IsotopeMaker: A Matlab program for isotopic data reduction

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ABSTRACT

Mass fractionation during isotope measurement by mass spectrometer hinders the acquirement of true isotopic composition and tedious and complex mathematical calculations are required to correct for mass bias. This study provides a Matlab program named "IsotopeMaker" for convenient isotopic data reductions. IsotopeMaker has two main aspects of application. For in situ LA-MC-ICP-MS isotopic analyses, IsotopeMaker can process Sr, Nd and Hf isotope data. For double spike data, IsotopeMaker provides a fast and convenient mass bias correction for all elements that have at least four isotopes. The visualization windows of IsotopeMaker make it easy to operate. Isotopic Sr, Nd and Hf data of a modern coral, a reference zircon and an in-house apatite and Mo isotopic data measured using the double spike method have been used to test the program capability.

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1. Introduction

Isotope geochemistry plays a fundamental role in Earth sciences. Both radiogenic and stable isotopes are used widely to determine the age of rocks, archeological objects, and to trace geological and environmental processes. Mass spectrometers are used to determine the isotopic composition for samples. Because the strength of chemical bonds is mass dependent, during sample atomization and ionization in mass spectrometer mass fractionation between different isotopes will occur [1]. Thus, the measured isotope ratios are not the true isotope ratios. Three different models for mass fractionation of isotopes, which are named linear law, power law and exponential law, are proposed by researchers [2–5]. Several methods are also proposed to correct mass fractionation. For radiogenic isotope systems having two or more natural non-radiogenic isotopes, the non-radiogenic isotopic ratios can be used to correct the mass fractionation in radiogenic isotopic ratios of the same element, such as strontium, which has three non-radiogenic isotopes ^{84}Sr, ^{86}Sr and ^{88}Sr, and one radiogenic isotope ^{87}Sr. For radiogenic isotope systems having fewer than two natural non-radiogenic isotopes, an artificially add-in element of similar mass is used to correct mass fractionation, such as lead, which has only one non-radiogenic isotope ^{204}Pb and the $^{203}Tl/^{205}Tl$ of an add-in reference solution is used to do mass fractionation correction. Another method named "double spike method" is thought to provide the most precise determination of isotopic ratios among different methods at present. In this method, a double spike, which is made by artificially concentrating two minor isotopes, is added in samples to correct mass fractionation. For example, a double spike for lead isotopic analysis may be mainly composed of ^{204}Pb and ^{206}Pb. However, this method can only be applied to elements with no less than four different isotopes. The "standard sample bracketing" (SSB) method is also widely used in isotope analysis. In this method, the mass bias of samples is assumed to be the same as that of the standards analyzed before and after samples.

At present, most commercial mass spectrometers have software to do online internal mass fractionation correction for isotopes in solution mode, such as strontium, neodymium and hafnium. In the last two decades, the in situ isotope analytic technique has undergone rapid development. One of the most used methods to conduct in situ isotopic measurement is laser ablation multiple collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). However, in laser sampling mode, many interferences from carrier gases (argon and helium) preclude precise isotope analysis using these commercial software. Many researchers create spreadsheet programs to process an off line in situ isotope data reduction [e.g., 6–9]. However, each of these spreadsheet programs is for one specific isotope system measurement and all are therefore not universally applicable. Although the double spike method can provide the most precise determination of isotope ratios, the complicated mathematical computation during data reduction makes its application difficult. Different data reduction programs are proposed for

