Estimation of optimal isotopic compositions of Sr, Ba, Nd and Sm spikes for double spike thermal ionization mass spectrometry by error propagation simulation

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ABSTRACT

Double spike thermal ionization mass spectrometry is a technique that can measure precisely the variation in stable isotopic composition of large atomic number elements. Precision of the double spike technique depends on the isotopic composition of the combined-spikes and also on analytical parameters such as sample-spike mixing factor and combination of the three isotope ratios used in the double spike analysis. Prior to preperation of the double spike, error propagation simulation through the double spike data analyses of Sr, Ba, Nd and Sm is carried out in order to estimate both optimal isotopic composition of the combined-spikes and optimal analytical conditions for these elements. The best isotopic compositions of combined spikes are $^{84}Sr/^{86}Sr_{double\ spike} \sim$ 2.5, $^{134}Ba/^{136}Ba_{double-spike} \sim$ 2.5, $^{150}Nd/^{145}Nd_{double\ spike} \sim$ 1.0 and $^{150}Sm/^{154}Sm_{double\ spike} \sim$ 0.47 for Sr, Ba, Nd and Sm, respectively. Optimal analytical conditions are also determined. Reliability of the simulation is confirmed by comparing the Sr error magnification factor of an actual double-spike analysis with the simulation results.

1. INTRODUCTION

Isotopic composition of an element may change by isotope fractionation that occurs through both chemical reactions and physical processes. Various isotope fractionation processes in nature cause variation of the isotopic composition of an element among natural geologic materials. Variations of the isotopic compositions of small atomic number elements (e.g. H, C, O and S) in natural geologic materials are widely used to trace geological and geochemical processes that the material has been subjected and also to discriminate the geological source of the material (e.g. Hoefs, 2004). Degree of isotope fractionation of an element depends on the relative mass difference of the isotopes (Bigeleisen and Mayer, 1947; Urey, 1947). Therefore, variation of the isotopic compositions of intermediate to large atomic number elements is expected to be very small compared to that of the small atomic number elements. Development of the multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and accompanying instrumental mass fractionation correction techniques made possible

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to measure very small variations in the isotopic compositions of intermediate atomic number elements such as Mg, Fe, Zn and Cu (Albarède, 2004; Beard and Johnson, 2004; Young and Galy, 2004). Studies of the isotopic variation of intermediate atomic number elements in nature are expanding by such techniques (Johnson et al., 2004).

An alternative analytical technique to precisely measure small isotopic variation of intermediate to large atomic number elements is the double spike thermal ionization mass spectrometry (DS-TIMS) technique. Application of the TIMS technique is limited to elements with relatively low first ionization potential. Thus, DS-TIMS technique cannot be applied for all elements that are studied by MC-ICP-MS technique. TIMS technique, however, has advantages over MC-ICP-MS technique in sensitivity, less severe isobaric interferences and higher analytical precision for measuring isotope ratios of elements that are easily ionized by thermal ionization (e.g. Sr and Nd). Isotope ratio measurement by TIMS technique contains instrumental mass fractionation issue. Therefore, use of the double spike technique (Dodson, 1963) is necessary to accurately correct for the instrumental mass fractionation during isotope ratio measurement by TIMS.

In the double spike technique, parameters such as the choice of two spiking masses of the double spike and isotopic composition of the double spike should be determined before preparing the double spike. Galer (1999) discussed the importance of determining an optimized condition for such parameters since these parameters control the precision of the double spike technique. Analytical conditions such as the choice of three isotope ratios used in the data analysis part of the double spike technique and the proportion of sample to the double spike in the "spiked" sample also affect the precision of the technique (Galer, 1999). These analytical conditions also need to be optimized to give most precise results. The degradation of the precision results from error magnification through the data analysis part of the double spike technique. Therefore, simulating the error magnification through the double spike analysis is a convenient way to estimate the optimal analytical parameters for a specific element (Galer, 1999; Rudge et al., 2009).

In this study, error propagation during the double spike analyses of Sr, Ba, Nd and Sm were simulated in order to determine optimal isotopic composition of the double spike and analytical conditions prior to the preperation of the actual double spike of these elements. Dependence of the degree of error magnification to the isotopic composition of the double spike and also to the analytical conditions is investigated for all four elements. Double-spike TIMS analysis of Sr reference reagent NBS 987 was performed to compare the simulation results with actual data and to check the reliability of the simulation. Optimal double spike isotopic compositions and analytical conditions are determined for Sr, Ba, Nd and Sm from the results of the error propagation simulation. Such data will be a basis of future high-precision double-spike analysis of Sr, Ba, Nd and Sm of geological materials.

2. THE DOUBLE SPIKE TECHNIQUE

The double spike technique, first proposed by Dodson (1963), is a rigorous method to correct for instrumental mass fractionation, which is inevitable in isotope ratio

mass spectrometry. Double spike technique allows determination of absolute isotopic composition of a sample by directly calculating the instrumental mass fractionation factor of a mass spectrometric measurement of the "natural "sample after a second mass spectrometric measurement was performed on a "spiked" sample. Application of the double spike technique is, basically, limited to elements that have four or more isotopes. Application to elements with three isotopes is possible by utilizing radioactive isotope or MC-ICPMS (e.g. Brennecka et $al.$, 2010; Bizzarro et $al.$, 2011). Knowledge of the accurate isotopic composition of the double spike is required to obtain absolute isotopic composition of a sample. However, this requirement is less severe because relative measurement against some reference material is sufficient for geochemical purposes (mass dependent uncertainty of the isotopic composition of the double spike is permissible in relative measurements; Wakaki and Tanaka, 2012). Numerous approaches to determine the instrumental mass fractionation factor from the mass spectrometric data are demonstrated in the literature (Dodson, 1963; Compston and Oversby, 1969; Hofmann 1971; Hamelin et $al.$, 1985; Johnson and Beard, 1999; Siebert et $al.$, 2001). Among those, matrix method (Hamelin et $al.$, 1985) gives the most simple and clear-cut solution. Details of the matrix method are summarized below.

Let an isotope ratio of an element be expressed as $R_i = m_i/m_0$. When an isotope ratio of a natural sample was measured on a mass spectrometer, the measured isotope ratio R_{in} is always deviated from the true isotope ratio R_{iN} by instrumental mass fractionation:

$$R_{iN} = R_{in} \left(1 + \alpha\Delta_i\right) , \qquad (3\text{-}1)$$

where α is an instrumental mass fractionation factor per atomic mass unit for the natural sample and Δ_i is the mass difference factor between numerator and denominator isotopes of ratio R_i. Instrumnental mass fractionation during TIMS measurement is best described by exponential law (Russel et $al.$, 1978). The use of the exponential law instead of the less-precise liner law in eq. (3-1) is not possible because the following equations will be too complex to obtain a solution by the matrix method. Therefore, approximation of the exponential law described in a liner style equation (exponential approximation mass fractionation law; Johnson and Beard, 1999) is introduced in place of the liner law. This can be done by defining the mass difference factor Δ_i in eq. (3-1) as $\Delta_i = (m_i - m_0) - (m_i - m_0)^2/2m_0$. The measured isotope ratio of a spiked sample R_{im} in another measurement is also deviated from its true value R_{iM}:

$$R_{iM} = R_{im} \left(1 + \alpha' \Delta_i\right) , \qquad (3\text{-}2)$$

where α' is an instrumental mass fractionation factor for the spiked sample. The true isotope ratio of the mixture R_{iM} can be expressed independently by a mixing factor Q between the sample and the double spike:

$$R_{iM} = Q\ R_{iS} + (1 - Q)\ R_{iN} , \qquad (3\text{-}3)$$

where R_{iS} is the true isotope ratio of the double spike. By introducing a new parameter q, where $q = 1/(1 - Q)$, Eq. (3-3) will be

$$R_{iN} - R_{iS} = q\ (R_{iM} - R_{iS}) . \qquad (3\text{-}4)$$

Combining Eqs. (3-1, 2 and 4) gives

$$q \ (R_{iS} - R_{im}) - \alpha' \ q \ (\Delta_i \ R_{im}) + \alpha \ (\Delta_i \ R_{in}) = R_{iS} - R_{in} \ . \qquad (3\text{-}5)$$

