}^{87}) / 1.126146. \quad (38)$$

Based on the principle of the isotope dilution method, we derive the following:

$$Ratio_{Mix}^{84/86} = \frac{Mol_{Spike} \cdot I_{Spike}^{84} + Mol_{Sam} \cdot I_{Sam}^{84}}{Mol_{Spike} \cdot I_{Spike}^{86} + Mol_{Sam} \cdot I_{Sam}^{86}} \quad (39)$$

where Mol_{Spike} and Mol_{Sam} represent the Sr molar quantities of the spike and the sample, respectively. By substituting Eqs. (36) and (37) into Eq. (39), we obtain:

$$Ratio_{Mix}^{84/86} = \frac{Mol_{Spike} \cdot I_{Spike}^{84} + Mol_{Sam} \cdot (100 - I_{Sam}^{84}) / 166.932903}{Mol_{Spike} \cdot I_{Spike}^{86} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 9.431709}. \quad (40)$$

If the mass fractionation that occurs during measurement obeys the exponential law, then Eqs. (2) and (40) can be combined as follows:

$$Ratio_{Measure}^{84/86} \cdot \left(\frac{84}{86}\right)^\beta - \frac{Mol_{Spike} \cdot I_{Spike}^{84} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 166.932903}{Mol_{Spike} \cdot I_{Spike}^{86} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 9.431709} = 0. \quad (41)$$

For $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$, similar equations are deduced:

$$Ratio_{Measure}^{87/86} \cdot \left(\frac{87}{86}\right)^\beta - \frac{Mol_{Spike} \cdot I_{Spike}^{87} + Mol_{Sam} \cdot I_{Sam}^{87}}{Mol_{Spike} \cdot I_{Spike}^{86} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 9.431709} = 0 \quad (42)$$

$$Ratio_{Measure}^{88/86} \cdot \left(\frac{88}{86}\right)^\beta - \frac{Mol_{Spike} \cdot I_{Spike}^{88} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 1.126146}{Mol_{Spike} \cdot I_{Spike}^{86} + Mol_{Sam} \cdot (100 - I_{Sam}^{87}) / 9.431709} = 0. \quad (43)$$

The following equations also apply:

$$Mol_{Spike} = M_{Spike}^{Sr} / Mass_{Spike} \quad (44)$$

$$M_{Spike}^{Sr} = C_{Spike} \cdot M_{Spike} \quad (45)$$

$$Mass_{Spike} = \frac{I_{Spike}^{84} \cdot M_{84} + I_{Spike}^{86} \cdot M_{86} + I_{Spike}^{87} \cdot M_{87} + I_{Spike}^{88} \cdot M_{88}}{100} \quad (46)$$

where M_{Spike}^{Sr} and $Mass_{Spike}$ represent the weight and the atomic weight of Sr in the added spike, respectively; C_{Spike}

Table 1. Isotopic compositions of the spikes used in this study

	$^{84}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{88}\text{Sr}/^{86}\text{Sr}$
^{84}Sr spike	15.0321	0.427624	3.40374
	$^{87}\text{Rb}/^{85}\text{Rb}$		
^{87}Rb spike	240.735		

Table 2. Cup configuration for Rb-Sr isotope analysis using Neptune Plus MC-ICP-MS

	L4	L3	L2	L1	C	H1	H2
Sr		^{83}Kr	^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr
Rb		^{83}Kr		^{85}Rb	^{86}Sr	^{87}Rb	

and M_{Spike} are the Sr concentration and weight of the added spike; and M_{84} , M_{86} , M_{87} and M_{88} are the atomic weights of ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr , respectively. Substituting Eqs. (45) and (46) into Eq. (44) results in:

$$\text{Mol}_{\text{Spike}} = 100 \cdot \frac{C_{\text{Spike}} \cdot M_{\text{Spike}}}{I_{\text{Spike}}^{84} \cdot M_{84} + I_{\text{Spike}}^{86} \cdot M_{86} + I_{\text{Spike}}^{87} \cdot M_{87} + I_{\text{Spike}}^{88} \cdot M_{88}}. \quad (47)$$