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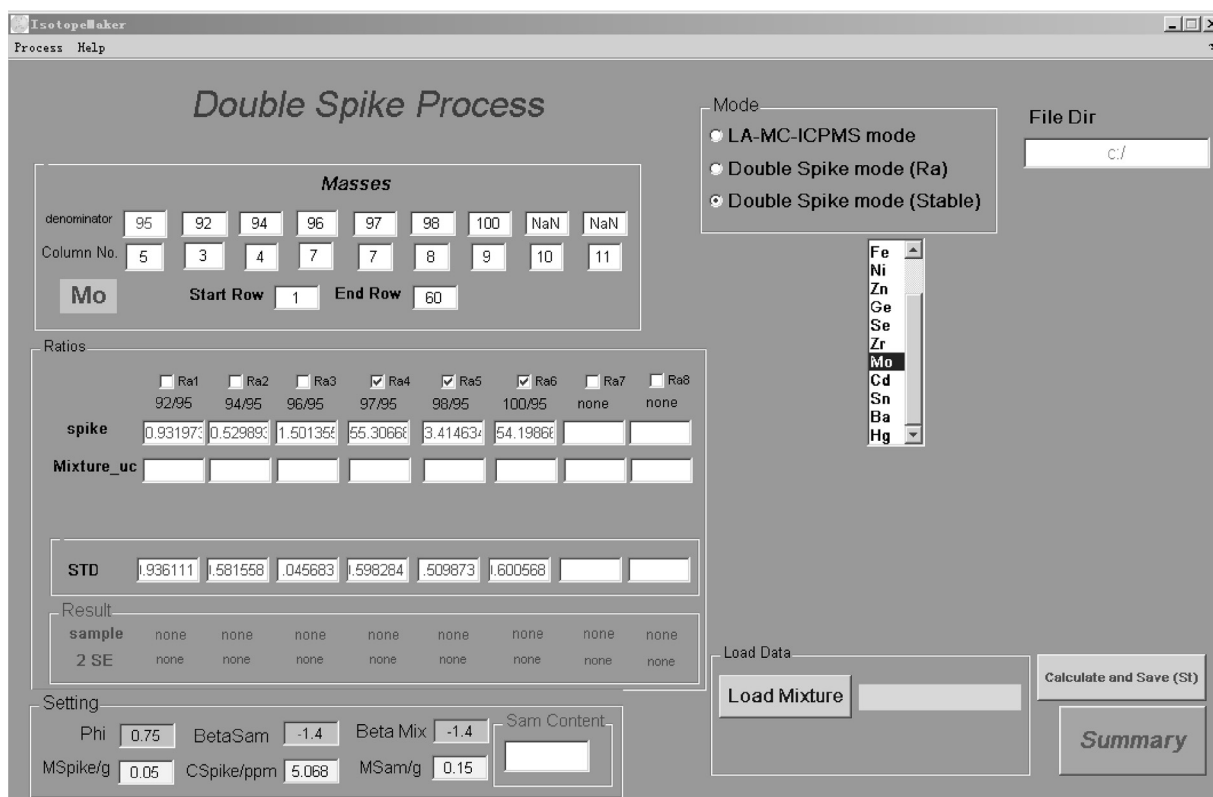*E-mail address:* zhangle@gig.ac.cn (L. Zhang).

Fig. 1. The main window of IsotopeMaker.

different isotope systems [e.g., 10–13]. However, each of these programs is also for a specific isotope system and can not replace each other. This paper presents here a new Matlab program named "IsotopeMaker" for processing laser sampled and double-spike mass spectrometer data (Fig. 1). IsotopeMaker has the following two functions: strontium, neodymium and hafnium isotope data reduction in in situ laser sampling studies; and mass bias correction for double-spike data. IsotopeMaker is designed to satisfy double-spike isotope analysis for all elements with four or more naturally occurring isotopes.

2. Data-reduction process

2.1. Laser sampling mass spectrometry data reduction

Compared to traditional isotope measurement in solution mode, in situ isotope measurement, which needs no tedious chemical preparation, is fast and can reveal isotopic heterogeneity at scales around 0.1 mm. This may be very important in magma processes studies, such as magma mixing and crustal contamination [14–16]. In recent years, the LA-MC-ICP-MS technique has been used extensively in a range of isotopic systems, such as Li, B, Mg, S, Fe, Sr, Nd, Hf and Pb [e.g., 6,17–23]. However, only Sr, Nd and Hf isotope measurements are available to use internal normalization to correct mass bias. The other isotope measurements use the SSB method to correct for mass bias. Because the mathematical computation of the SSB method is much simpler than that of correction method of internal normalization, only Sr, Nd and Hf isotope reduction processes are put in IsotopeMaker.