Three unknowns (q, α and α') are present in Eq. (3-5). Therefore, three independent isotope ratios of an element, each of which constructs three independent equations in the form of Eq. (3-5), are required to solve this equation. For the three isotope ratios (R_1, R_2 and R_3), Eq. (3-5) can be expressed in matrix form as

$$\mathbf{A} \cdot \begin{bmatrix} q \\ \alpha' \cdot q \\ \alpha \end{bmatrix} = b \ , \qquad (3\text{-}6)$$

where the matrix $\mathbf{A}$ and vector b are given by measured isotope ratios of natural and spiked samples as

$$\mathbf{A} = \begin{bmatrix} R_{1S} - R_{1m} & -\Delta_1 \cdot R_{1m} & \Delta_1 \cdot R_{1n} \\ R_{2S} - R_{2m} & -\Delta_2 \cdot R_{2m} & \Delta_2 \cdot R_{2n} \\ R_{3S} - R_{3m} & -\Delta_3 \cdot R_{3m} & \Delta_3 \cdot R_{3n} \end{bmatrix} \qquad (3\text{-}7)$$

and

$$b = \begin{bmatrix} R_{1S} - R_{1n} \\ R_{2S} - R_{2n} \\ R_{3S} - R_{3n} \end{bmatrix} , \qquad (3\text{-}8)$$

respectively. Solution of Eq. (3-6) will be then given by

$$\begin{bmatrix} q \\ \alpha' \cdot q \\ \alpha \end{bmatrix} = \mathbf{A}^{-1} \cdot b \ , \qquad (3\text{-}9)$$

where $\mathbf{A}^{-1}$ is the inverse matrix of $\mathbf{A}$. Finally, the true isotope ratio of the sample R_{iN} will be calculated with Eq. (3-1) by using measured isotope ratio of the natural sample R_{in}, and the instrumental mass fractionation factor α obtained from Eq. (3-9).

Uncertainty of the calculated true isotope ratio of the sample R_{iN} is estimated by propagating the uncertainties of the measured natural and spiked isotope ratios through Eqs. (3-5 to 9) by variance-covariance matrix procedure (Albarède and Provost, 1977; Hamelin *et al.*, 1985). Let an uncertainty of a measured isotope ratio R be expressed as σ_R. The variance-covariance matrix of measured isotope ratios of a natural sample (R_{1n}, R_{2n}, R_{3n}) is expressed by uncertainties of measured natural isotope ratios as

$$\mathbf{V}_{R_n} = \begin{bmatrix} \sigma_{R_{1n}}^2 & \sigma_{R_{1n}} \sigma_{R_{2n}} & \sigma_{R_{1n}} \sigma_{R_{3n}} \\ \sigma_{R_{1n}} \sigma_{R_{2n}} & \sigma_{R_{2n}}^2 & \sigma_{R_{2n}} \sigma_{R_{3n}} \\ \sigma_{R_{1n}} \sigma_{R_{3n}} & \sigma_{R_{2n}} \sigma_{R_{3n}} & \sigma_{R_{3n}}^2 \end{bmatrix} . \qquad (3\text{-}10)$$

The variance-covariance matrices of measured isotope ratios of a spiked sample (R_{1m}, R_{2m}, R_{3m}) and isotope ratios of the double spike (R_{1S}, R_{2S}, R_{3S}) are expressed in a similar manner. The variance-covariance matrix of the vector on the left side of Eq. (3-9) is expressed as

$$\mathbf{V}_q = \begin{bmatrix} \sigma_q^2 & \sigma_q\sigma_{q\alpha'} & \sigma_q\sigma_\alpha \\ \sigma_q\sigma_{q\alpha'} & \sigma_{q\alpha'}^2 & \sigma_{q\alpha'}\sigma_\alpha \\ \sigma_q\sigma_\alpha & \sigma_{q\alpha'}\sigma_\alpha & \sigma_\alpha^2 \end{bmatrix} .$$

(3-11)

This matrix can be calculated as

$$\mathbf{V}_q = \left(\boldsymbol{A}^{-1}\right) \cdot \left(q^2 \boldsymbol{V}_{R_S} + \boldsymbol{S}\cdot\boldsymbol{V}_{R_n}\cdot\boldsymbol{S} + \boldsymbol{P}\cdot\boldsymbol{V}_{R_m}\cdot\boldsymbol{P}\right)\cdot\left(\boldsymbol{A}^{-1}\right)^T ,$$

(3-12)

where $(A^{-1})^T$ is a transposed matrix of A^{-1} and S and P are

$$\boldsymbol{S} = \begin{bmatrix} 1+\Delta_1\alpha' & 0 & 0 \\ 0 & 1+\Delta_2\alpha & 0 \\ 0 & 0 & 1+\Delta_3\alpha \end{bmatrix} ,$$

(3-13)

and

$$\boldsymbol{P} = \begin{bmatrix} 1+q+\Delta_1 q\alpha' & 0 & 0 \\ 0 & 1+q+\Delta_2 q\alpha' & 0 \\ 0 & 0 & 1+q+\Delta_3 q\alpha' \end{bmatrix} ,$$

(3-14)

respectively (see Hamelin *et al.* (1985) for detail derivation of eq. 3-12). Using Eq. (3-12), uncertainty of the "calculated" instrumental mass fractionation factor of natural isotope ratio measurement, σ_α, can be calculated from the variance-covariance matrices of R_n, R_m and R_s (note that these variance-covariance matrices can be calculated by eq.3-10 using uncertainty values obtained from the isotope ratio measurement). Finally, using the calculated σ_α, the uncertainty of the true isotope ratio of the sample, R_{iN}, is calculated from simple error propagation through Eq. (3-1) as

$$\sigma_{R_{iN}}^2 = \sigma_{R_{in}}^2 + (R_{in}\Delta_i)^2 \cdot \sigma_\alpha^2 .$$

(3-15)

3. ERROR PROPAGATION SIMULATION

3.1. Parameters investigated in the simulation

As pointed out by Galer (1999), isotopic composition of the double spike and other analytical parameters affect the magnitude of error propagation during the calculation procedure described in the previous section. Error propagation through double spike calculation is simulated for four elements, Sr, Ba, Nd and Sm, to determine the parameters that give the smallest magnitude of error magnification. The parameters investigated in the simulation includes the isotopic composition of the double spike, combination of the three isotope ratios used in Eq. (3-6) and the sample-spike mixing factor Q. The investigated ranges of the parameters for each element are summarized in Table 1. Combination of the three isotope ratios used in Eq. (3-6) is selected with the requirement that the two spiked masses are always included within these three ratios. Isotope ratios of Sr and Nd are conventionally expressed relative to [86]Sr and [144]Nd. For Ba and Sm, [136]Ba, [148]Sm and [150]Sm are selected as a reference isotope because of the convenience of the isotope ratio measurement. The isotope ratios including three minor isotopes of Ba and Sm ([130]Ba, [132]Ba and [144]Sm) are excluded

Table 1 Summary of the parameters and their ranges investigated by error propagation simuration