Thus, except for β , I_{Sam}^{87} and Mol_{Sam} , all variables in Eqs. (41)–(43) are known or measured through mass spectrometry. Using the Newton-Raphson iterative method, values for β , I_{Sam}^{87} and Mol_{Sam} can be obtained. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the sample can then be derived with the following equation:

$$\text{Ratio}_{\text{Sam}}^{87/86} = I_{\text{Sam}}^{87} / I_{\text{Sam}}^{86} = 9.431709 \cdot I_{\text{Sam}}^{87} / (100 - I_{\text{Sam}}^{87}). \quad (48)$$

Calculating element abundance

Substituting I_{Sam}^{87} into Eqs. (36)–(38) provides the other three isotopic abundances of the sample (I_{Sam}^{84} , I_{Sam}^{86} and I_{Sam}^{88}). The total Sr abundance of the sample can then be determined as described by Zou (2007):

$$C_{\text{Sam}} = C_{\text{Spike}} \cdot \frac{\text{Ratio}_{\text{Spike}}^{87/86} - \text{Ratio}_{\text{Mix}}^{87/86}}{\text{Ratio}_{\text{Mix}}^{87/86} - \text{Ratio}_{\text{Sam}}^{87/86}} \cdot \frac{M_{\text{Spike}}}{M_{\text{Sam}}} \cdot \frac{\text{Mass}_{\text{Sam}}}{\text{Mass}_{\text{Spike}}} \cdot \frac{I_{\text{Spike}}^{87}}{I_{\text{Sam}}^{87}} \quad (49)$$

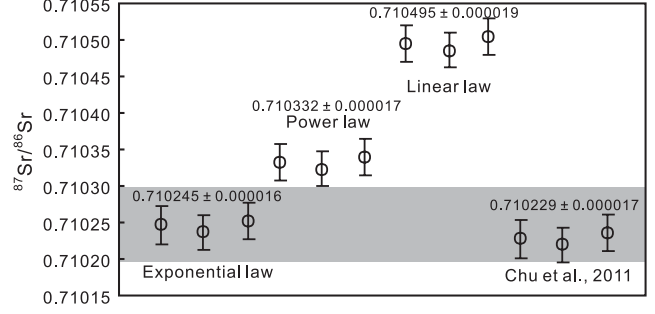


Fig. 1. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of SRM 987 corrected for mass fractionation using three different fractionation laws (the linear, power and exponential laws). The results for the same SRM 987 data calculated with the method proposed by Chu et al. (2011) are also shown for comparison. The gray area represents the reference value of SRM 987 (Woodhead and Hergt, 2001; Raczek et al., 2003; Elburg et al., 2005; Weis et al., 2005, 2006). The error bars correspond to 2 standard errors (2s).

where M_{Sam} and Mass_{Sam} are the weight of the added sample and the Sr atomic weight, respectively, and

$$\text{Mass}_{\text{Sam}} = \frac{I_{\text{Sam}}^{84} \cdot M_{84} + I_{\text{Sam}}^{86} \cdot M_{86} + I_{\text{Sam}}^{87} \cdot M_{87} + I_{\text{Sam}}^{88} \cdot M_{88}}{100}. \quad (50)$$

THE SINGLESPIKE SOFTWARE PACKAGE

For this study, we have developed a software package called SingleSpike, which is a MATLAB GUI, to help users apply the above iterative calculation method to process isotopic dilution data. The SingleSpike program uses isotopic ratios to correct for isotopic mass fractionation; the three mass fractionation laws (the linear, power and exponential laws) are available to make comparisons. The program package includes the following files: Singlespike.fig stores the GUI of SingleSpike, whereas SingleSpike.m is the main function. The folder “Element” records the natural and spike isotopic compositions for different isotope systems as well as certain running parameters. Before SingleSpike is used, these isotopic compositions should first be input. SingleSpike independently calculates isotopic ratios for each analytical cycle of the mass spectrometer. The internal precision (standard error) of each measurement cycle can directly represent the repeatability of measurements. SingleSpike yields output of the isotopic ratios of both the sample and the mixture. This program package and detailed instructions for its use are available at <http://www110.zippyshare.com/v/wxZkAwJO/file.html> and <https://pan.baidu.com/s/1o8AfDYq>.