2.1.1. Strontium isotope data reduction

LA-MC-ICP-MS Sr isotope analysis is mainly conducted on some Sr-enriched and Rb-depleted minerals, such as plagioclase, apatite, carbonate, allanite, coral and perovskite. During Sr isotope measurement, there are many kinds of interference which may shift the $^{87}Sr/^{86}Sr$ ratio. The most critical interferences are isobaric interferences of krypton and rubidium. For samples that have high concentrations of rare earth elements (REE, such as apatite), the doubly charged Er and Yb ions become considerable interferences. Some Ca dimers and Ca argides, Fe dioxides, as well as Ga and Zn oxides have masses that overlap with those of the Sr isotopes of interest. During Sr isotope measurements, the signals of Kr, Rb, Sr, Er and Yb are measured (Table 1). The following data reduction protocol for Sr isotope is similar to Ramos et al. [6]. Krypton, mainly from the working gas (argon and helium), has two isotopes ^{84}Kr and ^{86}Kr interfering ^{84}Sr and ^{86}Sr. IsotopeMaker uses the gas blank (the first 50 cycles of the raw data) to correct Kr interference [6,14,15,24]. ^{87}Rb, which decays to ^{87}Sr through β^- decay, is a large interference on ^{87}Sr. All previous LA-MC-ICP-MS studies used the peak stripping method for the Rb correction. ^{87}Rb was calculated using the measurement of ^{85}Rb (measured at the same time as the Sr isotopes) and the natural $^{85}Rb/^{87}Rb$ ratio (2.593 [25]), and then subtracted from the signal at mass 87. It is assumed that Rb has a similar mass bias factor as Sr [6,26]. Samples that have high concentrations of REE may need to evaluate the influence of the doubly charged Er and Yb. The important interferences are $^{168}Er^{2+}$ and $^{168}Yb^{2+}$, $^{170}Er^{2+}$, $^{172}Yb^{2+}$, $^{174}Yb^{2+}$ and $^{176}Yb^{2+}$, which interfere with ^{84}Sr, ^{85}Rb, ^{86}Sr, ^{87}Sr and ^{88}Sr respectively. Previous studies using $^{167}Er^{2+}$ (83.5), $^{171}Yb^{2+}$ (85.5) and $^{173}Yb^{2+}$ (86.5) successfully corrected the interferences of Er^{2+} and Yb^{2+} [6,26]. The measured counts of $^{171}Yb^{2+}$ and $^{173}Yb^{2+}$ are used to calculate the mass bias factor for both Er and Yb and the peak stripping method is used to correct the interferences of Er and Yb. Though Woodhead et al. [27] observed the interferences of Ca dimers (e.g. $^{43}Ca^{44}Ca^+$) and Ca argides (e.g. $^{44}Ca^{40}Ar^+$) during Sr isotope measurements on carbonates, other studies suggest a very limited role for interfering Ca dimers and Ca argides [6,28]. IsotopeMaker does not therefore consider Ca dimers and Ca argides interferences. Other

Table 1
Potential interferences and cup configurations for Sr, Nd and Hf isotopic measurement.

		L4	L3	L2	L1	C	H1	H2	H3	H4
		83	83.5	84	85	85.5	86	86.5	87	88
Sr Interferences				^{84}Sr			^{86}Sr		^{87}Sr	^{88}Sr
	Rb				^{85}Rb				^{87}Rb	
	Kr	^{83}Kr		^{84}Kr			^{86}Kr			
	Er	^{166}Er	^{167}Er	^{168}Er	^{170}Er					
	Yb			^{168}Yb	^{170}Yb	^{171}Yb	^{172}Yb	^{173}Yb	^{174}Yb	^{176}Yb
		142	143	144	145	146	147	148	149	
Nd Interferences		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd		^{148}Nd		
	Sm			^{144}Sm			^{147}Sm		^{149}Sm	
	Ce	^{142}Ce								
		171	173	174	175	176	177	178	179	180
Hf Interferences				^{174}Hf		^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf
	Yb	^{171}Yb	^{173}Yb			^{176}Yb				
	Lu				^{175}Lu	^{176}Lu				