element	double spike	isotopic composition of the DS		R_1	R_2	R_3	Q
Sr	^{84}Sr-^{86}Sr	^{84}Sr/^{86}Sr = 0.1 to 10	C_{Sr}	$^{84}Sr/^{86}Sr$	^{87}Sr/^{86}Sr	^{88}Sr/^{86}Sr	0 to 1
Ba	^{134}Ba-^{136}Ba	^{134}Ba/^{136}Ba = 0.1 to 10	C_{Ba1}	$^{134}Ba/^{136}Ba$	^{135}Ba/^{136}Ba	^{137}Ba/^{136}Ba	0 to 1
			C_{Ba2}	$^{134}Ba/^{136}Ba$	^{135}Ba/^{136}Ba	^{138}Ba/^{136}Ba	0 to 1
			C_{Ba3}	$^{134}Ba/^{136}Ba$	^{137}Ba/^{136}Ba	^{138}Ba/^{136}Ba	0 to 1
Nd	^{145}Nd-^{150}Nd	^{150}Nd/^{145}Nd = 0.1 to 10	C_{Nd1}	^{142}Nd/^{144}Nd	$^{145}Nd/^{144}Nd$	$^{150}Nd/^{144}Nd$	0 to 1
			C_{Nd2}	^{143}Nd/^{144}Nd	$^{145}Nd/^{144}Nd$	$^{150}Nd/^{144}Nd$	0 to 1
			C_{Nd3}	$^{145}Nd/^{144}Nd$	^{146}Nd/^{144}Nd	$^{150}Nd/^{144}Nd$	0 to 1
			C_{Nd4}	$^{145}Nd/^{144}Nd$	^{148}Nd/^{144}Nd	$^{150}Nd/^{144}Nd$	0 to 1
Sm	^{149}Sm-^{150}Sm	^{149}Sm/^{150}Sm = 0.1 to 10	C_{Sm1}	^{147}Sm/^{148}Sm	$^{149}Sm/^{148}Sm$	$^{150}Sm/^{148}Sm$	0 to 1
			C_{Sm2}	$^{149}Sm/^{148}Sm$	$^{150}Sm/^{148}Sm$	^{152}Sm/^{148}Sm	0 to 1
			C_{Sm3}	$^{149}Sm/^{148}Sm$	$^{150}Sm/^{148}Sm$	^{154}Sm/^{148}Sm	0 to 1
			C_{Sm4}	^{147}Sm/^{150}Sm	^{148}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	0 to 1
			C_{Sm5}	^{147}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	^{152}Sm/^{150}Sm	0 to 1
			C_{Sm6}	^{147}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	^{154}Sm/^{150}Sm	0 to 1
			C_{Sm7}	^{148}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	^{152}Sm/^{150}Sm	0 to 1
			C_{Sm8}	^{148}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	^{154}Sm/^{150}Sm	0 to 1
			C_{Sm9}	$^{149}Sm/^{150}Sm$	^{152}Sm/^{150}Sm	^{154}Sm/^{150}Sm	0 to 1
	^{149}Sm-^{154}Sm	^{149}Sm/^{154}Sm = 0.1 to 10	C_{Sm10}	^{147}Sm/^{148}Sm	$^{149}Sm/^{148}Sm$	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm11}	$^{149}Sm/^{148}Sm$	^{150}Sm/^{148}Sm	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm12}	$^{149}Sm/^{148}Sm$	^{152}Sm/^{148}Sm	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm13}	^{147}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm14}	^{148}Sm/^{150}Sm	$^{149}Sm/^{150}Sm$	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm15}	$^{149}Sm/^{150}Sm$	^{152}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
	^{150}Sm-^{154}Sm	^{150}Sm/^{154}Sm = 0.1 to 10	C_{Sm16}	^{147}Sm/^{148}Sm	$^{150}Sm/^{148}Sm$	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm17}	^{149}Sm/^{148}Sm	$^{150}Sm/^{148}Sm$	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm18}	$^{150}Sm/^{148}Sm$	^{152}Sm/^{148}Sm	$^{154}Sm/^{148}Sm$	0 to 1
			C_{Sm19}	^{147}Sm/^{150}Sm	^{148}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm20}	^{147}Sm/^{150}Sm	^{149}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm21}	^{147}Sm/^{150}Sm	^{152}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm22}	^{148}Sm/^{150}Sm	^{149}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm23}	^{148}Sm/^{150}Sm	^{152}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1
			C_{Sm24}	^{149}Sm/^{150}Sm	^{152}Sm/^{150}Sm	$^{154}Sm/^{150}Sm$	0 to 1

from the investigated parameter, because of the difficulty in the actual isotope ratio measurement of these isotopes.

Choice of the double spike is another important factor that controls the magnitude of error magnification. However, this choice is practically limited by the availability of spikes. Spikes available at the beginning of this study were limited to ^{84}Sr, ^{86}Sr, ^{134}Ba, ^{136}Ba, ^{145}Nd, ^{150}Nd, ^{149}Sm, ^{150}Sm and ^{154}Sm. Therefore, only the possible combination of a double spike that can be produced by these single spikes is investigated in this simulation. The isotopic compositions of the single spikes are summarized in Table 2. In the simulation, the variable parameter R_S (isotope ratio of the double spike) is

Table 2   Sr, Ba, Nd and Sm isotopic compositions of spikes and natural sample used for calculation

Sr		^{84}Sr	^{86}Sr	^{87}Sr	^{88}Sr		
	natural[*a]	0.56	9.86	7.00	82.58		
	^{84}Sr spike	99.65	0.14	0.03	0.18		
	^{86}Sr spike	0.01	96.40	1.33	2.26		

Ba		^{130}Ba	^{132}Ba	^{134}Ba	^{135}Ba	^{136}Ba	^{137}Ba	^{138}Ba
	natural[*a]	0.11	0.10	2.42	6.59	7.85	11.23	71.70
	^{134}Ba spike	–	–	88.10	5.36	1.21	1.07	4.26
	^{136}Ba spike	–	–	0.04	0.75	95.40	1.53	2.28

Nd		^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
	natural[*a]	27.2	12.2	23.8	8.3	17.2	5.7	5.6
	^{145}Nd spike	0.93	0.59	2.53	91.85	3.66	0.29	0.15
	^{150}Nd spike	0.77	0.39	0.88	0.34	0.84	0.66	96.13

Sm		^{144}Sm	^{147}Sm	^{148}Sm	^{149}Sm	^{150}Sm	^{152}Sm	^{154}Sm	
	natural[*a]	3.07	14.99	11.24	13.82	7.38	26.75	22.75	
	^{149}Sm spike	0.01	0.33	0.53	97.60	0.55	0.66	0.32	
	^{150}Sm spike	0.002	0.002	0.006	0.04	99.93	0.01	0.01	
	^{154}Sm spike	0.02	0.16	0.17	0.19	0.13	0.73	98.60	(%)

[*a] Natural isotopic composition was taken from Rosman and Taylor (1998).

defined by mixing these two single spikes in various proportions.

The isotopic compositions of natural Sr, Ba, Nd and Sm (Table 2) as well as instrumental mass fractionation factors of natural measurement and spiked measurement (α and α') are treated as a constant in the simulation. Instrumental mass fractionation factors are fixed to 0.0001. Although the instrumental mass fractionation factors are variable in Eq. (3-6), we confirmed that changing these fractionation factors within the range from –0.01 to 0.01 (note that practical isotopic fractionation factor in TIMS measurement is much smaller than this range) causes negligibly small changes on the error magnification.

3.2. Error model

As shown in the previous section (section 2), sources of the error, which finally propagate onto the true isotope ratio of the sample R_{iN} through double spike calculation, are errors of the isotope ratios of natural and spiked measurements (R_{1n}, R_{2n}, R_{3n}, R_{1m}, R_{2m} and R_{3m}) as well as the uncertainty in the isotope ratios of the spike (R_{1S}, R_{2S} and R_{3S}). The errors of these isotope ratios are modeled using the isotope ratios itself following Ludwig (1997). Assuming that the ion-counting noise has a Poisson distribution, the variance of a measured ion beam intensity h can be approximated as

$$\alpha_h^2 \propto h \ . \tag{3-16}$$

The uncertainty of a ratio of two ion beams $R_i = h_i/h_0$ can be obtained by simple

error propagation as

$$\sigma_{R_i}^2 = f \cdot R_i(1 + R_i)/h_0 \,, \tag{3-17}$$

where f is a proportionality constant. For the ease of the calculation, total intensity of the ion beam of an element is assumed to be constant. This assumption mirrors the actual analytical condition where the amount of element measured in a single mass spectrometric run is kept to be constant. With this assumption, the peak intensity of the denominator isotope will be proportional to the isotopic abundance of the denominator isotope (Ab_0) that can be written as

$$Ab_0 = \frac{1}{1 + \Sigma R_i} \,, \tag{3-18}$$

where ΣR_i is sum of all isotope ratios of an element. Equations (3-17 and 18) gives

$$\sigma_{R_i}^2 = f \cdot (1 + \Sigma R_i) R_i(1 + R_i) \,. \tag{3-19}$$

3.3. Error propagation simulation

The input data of the simulation are isotope ratios of the natural sample (R_N, fixed), isotope ratios of the double spike (R_S) and the sample-spike mixing factor Q. First, isotope ratio of sample-spike mixture (R_M) is calculated from these parameters. The "measured" isotope ratios of natural sample (R_n) and sample-spike mixture (R_m) are calculated by fixed mass fractionation factors α and α'). Errors of the "measured" isotope ratios are modeled by the method described in the previous section (eq. 3-19). Error of the "calculated" instrumental mass fractionation factor of natural isotope ratio measurement, σ_α, is then calculated by propagating the modeled errors. Covariance terms that appear in the variance-covariance matrix (eq. 3-10) are difficult to model and thus assumed as 0. In typical isotope ratio measurement by TIMS, the two measured isotope ratios of an element are not correlated, if the within run mass fractionation is properly corrected by internal normalization using exponential law (Fig. 1). In such case, the covarience of the two measured isotope ratios is small and can be approximated by 0. The Error of the true isotope ratio of the sample, R_{iN}, is calculated from eq. (3-19) using the calculated σ_α and the modeled $\sigma_{R_{in}}$. Finally, error magnification factor of an isotope ratio Ri is calculated as

$$\gamma_{R_i} = \sqrt{\sigma_{R_{iN}}^2 / \sigma_{R_{in}}^2} \,, \tag{3-20}$$

for a given set of analytical conditions.