Table 3. Rb and Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of USGS reference materials measured in this study and published values from literature

Sample	Rb (ppm)		Sr (ppm)		$^{84}\text{Sr}/^{86}\text{Sr}$ of mixture	$^{87}\text{Sr}/^{86}\text{Sr}$	
	This study	Literature values	This study	Literature values		This study	Literature values ^a
AGV-2	65.1	66.3 ± 0.80 ^b	662.1	661 ± 2.6 ^b	1.24235	0.704012	0.703987(16) ^c
	64.9		658.8		0.95423	0.704001	0.703931(34) ^f
	64.7		663.9		0.98595	0.704021	0.704079 ^e
BCR-2	46.3	47 ^b	337.6	340 ^b	0.74521	0.705005	0.705003(08) ^c
	46.8	44.75 ± 7.38 ^c	335.1	323.7 ± 52.6 ^c	0.88642	0.704989	0.705019(16) ^e
	46.5	47.3 ^d	338.5	339 ^d	0.65487	0.705011	0.704958(34) ^f 0.705015 ^g
BHVO-2	9.02	9.08 ^b	395.8	396 ^b	0.62548	0.703474	0.703469(14) ^c
	9.11	9.18 ± 0.16 ^c	394.2	397 ± 5.2 ^c	0.69562	0.703481	0.703487(19) ^e
	9.08	8.56 ^d	397.9	394 ^d	0.71452	0.703465	0.703435(34) ^f 0.703481(34) ^h

^aThe numbers inside parentheses are 2 standard deviation corresponding to the last two digits of the values.

^bRaczek et al. (2001); ^cElburg et al. (2005); ^dWillbold and Jochum (2005); ^eWeis et al. (2006); ^fRaczek et al. (2003); ^gBalcaen et al. (2005); ^hWeis et al. (2005).

EXPERIMENTAL PROCEDURE AND RESULTS

Materials and reagents

Sr isotopic compositions of three United State Geological Survey (USGS) geological reference materials (BHVO-2, BCR-2 and AGV-2) were measured to evaluate and verify the newly developed method and program. We also selected several minerals from two rock samples with known ages (the Plešovice granulite (Sláma et al., 2008) and the Qinghu granite (Li et al., 2013)) to construct Rb-Sr isochrons.

Deionized water used in the experiment was purified with a Millipore system to yield a resistivity of 18.2 MΩ at 25°C. BV-III-grade hydrofluoric acid (HF), hydrochloric acid (HCl) and nitric acid (HNO₃) (all from the Beijing Institute of Chemical Reagents) were purified via sub-boiling using a Savillex DST-1000 system.

Sample digestion

For each sample, about 30–100 mg of sample powder was weighed and poured into a pre-cleaned 15-mL PFA beaker. Weighed aliquots (~50–100 mg) of the mixed ^{84}Sr - ^{85}Rb -enriched spike were added to the samples, which were then gently evaporated to dryness. Table 1 shows the isotopic composition of the spike. Next, 1 mL of 7 M HNO₃ and 2 mL of concentrated HF were added. The beakers were tightly capped and heated on a hotplate at about 120°C for 7 days. The beakers were then opened and dried on the hotplate, 1 mL of 14 M HNO₃ was added to each sample, and they were then dried a second time. After that, 1 mL of 14 M HNO₃ was added again to each

sample, and the beakers were capped and placed on the hotplate for 4 hours. Each beaker was then opened and dried a third time. Finally, 1.5 mL of 2 M HCl was added and the beakers were capped and placed on the hotplate for 2 hours prior to chemical separation.