interferences such as Fe dioxides (^{54}Fe^{16}O$_2$), Ga and Zn oxides (^{71}Ga^{16}O and ^{68}Zn^{16}O) have a very limited effect on Sr isotope ratio measurement [6,26]. Thus IsotopeMaker does not correct laser ablation results for each of these species. Using an exponential mass bias law, all ratios are corrected to ^{86}Sr/^{88}Sr = 0.1194. For each analysis, IsotopeMaker outputs three ratios, ^{87}Rb/^{86}Sr, ^{84}Sr/^{86}Sr and ^{87}Sr/^{86}Sr. The ^{87}Rb/^{86}Sr ratio reflects Rb content relative to Sr content in samples and if this ratio is too high, the result of ^{87}Sr/^{86}Sr may not be correct. Previous studies indicate accurate corrections for ^{87}Rb can be acquired for samples with Rb/Sr < 0.02 (equal to ^{87}Rb/^{86}Sr < 0.06) [6,14]. Because both ^{84}Sr and ^{86}Sr are stable isotopes, the calculated ^{84}Sr/^{86}Sr can be compared to the accepted natural value (~0.0565 [29]) to assess whether the data reduction is correct or not.

2.1.2. Neodymium isotope data reduction

LA-MC-ICP-MS may be used to measure Nd isotopes in minerals enriched in REE (such as apatite, monazite and perovskite). During Nd isotope measurements, the only interference is from ^{144}Sm which overlaps with ^{144}Nd. Although ^{142}Ce interferes with ^{142}Nd, Nd isotope ratios involving ^{142}Nd are not commonly used. The interference of ^{142}Ce is therefore not taken into consideration. Several studies have established Nd isotope measurement techniques using LA-MC-ICP-MS [21,30]. Both Sm and Nd are measured in Nd isotope measurements (Table 1). The peak stripping method is applied to correct the isobaric interference of ^{144}Sm on ^{144}Nd. The mass bias factor of Sm is calculated from the measured isotopic ratio of ^{147}Sm/^{149}Sm and its accepted value (1.08507 [2]). ^{144}Sm is then derived from the measured ^{147}Sm, the natural ratio of ^{144}Sm/^{147}Sm (0.20504 [2]) and the calculated mass bias factor of Sm. Then using an exponential mass bias law all ratios are corrected to the natural ^{146}Nd/^{144}Nd ratio of 0.7219. For each analysis, IsotopeMaker outputs three ratios, ^{147}Sm/^{144}Nd, ^{145}Nd/^{144}Nd and ^{143}Nd/^{144}Nd. ^{147}Sm/^{144}Nd is used to calculate the initial ^{143}Nd/^{144}Nd for ancient samples. Like ^{84}Sr/^{86}Sr, ^{145}Nd/^{144}Nd is used to assess whether the data reduction is correct or not. The accepted value measured by thermal ionization mass spectrometer (TIMS) for ^{145}Nd/^{144}Nd is 0.348417 [2].

2.1.3. Hafnium isotope data reduction

At present, in situ Hf isotope measurement by LA-MC-ICP-MS is mainly performed on zircon, which is a Hf-enriched and resistant mineral, occurring as an accessory mineral in various kinds of rocks [20,31]. Recently, the technique has also been used to study the Hf isotopic composition of rutile [32]. During Hf isotope measurement, Yb, Lu and Hf are measured simultaneously (Table 1). IsotopeMaker takes a similar data reduction protocol as that in Wu et al. [20]. ^{173}Yb

and ^{175}Lu were used to correct the isobaric interference of ^{176}Yb and ^{176}Lu on ^{176}Hf. The natural ratio values of ^{176}Yb/^{173}Yb and ^{176}Lu/^{175}Lu used by IsotopeMaker are 0.79381 [33] and 0.02656 [20]. The mass bias factor of Yb is calculated from the measured ^{173}Yb/^{171}Yb and the natural ratio of 1.13268 [34]. The mass bias factor of Lu is assumed to be the same as that of Yb. The ^{176}Hf/^{177}Hf was normalized to ^{179}Hf/^{177}Hf of 0.7325 using an exponential law for mass bias correction. For each analysis, IsotopeMaker outputs three ratios, ^{176}Yb/^{177}Hf, ^{175}Lu/^{177}Hf and ^{176}Hf/^{177}Hf. ^{175}Lu/^{177}Hf is used to calculate the initial ^{176}Hf/^{177}Hf, though normally this ratio is small and the age-correction changes the value of ^{176}Hf/^{177}Hf very slightly.