4. DOUBLE SPIKE TIMS ANALYSIS OF STRONTIUM

To compare the simulation results with actual data, double spike-TIMS analysis of Sr is carried out. Sr isotopic composition of the standard reference material NBS 987 was analyzed multiple times by changing the sample-spike mixing factor Q and using an ^{84}Sr-^{86}Sr double spike with fixed isotopic compositions. The isotope composition of the double spike is calibrated against NBS 987 assuming ^{86}Sr/^{88}Sr$_{NBS\,987}$ = 0.1194 following the method described in Wakaki and Tanaka (2012). The isotope ratios of the double spike are shown in table 3 together with the measured isotope ratios of NBS 987 used
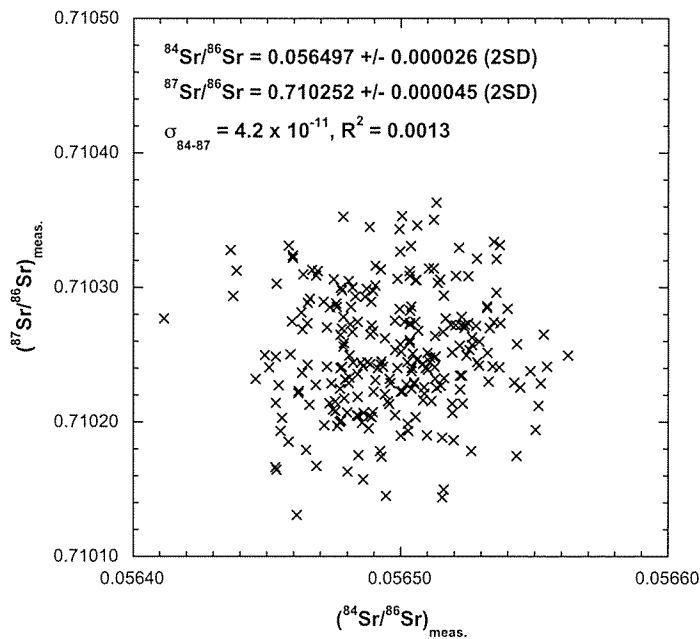
Fig. 1 Strontium isotope ratios ($^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$) of NBS 987 reference material measured using VG sector 54-30 TIMS at Nagoya University. Internal normalization using exponential law and $^{88}Sr/^{86}Sr = 0.1194$ was applied to correct for instrumental mass fractionation during the measurement. A single measurement consists of 250 cycles of 8 seconds integrations, and the results of the 250 cycles are plotted as crosses. The covariation term ($\sigma_{84\text{-}87}$) and R^2 value between the measured $^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios are very small indicating that these measured ratios are not correlated.

Table 3 Isotopic composition of the $^{84}Sr\text{-}^{86}Sr$ double spike and NBS 987.

Sample	$^{84}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{88}Sr/^{86}Sr$	n
$^{84}Sr\text{-}^{86}Sr$ double spike	3.09240 (12)	0.014903 (18)	0.03012 (22)	4
NBS 987	0.056494 (5)	0.710264 (7)	$\equiv$ 8.375209	4

Errors indicated in the parentheses are 2SE of the multiple analyses.
Sr isotope ratios of NBS 987 was measured by internal normalization assuming $^{88}Sr/^{86}Sr = 8.375209$.

in the calibration. Aliquots of NBS 987 were spiked with different amounts of $^{84}Sr\text{-}^{86}Sr$ double spike. NBS 987 and NBS 987-double spike mixtures were measured for its Sr isotope ratios ($^{84}Sr/^{86}Sr$, $^{87}Sr/^{86}Sr$ and $^{88}Sr/^{86}Sr$) on the VG Sector 54-30 TIMS at Nagoya University and stable isotopic composition of NBS 987 is calculated by the refined double spike method described in Wakaki and Tanaka (2012). Error magnification factor is also calculated by eq. 3-20 for each of the analysis. Because the Sr isotope ratios are measured using internal normalization with $^{88}Sr/^{86}Sr$ (see Wakaki and Tanaka (2012) for details of the refined double spike method), the errors of the measured $^{88}Sr/^{86}Sr$ ratio is passed on to the measured $^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$. Therefore, error

magnification factor of $^{88}Sr/^{86}Sr$ could not be defined. The stable isotopic results are expressed with relative to the average of all NBS 987 analyses using the conventional delta notation, defined as $\delta^{88}Sr = [(^{88}Sr/^{86}Sr)_{sample}/(^{88}Sr/^{86}Sr)_{NBS\ 987} - 1] \times 10^3$ (per mil). Errors of the delta values are estimated by taking into account both the internal error (2SE) of a measurement and the reproducibility of the standard analysis (2SD), and reported as 2 standard deviations.

5. RESULTS AND DISCUSSION

5.1. Error propagation simulation

5.1.1. Optimal double spike isotopic composition of Strontium

Strontium has four stable isotopes and thus only has three independent isotope ratios. There are no choices for the three isotope ratios used in Eq. (3-6). Therefore, parameters investigated for Sr are isotopic composition of the double spike and the sample-spike mixing factor Q. The results of the error propagation simulation for Sr are shown as $\gamma^{88}Sr/^{86}Sr$ (the error magnification factor of $^{88}Sr/^{86}Sr$ ratio) contoured against two parameters, the $^{84}Sr/^{86}Sr$ ratio of the double spike and the sample-spike mixing factor, in Fig. 2a. The results of $\gamma^{84}Sr/^{86}Sr$ and $\gamma^{87}Sr/^{86}Sr$ are also shown in Figs. 2b and 2c. These results show that the error magnification factor depends strongly on both the isotopic composition of the double spike and the mixing factor Q. The contour patterns of $\gamma^{88}Sr/^{86}Sr$, $\gamma^{84}Sr/^{86}Sr$ and $\gamma^{87}Sr/^{86}Sr$ are essentially identical (Figs. 2a-c). This is because the investigated parameters affect σ_α (Eq. 3-12) and the change of σ_α transfers similarly to all three γ values (Eq. 3-15). The minimum value of $\gamma^{88}Sr/^{86}Sr$ is 1.96. This value is obtained from Q = 0.47 and $^{84}Sr/^{86}Sr_{double\ spike} \sim 2.5$. The range of parameters that gives similar $\gamma^{88}Sr/^{86}Sr$ values ($\gamma^{88}Sr/^{86}Sr < 2.0$) are 0.46 < Q < 0.49 and $1.6 < {}^{84}Sr/^{86}Sr_{double\ spike} < 4.5$. These ranges of parameters are optimal for the DS-TIMS analysis using ^{88}Sr-^{86}Sr double spike (Table 4).
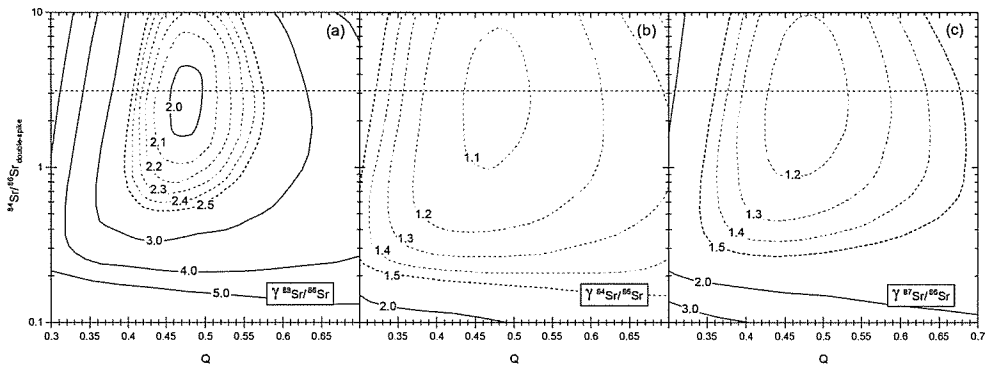

Fig. 2   Error magnification factors of a) $^{88}Sr/^{86}Sr$ ratio ($\gamma^{88}Sr/^{86}Sr$), b) $^{84}Sr/^{86}Sr$ ratio ($\gamma^{84}Sr/^{86}Sr$) and c) $^{87}Sr/^{86}Sr$ ratio ($\gamma^{87}Sr/^{86}Sr$) are contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q. Horizontal dashed line indicates isotopic composition of the double spike used in the actual analysis.