Ion-exchange chromatography

Purification of Sr was carried out through ion chromatography with AG50W-X12 resin. The resin was washed in turn with 18 mL of 6 M HCl, 10 mL of Milli-Q water and 2 mL of 2 M HCl. After that, centrifuged sample solutions were loaded on the resin column. Then, the resin was washed with 3 mL of 2 M HCl to remove matrix elements (e.g., Si, Al, Mg and Fe). Rb was then eluted with 1.5 mL of 2 M HCl. Next, the resin was washed with 8 mL of 2 M HCl to remove any residual Rb. The Sr fraction was then eluted with 3 mL of 2.5 M HCl. This purification procedure was repeated twice for samples with Rb/Sr ratios greater than 1 to ensure complete separation of Rb from Sr. Finally, samples were evaporated to dryness. Before MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometer) measurement, Rb and Sr were extracted with 2% HNO₃. Total procedure blanks were <0.1 ng for Sr and <0.05 ng for Rb, which were negligible with respect to the sample weights.

Mass spectrometry

Rb and Sr isotopic measurements were conducted with a Thermo Scientific Neptune Plus MC-ICP-MS at the State Key Laboratory of Isotope Geochemistry of the Guangzhou Institute of Geochemistry (GIG), Chinese

Table 4. Rb-Sr isotope data for minerals from the Plešovice granulite and the Qinghu granite

Sample	Mineral	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}^*$	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE
Plešovice granulite	Biotite	762.1	109.6	20.345	0.82384	0.00002
	K-feldspar	603.2	253.9	6.909	0.75979	0.00002
	K-feldspar	581.3	243.5	6.943	0.76033	0.00002
	K-feldspar	582.6	255.1	6.642	0.75882	0.00002
Qinghu granite	K-feldspar	489.5	730.5	1.805	0.70802	0.00002
	Plagioclase	71.43	812.5	0.2367	0.70452	0.00002
	Apatite	0.700	369.7	0.005	0.70401	0.00002

*The $^{87}\text{Rb}/^{86}\text{Sr}$ isotopic ratios were calculated from measured Rb and Sr concentrations and isotopic compositions.

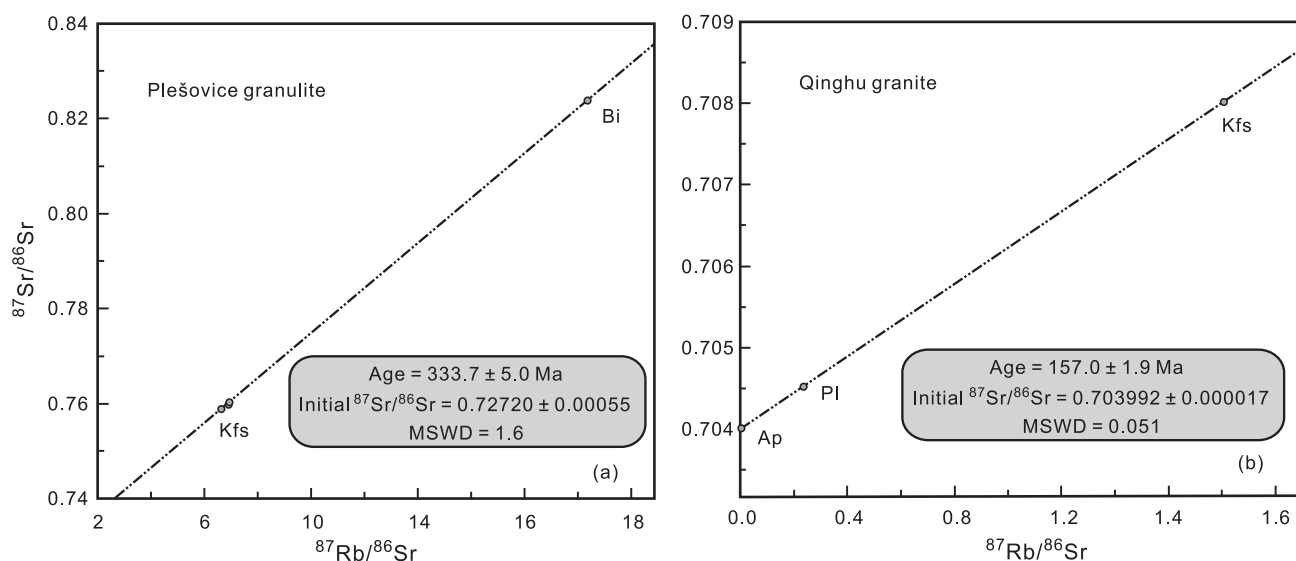


Fig. 2. Rb-Sr mineral isochrons of (a) the Plešovice granulite and (b) the Qinghu granite. The Isoplot software package (Ludwig, 2003) was used to calculate the isochron ages with a decay constant of ^{87}Rb of 1.42×10^{-11} (Steiger and Jager, 1977). Input error for $^{87}\text{Rb}/^{86}\text{Sr}$ is 1%, and individual errors are smaller than the size of the symbols.