2.2. Double-spike method data reduction

The double spike technique was first proposed by Dodson [35] to correct the instrumental mass bias on isotope measurements. As non-traditional stable isotope studies have grown in importance in Earth science over the last two decades, the double spike technique got much attention in the aspect of instrumental mass bias correction [36]. A double spike is a solution that contains a known concentration of the element, artificially enriched in two of its minor isotopes. The double spike method consists of mixing a natural sample with a double spike and measuring the isotopic ratios of the mixture using mass spectrometry, providing very precise quantitative determination not only of the concentrations of elements but also of the isotopic ratios. This technique needs the analyzed elements to have at least four isotopes. For radiogenic isotope systems, such as strontium and lead, the double spike method needs two runs: one run is to measure the un-spiked sample and the other run is to measure the spiked mixture [1]. For

Table 2
Symbols used in double spike data reduction.

Symbol	Meaning
Phi_i	Atomic proportion of the isotope i in a mixture contributed by the spike
R_{ij}	True isotopic ratio of isotopes i and j with masses m_i and m_j
r_{ij}	Isotopic ratio measured by mass spectrometer
β	Mass fractionation factor
C	The element concentrations in sample
M	The weight of sample
W	The atomic weights of the element
μ	The isotope abundances of isotope j

The superscripts of *sp*, *sam* and *mix* refer to spike, sample and mixture of spike and sample.
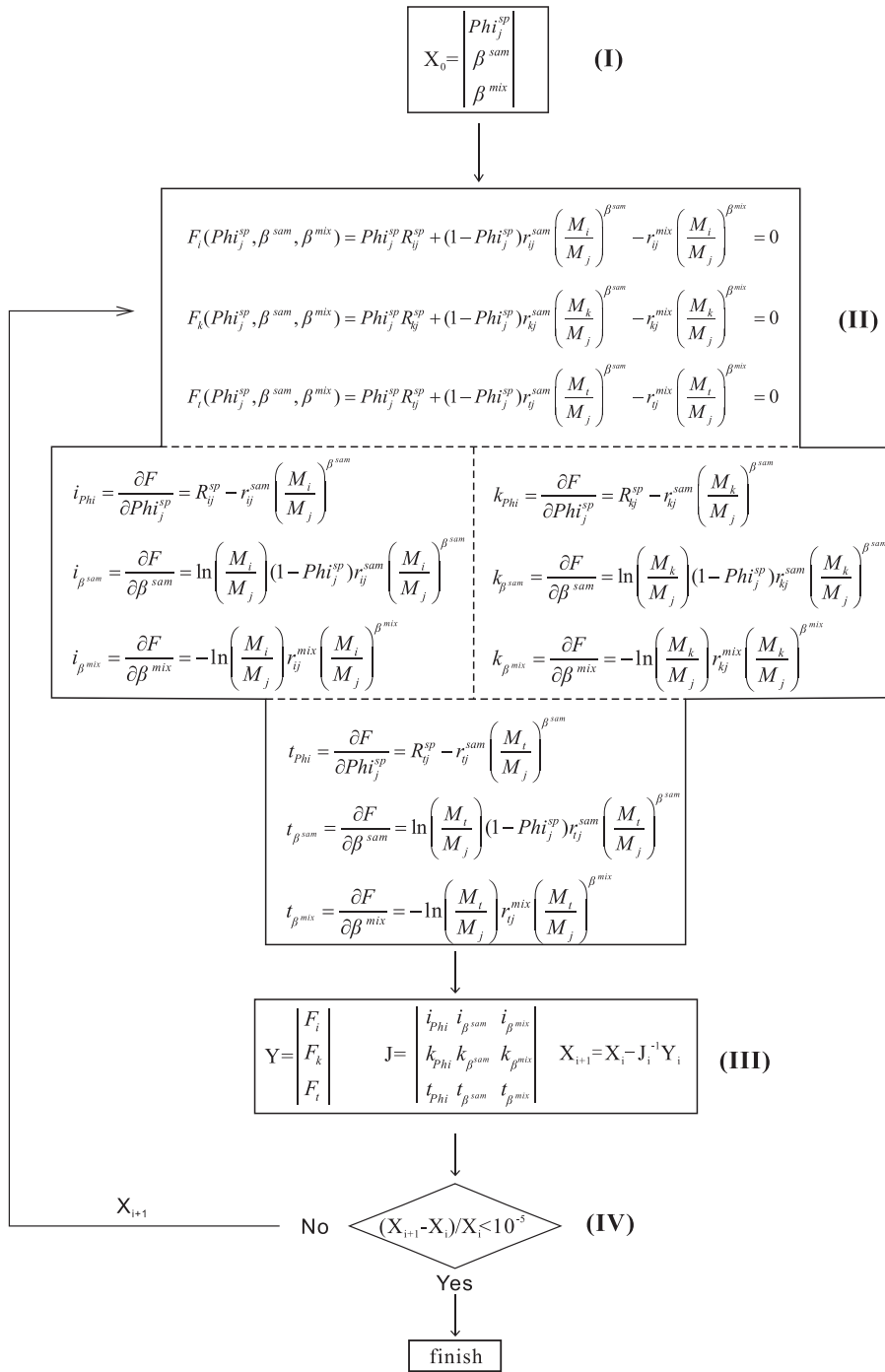
Fig. 2. Flow chart of the numerical algorithm applied to double spike data reduction (after Albarède and Beard [36]).