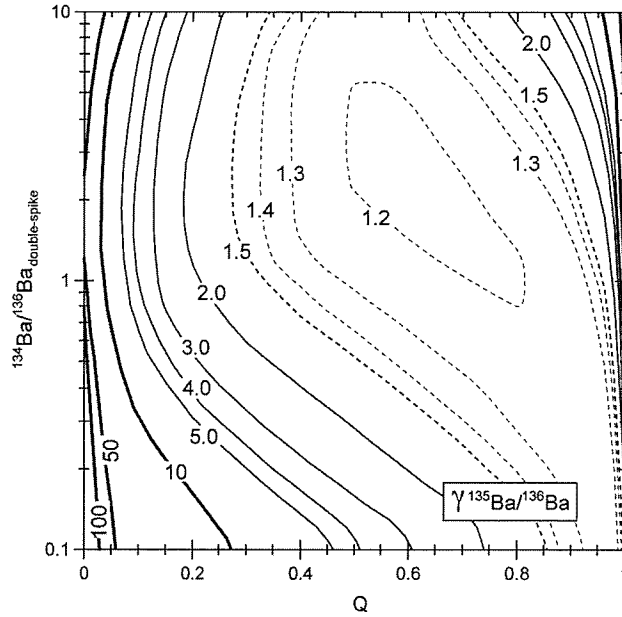### 5.1.2. Optimal double spike isotopic composition of Barium

Barium has seven stable isotopes. Excluding the two minor isotopes ^{130}Ba and ^{132}Ba, there are four independent isotope ratios. One of the spiked isotopes, ^{136}Ba, is the reference isotope of the isotope ratio. The other spiked isotope is ^{134}Ba. There are three possible combinations of three isotope ratios for calculation (C_{Ba1} to C_{Ba3} in Table 1). The error magnification factor of ^{135}Ba/^{136}Ba (γ ^{135}Ba/^{136}Ba) is first calculated for a fixed mixing factor Q to compare the results between the combinations of three isotope ratios. One example of such calculations is shown in Fig. 3. Among the three combinations, C_{Ba2} (^{134}Ba/^{136}Ba, ^{135}Ba/^{136}Ba and ^{138}Ba/^{136}Ba) gives the smallest error magnification factors for any Q values (Fig. 3). The γ ^{135}Ba/^{136}Ba values calculated for

Table 4 Best and optimal analytical conditions for DS-TIMS analyses of Sr, Ba, Nd and Sm

element		double spike	isotopic composition of the DS	combinatin of isotope ratios used for calculation			Q
					R_1	R_2	R_3	
Sr	best	^{84}Sr-^{86}Sr	^{84}Sr/^{86}Sr = 2.5	C_{Sr}	*^{84}Sr/^{86}Sr*	^{87}Sr/^{86}Sr	^{88}Sr/^{86}Sr	0.47
	optimal		^{84}Sr/^{86}Sr = 1.6–4.5	C_{Sr}	*^{84}Sr/^{86}Sr*	^{87}Sr/^{86}Sr	^{88}Sr/^{86}Sr	0.46—0.49
Ba	best	^{134}Ba-^{136}Ba	^{134}Ba/^{136}Ba = 2.5	C_{Ba2}	*^{134}Ba/^{136}Ba*	^{135}Ba/^{136}Ba	^{138}Ba/^{136}Ba	0.60
	optimal		^{134}Ba/^{136}Ba = 0.80–5.0	C_{Ba2}	*^{134}Ba/^{136}Ba*	^{135}Ba/^{136}Ba	^{138}Ba/^{136}Ba	0.50–0.80
Nd	best	^{145}Nd-^{150}Nd	^{150}Nd/^{145}Nd = 1.0	C_{Nd1}	*^{145}Nd/^{144}Nd*	^{148}Nd/^{144}Nd	*^{150}Nd/^{144}Nd*	0.04
	optimal		^{150}Nd/^{145}Nd = 0.40–3.0	C_{Nd1}	*^{145}Nd/^{144}Nd*	^{148}Nd/^{144}Nd	*^{150}Nd/^{144}Nd*	0.025–0.09
	optimal		^{150}Nd/^{145}Nd = 0.50–1.7	C_{Nd1}	^{142}Nd/^{144}Nd	*^{145}Nd/^{144}Nd*	*^{150}Nd/^{144}Nd*	0.04–0.095
Sm	best	^{150}Sm-^{154}Sm	^{150}Sm/^{154}Sm = 0.47	C_{Sm21}	^{147}Sm/^{150}Sm	^{152}Sm/^{150}Sm	*^{154}Sm/^{150}Sm*	0.90
	optimal		^{150}Sm/^{154}Sm = 0.11–2.7	C_{Sm21}	^{147}Sm/^{150}Sm	^{152}Sm/^{150}Sm	*^{154}Sm/^{150}Sm*	0.70–0.98
	optimal	^{149}Sm-^{150}Sm	^{149}Sm/^{150}Sm = 0.55–2.0	C_{Sm6}	^{147}Sm/^{150}Sm	*^{149}Sm/^{150}Sm*	^{154}Sm/^{150}Sm	0.92–0.98
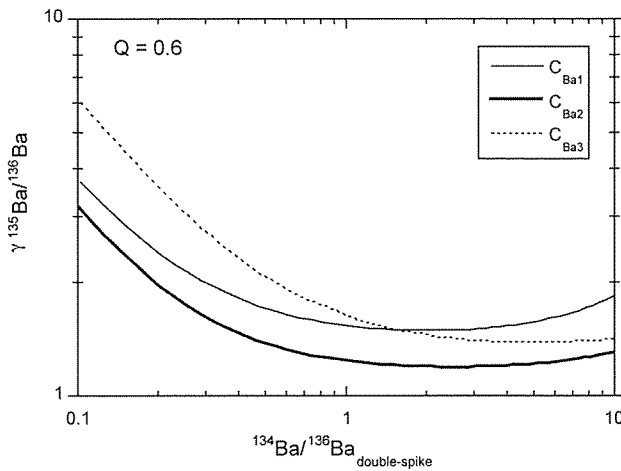
Fig. 3 Error magnification factor of ^{135}Ba/^{136}Ba (γ ^{135}Ba/^{136}Ba) calculated for Q = 0.6 is plotted against the isotopic composition of the double spike. Results calculated by different combination of the three isotope ratios (see Table 1) are plotted in different lines.
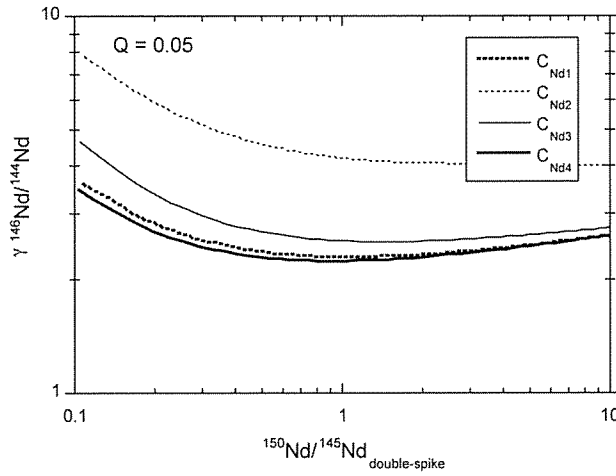
Fig. 4 Error magnification factor of ^{135}Ba/^{136}Ba ($\gamma\,^{135}$Ba/^{136}Ba) calculated by combination C_{Ba2} (^{134}Ba/^{136}Ba, ^{135}Ba/^{136}Ba and ^{138}Ba/^{136}Ba) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.

various isotopic compositions and Q values using the combination C_{Ba2} are shown in Fig. 4. The asymmetric shape of the contours in Fig. 4 indicates that optimal Q values may change depending on the isotopic compositions of the double spike. The minimum value of $\gamma\,^{135}$Ba/^{136}Ba is 1.18. This value is obtained from Q = 0.60 and ^{134}Ba/^{136}Ba$_{double\ spike}$ ~ 2.5. The range of parameters that gives similar $\gamma\,^{135}$Ba/^{136}Ba values ($\gamma\,^{135}$Ba/^{136}Ba < 1.2) are 0.50 < Q < 0.80 and 0.80 < ^{134}Ba/^{136}Ba$_{double\ spike}$ < 5.0. The optimal parameters for Ba analysis are summarized in Table 4.