Academy of Sciences. A MicroMist PFA nebulizer (50 $\mu\text{L}/\text{min}$) and a quartz cyclonic spray chamber were used to introduce sample solutions in 2% HNO_3 into the mass spectrometer. Table 2 provides the instrumental configurations for Rb and Sr isotopic measurements. During the measurements, the intensities of ^{85}Rb and ^{88}Sr were about 1 and 5 volts, respectively. The Rb and Sr isotope analyses consisted of 30 and 65 cycles, respectively, with an integration time of 4.2 s per cycle. Fifteen analyses of NIST SRM (National Institute of Standard and Technology, standard reference material) 987 yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio value of 0.710252 ± 0.000020 (two standard deviations (2SD)). The raw data of Sr measurements were exported and reduced with SingleSpike. Mass fractionation of Rb is not corrected in the SingleSpike software; therefore, a standard-sample-standard bracketing method was used to make this correction.

Results

Three analyses of the spiked SRM 987 were corrected for mass fractionation using SingleSpike with the linear, power and exponential laws, respectively (Fig. 1). Only the results corrected with the exponential law agree with the reference value. The power and linear laws were insufficient to correct for mass fractionation during MC-ICP-MS measurement (Chu *et al.*, 2011). Therefore, the following data were all corrected using the exponential law. Figure 1 also shows the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of SRM 987 calculated with the method proposed by Chu *et al.* (2011). Chu *et al.* (2011) deduced an algebraic solution with the exponential law without iterative calculation. However, their method requires first applying the power law to estimate the mass bias factor, which may introduce error into the final results. The results of the three SRM 987 analyses calculated with the method of Chu *et al.* (2011)

are approximately 16 ppm lower than the results of this study (Fig. 1). Although the results of the two studies are identical within analytical error, our results are closer to the mean value of the accepted $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of SRM 987.

Three duplicates of each USGS geological reference material were measured. The results of this study and the data published in existing literature are summarized in Table 3 for comparison. The results for the concentrations of Rb and Sr and the Sr isotopic compositions are in good agreement with the values obtained in previous studies. The replicate values of Rb-Sr concentrations for the reference materials are within 1%, and the laboratory biases in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are lower than 20 ppm (2SD).

To further test the newly developed analytical protocol, we established Rb-Sr mineral isochron ages for the Plešovice granulite (from the Czech Republic) and the Qinhu granite (from China). Biotite and K-feldspar were selected for the Plešovice granulite, and apatite, plagioclase and K-feldspar were selected for the Qinhu granite, to construct these Rb-Sr isochrons. As shown in Table 4 and Fig. 2, the separated minerals yielded Rb-Sr isochron ages of 333.7 ± 5.0 Ma and 157.0 ± 1.9 Ma for the Plešovice granulite and the Qinhu granite, respectively, which are consistent with the accepted zircon U-Pb ages of these samples, 337.15 ± 0.37 Ma (Sláma *et al.*, 2008) and 159.5 ± 0.2 Ma (Li *et al.*, 2013), respectively. These results demonstrate the applicability and prospects of our methodology.

CONCLUSIONS

We have presented two iterative methods for isotope dilution analysis of elements with at least two internal reference isotopic ratios. Three different mass fractionation laws were applied in the calculation methods. However, only the exponential law accurately corrects for mass fractionation during MC-ICP-MS measurement. In addition, a MATLAB GUI program was created for isotope dilution data processing. The analytical results for three USGS reference materials and two rock samples with known ages demonstrate the validity of the methods presented in this study.

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