stable isotope system, such as chromium, iron and molybdenum, only one run measuring the spiked mixture is need to acquire mass bias corrected isotopic ratios [36,37].

For convenience, the meanings of the symbols used in the following equations for double spike data reduction are displayed in Table 2.

2.2.1. Double-spike method data reduction for isotope systems including radiogenic isotopes

For radiogenic isotope systems, r_{ij}^{sam} and r_{ij}^{mix} are measured using a mass spectrometer. Phi_j is the proportion of the isotope j in the mixture contributed by the spike. Then the proportion of

the isotope j contributed by the sample is $(1 - Phi_j)$. Based on mass balance, we have

$$Phi_j^{sp} R_{ij}^{sp} + (1 - Phi_j^{sp})R_{ij}^{sam} = R_{ij}^{mix} \tag{1}$$

Assuming the mass fractionation obeys the exponential law:

$$R_{ij} = r_{ij}\left(\frac{M_i}{M_j}\right)^{\beta} \tag{2}$$

Substitution of (2) in to (1), we obtain

$$Phi_j^{sp} R_{ij}^{sp} + (1 - Phi_j^{sp})r_{ij}^{sam}\left(\frac{M_i}{M_j}\right)^{\beta sam} = r_{ij}^{mix}\left(\frac{M_i}{M_j}\right)^{\beta mix}$$
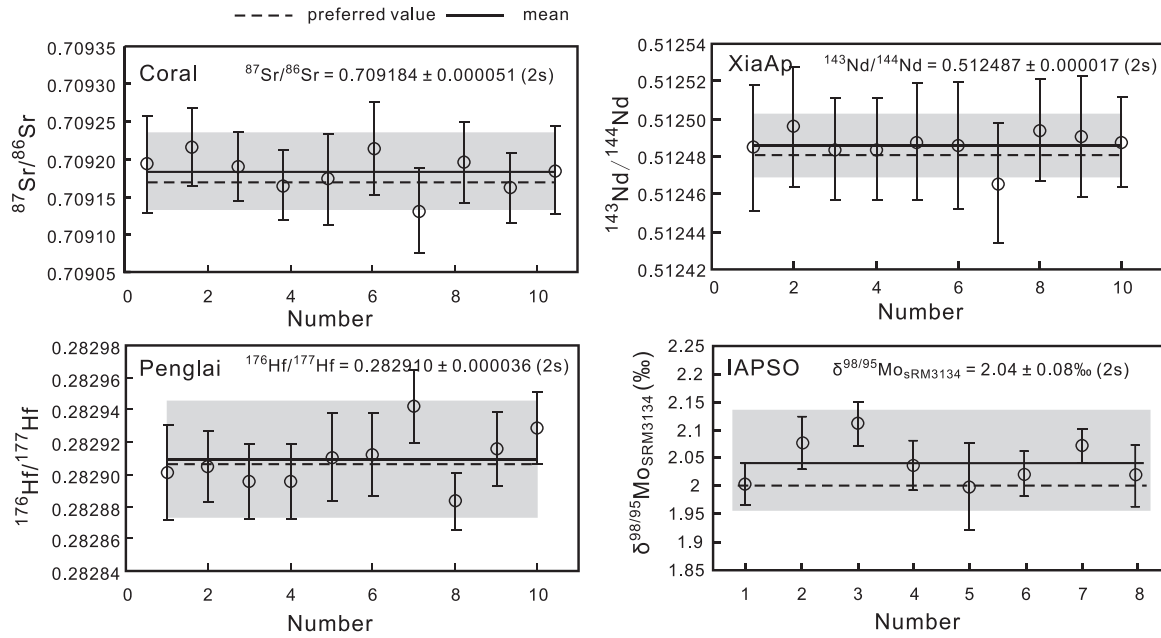
Fig. 3. The isotopic results of several reference materials calculated by IsotopeMaker. The preferred values of modern coral, Penglai and IAPSO are from Christensen et al. [39], Li et al. [40] and Li et al. [12]. For XiaAp, the preferred value was measured by MC-ICP-MS in solution mode. The error bars correspond to 2 standard error (2s).

Then we define:

$$F_i(Phi_j^{sp}, \beta^{sam}, \beta^{mix})$$