5.1.3. Optimal double spike isotopic composition of Neodymium

Neodymium has seven stable isotopes and has six independent isotope ratios. Including the two spiked isotopes (^{145}Nd and ^{150}Nd), there are four possible combinations of three isotope ratios used for calculation (C_{Nd1} to C_{Nd4} in Table 1). The error magnification factor of ^{146}Nd/^{144}Nd ($\gamma\,^{146}$Nd/^{144}Nd) is first calculated for a fixed mixing factor Q to compare the results between these combinations. One example of such calculations is shown in Fig. 5. The combination C_{Nd4} (^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd) gives the smallest error magnification factors (Fig. 5). The $\gamma\,^{146}$Nd/^{144}Nd values calculated using the combination C_{Nd4} are shown in Fig. 6. The minimum value of $\gamma\,^{146}$Nd/^{144}Nd is 2.22. This value is obtained from Q = 0.04 and ^{150}Nd/^{145}Nd$_{double\ spike}$ ~ 1.0. The range of parameters that gives similar $\gamma\,^{146}$Nd/^{144}Nd values ($\gamma\,^{146}$Nd/^{144}Nd < 2.3) are 0.025 < Q < 0.09 and 0.40 < ^{150}Nd/^{145}Nd$_{double\ spike}$ < 3.0. The optimal parameters for Nd analysis are summarized in Table 4.
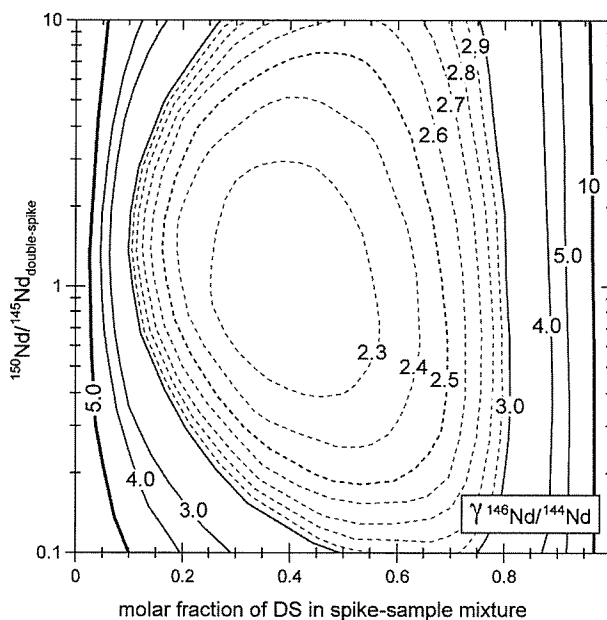
Fig. 5 Error magnification factor of ^{146}Nd/^{144}Nd ($\gamma\,^{146}$Nd/^{144}Nd) calculated for Q = 0.05 is plotted against the isotopic composition of the double spike. Results calculated by different combination of the three isotope ratios (see Table 1) are plotted in different lines.
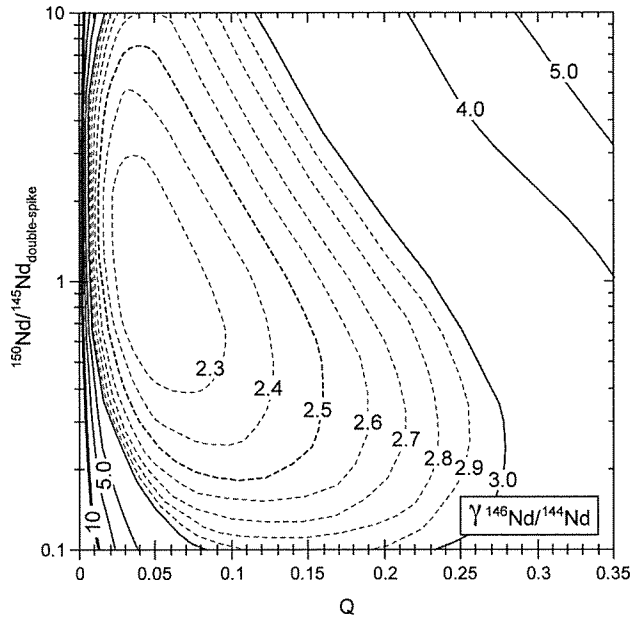
Fig. 6 Error magnification factor of ^{146}Nd/^{144}Nd ($\gamma\,^{146}$Nd/^{144}Nd) calculated by combination C_{Nd4} (^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.

The optimal value of the sample-spike mixing factor is close to 0 and seems to indicate that the propotion of the spike in the sample-spike mixture is quite small.
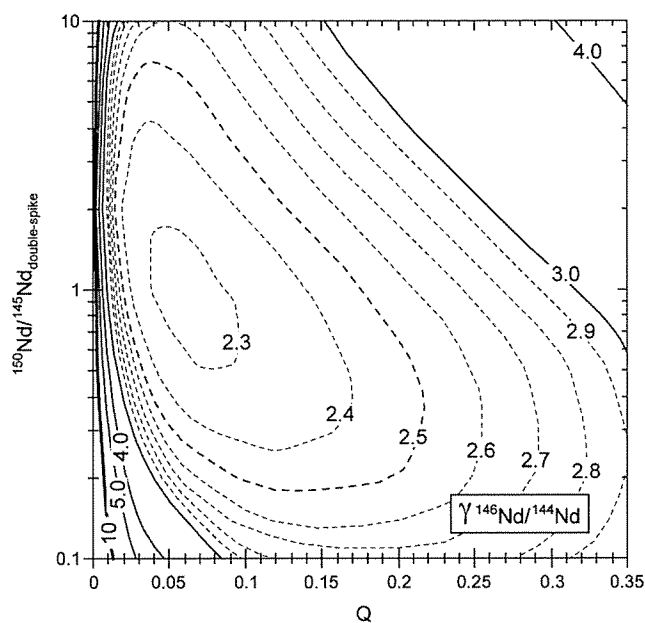
Fig. 7   Error magnification factor of $^{146}Nd/^{144}Nd$ ($\gamma\,^{146}Nd/^{144}Nd$) calculated by combination C_{Nd4} ($^{145}Nd/^{144}Nd$, $^{148}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) is contoured against two parameters, the isotopic composition of the double spike and molar fraction of the double spike in sample-spike mixture.

The mixing factor Q is defined by isotope ratios (Eq. 3-3) and does not directly reflects the molar mixing proportions between the spike and the sample.   The $\gamma\,^{146}Nd/^{144}Nd$ values are plotted against the molar fraction of the spike in the sample-spike mixture in Fig. 7 instead of the mixing factor Q.   The optimal Q value of Q = 0.04 corresponds to 37 mol % of the spike in the sample-spike mixture.

In Fig. 5, combinations C_{Nd1} ($^{142}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) and C_{Nd3} ($^{145}Nd/^{144}Nd$, $^{146}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) show similar but slightly degraded results to results of the optimal combination C_{Nd4}.   The $\gamma\,^{146}Nd/^{144}Nd$ values calculated using the combinations C_{Nd1} and C_{Nd3} are shown as a reference in Fig. 8 and Fig. 9, respectively. The range of parameters that gives optimal conditions for C_{Nd1} ($\gamma\,^{146}Nd/^{144}Nd$ < 2.3) are 0.04 < Q < 0.095 and 0.50 < $^{150}Nd/^{145}Nd$ double spike < 1.7.   The range of parameters that gives optimal conditions for C_{Nd3} ($\gamma\,^{146}Nd/^{144}Nd$ < 2.5) are 0.03 < Q < 0.04 and 1.5 < $^{150}Nd/^{145}Nd_{double\ spike}$ < 2.5.   These results show that optimal double spike isotopic composition and sample-spike mixing ratios change slightly by the combinations of the isotope ratios used in the calculation.

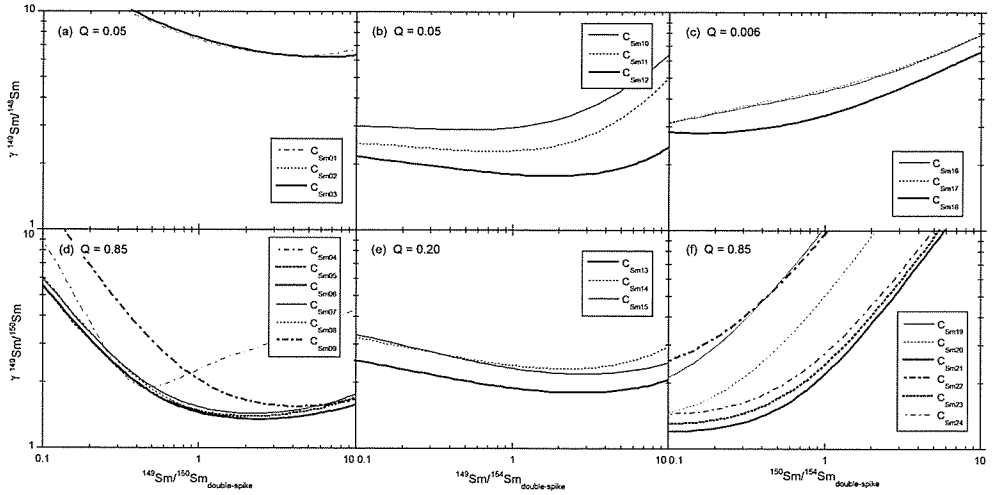### 5.1.4. Optimal double spike isotopic composition of Samarium

Samarium has seven stable isotopes.   It has five independent isotope ratios, excluding the minor isotope ^{144}Sm.   Three types of double spikes and two pairs of isotope ratios with different reference isotopes (^{148}Sm and ^{150}Sm) are examined.   Twenty-four possible combinations of three isotope ratios exist under such condition (Table 1).