$$= Phi_j^{sp} R_{ij}^{sp} + (1 - Phi_j^{sp}) r_{ij}^{sam} \left(\frac{M_i}{M_j} \right)^{\beta^{sam}} - r_{ij}^{mix} \left(\frac{M_i}{M_j} \right)^{\beta^{mix}} = 0 \quad (3)$$

The derivatives of F_i with respect to Phi_j^{sp}, β^{sam} and β^{mix} are

$$i_{Phi} = \frac{\partial F}{\partial Phi_j^{sp}} = R_{ij}^{sp} - r_{ij}^{sam} \left(\frac{M_i}{M_j} \right)^{\beta^{sam}} \quad (4)$$

$$i_{\beta^{sam}} = \frac{\partial F}{\partial \beta^{sam}} = \ln \left(\frac{M_i}{M_j} \right) (1 - Phi_j^{sp}) r_{ij}^{sam} \left(\frac{M_i}{M_j} \right)^{\beta^{sam}} \quad (5)$$

$$i_{\beta^{mix}} = \frac{\partial F}{\partial \beta^{mix}} = - \ln \left(\frac{M_i}{M_j} \right) r_{ij}^{mix} \left(\frac{M_i}{M_j} \right)^{\beta^{mix}} \quad (6)$$

In Eq. (3), r^{sam} and r^{mix} are measured by mass spectrometry and there are three unknown variables (Phi_j^{sp}, β^{sam} and β^{mix}). For another two ratios R_{kj} and R_{tj}, two similar sets of function F and their derivatives can be written (Fig. 2). To start the calculation, it needs a set of starting values (Phi_j^{sp}, β^{sam} and β^{mix}). Substitute these starting values into the equations of part II in Fig. 2, whose left hand sides will form a 3×1 and 3×3 matrixes (Y and J in Fig. 2). Based on the equation of part III in Fig. 2, there forms a new set of Phi_j^{sp}, β^{sam} and β^{mix}. Repeat these steps until the condition of part IV in Fig. 2 is satisfied. Then substitute the final Phi_j^{sp}, β^{sam} and β^{mix} into Eqs. (1) and (2), the sample's isotopic ratios will be obtained.

2.2.2. Double-spike method data reduction for stable isotope systems

For stable isotope system, only one run, measuring the spiked mixture, is required to acquire mass bias corrected isotopic ratios [36,37]. Traditionally, stable isotope ratios are normalized to a reference material and expressed in δ notation. For example, the ratio of $^{98}Mo/^{95}Mo$ is expressed as:

$$\delta^{98/95}Mo(‰) = \left[\frac{(^{98}Mo/^{95}Mo)_{sample}}{(^{98}Mo/^{95}Mo)_{SRM3134}} - 1 \right] \times 1000 \quad (7)$$

In Eq. (3), for stable isotope r^{mix} is measured by mass spectrometry and r^{sam} refers to an isotopic ratio of a reference material for stable isotope system. For example, in the case of Mo isotope measurement, reference NIST SRM 3134 is the reference material. During measurement, both spiked sample and spiked reference solution are analyzed. The data reduction is the same as that for radiogenic isotope systems. Using the mass bias corrected isotopic ratios of the sample and the reference solution, the δ value can be obtained.

One advantage of the double spike method is that the concentration of the measured element can be acquired at the same time. IsotopeMaker uses the following equation deduced by Zou [1] to calculate the element concentration.

$$C_{sam} = C_{spike} \frac{R^{sp} - R^{mix}}{R^{mix} - R^{sam}} \frac{M^{sp}}{M^{sam}} \frac{W^{sam}}{W^{sp}} \frac{\mu_{sp}^j}{\mu_N^j} \quad (8)$$

C_{sam} and C_{spike} are the element concentrations in the spike and sample. M^{sp} and M^{sam} are the weight of the spike and the weight of the sample, respectively. W^{sam} and W^{sp} are the atomic weights of the element in the sample and spike, respectively. μ_{sp}^j and μ_N^j are the isotope abundances of isotope j in the spike and sample, respectively. Note that j is the isotope on the denominator of the isotopic ratios.

Nineteen elements are preinstalled in IsotopeMaker. However, this does not mean that elements other than the preinstalled 19 elements cannot be calculated. To input a new element into IsotopeMaker, users just need to create an .xls file to save the new element setting. Because the isotopic compositions of the double spikes and reference materials may be not the same in different laboratories, users should first change the isotopic ratios of the double spikes and reference materials in the .xls files. Because IsotopeMaker does not consider any interference when dealing with

double spike data, careful chemical processes are needed to separate the interested elements from sample matrix.

IsotopeMaker calculates isotopic ratios of every cycle in each analysis independently. The internal precision (standard error) derived from every cycle calculation can directly reflect the measurement repeatability.

3. Application

To test IsotopeMaker, raw data of several reference materials measured by (LA)-MC-ICP-MS were input into IsotopeMaker. Ten analyses each of a modern coral, an in-house reference apatite and reference zircon Penglai were used to test the calculation for in situ Sr, Nd and Hf isotopic analyses. The detailed instrumental settings for Sr, Nd and Hf isotope analyses are similar to Ramos et al. [6], Yang et al. [21] and Wang et al. [38], respectively. The mean values of the 10 analyses for the ratios of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ of each reference sample are 0.709184 ± 0.000051 (2 standard deviation, 2SD), 0.512487 ± 0.000017 (2SD) and 0.282910 ± 0.000036 (2SD), which agree with the preferred values [39,40] within 2 standard deviation (Fig. 3). Eight repeated Mo isotopic analyses of IAPSO Atlantic seawater were used to assess the data reduction for double-spike method of IsotopeMaker. The chemical procedure and instrumental setting for Mo isotopic analysis have been described in a previous study [12]. The mean value of $\delta^{98/95}Mo_{SRM3134}$ of the eight analyses is 2.04 ± 0.08 (2SD) agreeing with the result measured by Li et al. [12].

4. Conclusion

IsotopeMaker is a matlab program for mass spectrometer isotopic data reduction which includes two main aspects of application. For in situ LA-MC-ICP-MS isotopic analyses, IsotopeMaker can process Sr, Nd and Hf isotopic data reduction. For double spike data, IsotopeMaker provides fast and convenient mass bias correction for all elements with at least four natural isotopes. The source codes, test data and the instructions for Isotopemaker are provided as Supplementary materials. Anyone interested in IsotopeMaker are encouraged to contact the authors by E-mail.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2015.09.019.

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