Fig. 8 Error magnification factor of $^{146}Nd/^{144}Nd$ ($\gamma^{146}Nd/^{144}Nd$) calculated by combination C_{Nd1} ($^{142}Nd/^{144}Nd$, $^{145}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.
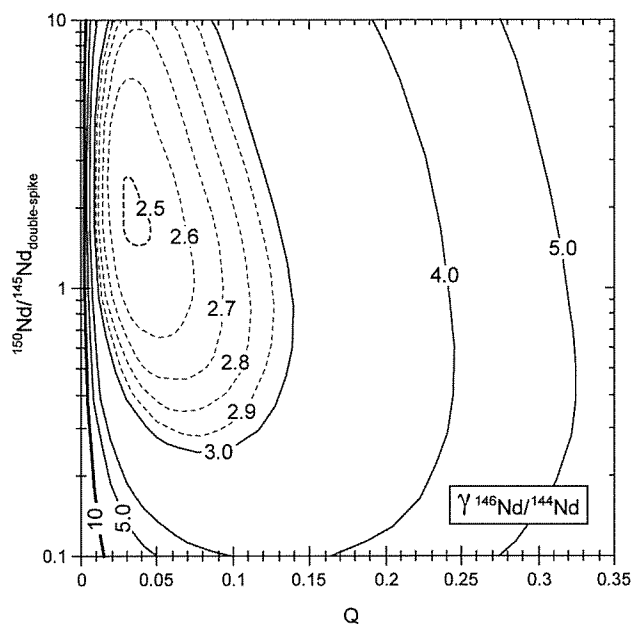
Fig. 9 Error magnification factor of $^{146}Nd/^{144}Nd$ ($\gamma^{146}Nd/^{144}Nd$) calculated by combination C_{Nd3} ($^{145}Nd/^{144}Nd$, $^{146}Nd/^{144}Nd$ and $^{150}Nd/^{144}Nd$) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.

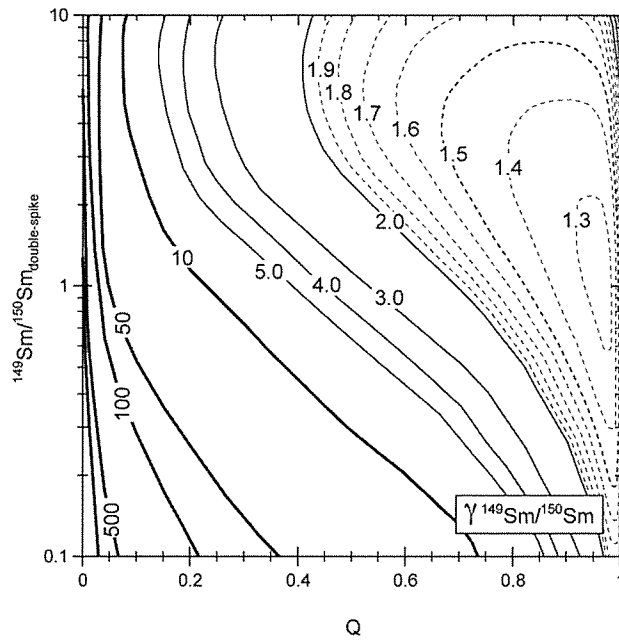**Fig. 10** Error magnification factor of ^{149}Sm/^{148}Sm (γ^{149}Sm/^{148}Sm) calculated for (a) ^{149}Sm-^{150}Sm double spike and Q = 0.05, (b) ^{149}Sm-^{154}Sm double spike and Q = 0.05 and (c) ^{150}Sm-^{154}Sm double spike and Q = 0.006 are plotted against the isotopic composition of the double spike. Error magnification factor of ^{149}Sm/^{150}Sm (γ^{149}Sm/^{150}Sm) calculated for (d) ^{149}Sm-^{150}Sm double spike and Q = 0.85, (e) ^{149}Sm-^{154}Sm double spike and Q = 0.20 and (f) ^{150}Sm-^{154}Sm double spike and Q = 0.85 are plotted against the isotopic composition of the double spike. The fixed Q values are selected to show the smallest error magnification for a given set of double spike and reference isotope pairs.

First, the error magnification factor of ^{149}Sm/^{148}Sm (γ^{149}Sm/^{148}Sm) is calculated using different combinations at a fixed mixing factor Q for each of the three double spikes using ^{148}Sm as a reference isotope of isotope ratios (Figs. 10a-c). The error magnification factor of ^{149}Sm/^{150}Sm (γ^{149}Sm/^{150}Sm) is also calculated using different combinations at a fixed mixing factor Q for each of the three double spikes using ^{150}Sm as a reference isotope of isotope ratios (Figs. 10d-f). The Q values which show the smallest error magnification for a given set of double soike and reference isotope pairs are selected for the fixed values. Small error magnification factors are observed for ^{149}Sm-^{150}Sm double spike with combination C_{Sm6} (^{147}Sm/^{150}Sm, ^{149}Sm/^{150}Sm and ^{154}Sm/^{150}Sm; Fig. 10d) and for ^{150}Sm-^{154}Sm double spike with combination C_{Sm21} (^{147}Sm/^{150}Sm, ^{152}Sm/^{150}Sm and ^{154}Sm/^{150}Sm; Fig. 10f). These two conditions are examined further.

Small error magnification factor is obtained in the case where the reference isotope was spiked. If the reference isotope was spiked, all three isotope ratios used in the calculation will change by adding the double spike. If the reference isotope was not spiked, however, only the two "spiked" isotope ratio will change by adding the double spike (the third isotope ratio will be similar between the sample and the sample-spike mixture). Therefore, the calculation of eq. 3-9 will be more precise in the case when the reference isotope was spiked. The difference observed in the error magnification factor likely reflects the precision of the calculation of eq. 3-9.

The γ^{149}Sm/^{150}Sm values calculated for ^{149}Sm-^{150}Sm double-spike using combination C_{Sm6} are shown in Fig. 11. The minimum value of γ^{149}Sm/^{150}Sm is 1.28. This value is

Fig. 11 Error magnification factor of $^{149}Sm/^{148}Sm$ ($\gamma^{149}Sm/^{148}Sm$) calculated for ^{149}Sm-^{150}Sm double spike by combination C_{Sm6} ($^{147}Sm/^{150}Sm$, $^{149}Sm/^{150}Sm$ and $^{154}Sm/^{150}Sm$) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.

obtained from Q = 0.96 and $^{149}Sm/^{150}Sm$ double spike ~ 1.1. The range of parameters that gives similar $\gamma^{149}Sm/^{150}Sm$ values ($\gamma^{149}Sm/^{150}Sm$ < 1.3) are 0.92 < Q < 0.98 and 0.55 < $^{149}Sm/^{150}Sm_{double\ spike}$ < 2.0. The $\gamma^{149}Sm/^{150}Sm$ values calculated for ^{150}Sm-^{154}Sm double spike using combination C_{Sm21} are shown in Fig. 12. The minimum value of $\gamma^{149}Sm/^{150}Sm$ is 1.12. This value is obtained from Q = 0.90 and $^{150}Sm/^{154}Sm$ double spike ~ 0.47. The range of parameters that gives similar $\gamma^{149}Sm/^{150}Sm$ values ($\gamma^{149}Sm/^{150}Sm$ < 1.15) are 0.70 < Q < 0.98 and 0.11 < $^{150}Sm/^{154}Sm$ double spike < 2.7. The results of ^{150}Sm-^{154}Sm double spike give the smallest $\gamma^{149}Sm/^{150}Sm$ among the examined conditions. The optimal parameters for Sm analysis are summarized in Table 4.

5.2. double spike-TIMS analysis of Sr standard reference material NBS 987

The results of double spike-TIMS analysis of Sr standard reagent NBS 987 is shown in table 5. In total, 35 independent analyses were performed for sample-spike mixing factors (Q) ranging from 0.24 to 0.68. All the delta values scatter around 0 and no systematic shift of isotopic composition, depending on Q values, is observed. The error magnification factors for $^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$, on the other hand, change systematically depending on Q values.

5.3. Comparison of simulation results of Sr and mass spectrometric data

The $^{84}Sr/^{86}Sr$ ratio of the double spike used in the experiment is ~3.09, which
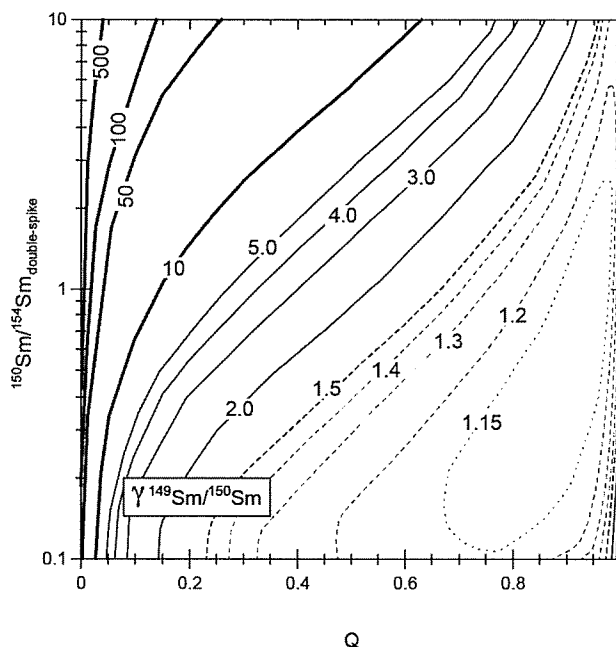
Fig. 12 Error magnification factor of ^{149}Sm/^{150}Sm (γ ^{149}Sm/^{150}Sm) calculated for ^{150}Sm-^{154}Sm double spike by combination CS$_{m2i}$ (^{147}Sm/^{150}Sm, ^{152}Sm/^{150}Sm and ^{154}Sm/^{150}Sm) is contoured against two parameters, the isotopic composition of the double spike and the sample-spike mixing factor Q.

is within the optimal range estimated by the error propagation simulation (Fig. 2). Dependence of the Sr error magnification factors on the sample-spike mixing factor Q is simulated for this particular double spike isotopic composition (shown in table 3) and shown in Fig. 13. Also shown in Fig. 13 are the error magnification factors of the actual NBS 987 measurements. The measured γ ^{87}Sr/^{86}Sr values agree well with the simulation results. The measured γ ^{84}Sr/^{86}Sr values deviate slightly to the lower side of the simulated profile, but well reproduce the concave shape and the peak position of the simulated profile. The actual Sr isotopic measurement was done by a slightly different method, which includes internal normalization (Wakaki and Tanaka, 2012). Because of the normalization, the error of the measured ^{88}Sr/^{86}Sr is passed on to the errors of the measured ^{84}Sr/^{86}Sr and ^{87}Sr/^{86}Sr ratios. This difference of the errors between the model and the measurement may slightly affect the degree of error propagation. Although the error model does not perfectly reproduce the actual measurement error, the close agreement of the simulation results and the measured error magnification factors indicates that the optimal double spike isotopic composition and other analytical parameters estimated by the simulation are reliable.

6. SUMMARY

Optimal analytical parameters for the double spike analyses of Sr, Ba, Nd and Sm

Table 5 Relative isotopic composition and error magnification factors of NBS 987.

Q	$\delta^{84}Sr$	(2SD)	$\delta^{87}Sr$	(2SD)	$\delta^{88}Sr$	(2SD)	$\gamma^{84}Sr/^{86}Sr$	$\gamma^{87}Sr/^{86}Sr$
0.24	−0.07 ± 0.23		−0.02 ± 0.04		−0.02 ± 0.07		1.44	4.14
0.24	0.14 ± 0.23		−0.01 ± 0.03		−0.01 ± 0.06		1.34	3.16
0.24	−0.05 ± 0.23		0.01 ± 0.04		0.02 ± 0.07		1.59	4.06
0.33	0.00 ± 0.23		−0.01 ± 0.03		−0.03 ± 0.05		1.15	2.04
0.33	−0.07 ± 0.23		−0.02 ± 0.03		−0.02 ± 0.05		1.13	2.29
0.33	0.19 ± 0.23		−0.03 ± 0.03		−0.05 ± 0.05		1.15	2.13
0.33	0.01 ± 0.15		0.00 ± 0.04		−0.01 ± 0.05		1.20	2.25
0.47	−0.02 ± 0.15		0.01 ± 0.04		0.03 ± 0.05		1.03	1.24
0.47	−0.02 ± 0.15		−0.03 ± 0.04		−0.02 ± 0.05		1.03	1.33
0.47	0.07 ± 0.15		−0.01 ± 0.04		−0.02 ± 0.05		1.03	1.26
0.47	0.05 ± 0.15		0.00 ± 0.04		0.00 ± 0.05		1.03	1.26
0.47	−0.04 ± 0.14		0.02 ± 0.04		0.04 ± 0.05		1.03	1.35
0.47	−0.14 ± 0.14		0.01 ± 0.04		−0.01 ± 0.05		1.02	1.24
0.47	0.02 ± 0.15		0.02 ± 0.04		0.03 ± 0.05		1.04	1.31
0.47	0.07 ± 0.16		−0.02 ± 0.04		−0.04 ± 0.05		1.03	1.37
0.47	−0.04 ± 0.22		0.01 ± 0.02		0.01 ± 0.04		1.03	1.27
0.47	−0.11 ± 0.23		0.00 ± 0.02		0.02 ± 0.04		1.03	1.34
0.47	0.14 ± 0.23		−0.01 ± 0.02		−0.01 ± 0.04		1.03	1.32
0.47	0.01 ± 0.23		0.00 ± 0.03		−0.02 ± 0.05		1.06	1.65
0.50	−0.08 ± 0.15		0.00 ± 0.03		−0.02 ± 0.04		1.02	1.31
0.50	0.08 ± 0.15		−0.01 ± 0.03		−0.01 ± 0.04		1.02	1.22
0.50	−0.01 ± 0.15		0.00 ± 0.03		0.01 ± 0.04		1.03	1.28
0.50	0.00 ± 0.15		0.03 ± 0.03		0.03 ± 0.04		1.03	1.28
0.50	0.11 ± 0.15		−0.03 ± 0.03		−0.04 ± 0.04		1.03	1.26
0.50	0.03 ± 0.15		0.00 ± 0.03		0.01 ± 0.04		1.03	1.32
0.50	0.03 ± 0.15		0.00 ± 0.03		0.01 ± 0.04		1.03	1.36
0.50	0.01 ± 0.16		0.00 ± 0.03		0.01 ± 0.04		1.01	1.14
0.50	−0.08 ± 0.15		0.01 ± 0.03		0.00 ± 0.04		1.03	1.31
0.50	−0.10 ± 0.15		0.01 ± 0.03		0.01 ± 0.04		1.03	1.30
0.50	−0.02 ± 0.22		0.00 ± 0.02		−0.01 ± 0.04		1.02	1.23
0.50	−0.09 ± 0.23		−0.01 ± 0.02		0.00 ± 0.04		1.02	1.25
0.68	0.00 ± 0.22		−0.01 ± 0.02		−0.03 ± 0.04		1.07	1.60
0.68	−0.02 ± 0.23		−0.04 ± 0.02		−0.07 ± 0.04		1.06	1.66
0.68	0.19 ± 0.23		−0.04 ± 0.02		−0.05 ± 0.04		1.06	1.58
0.68	−0.01 ± 0.23		0.01 ± 0.02		0.00 ± 0.04		1.05	1.58
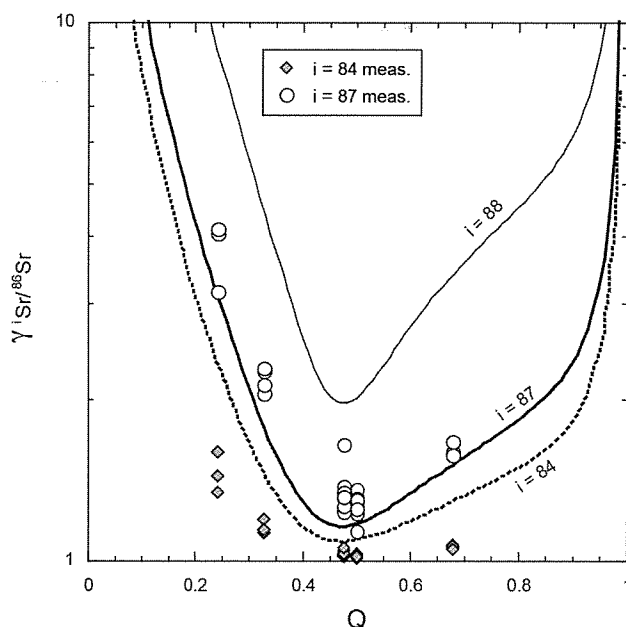
Fig. 13 Comparison of Sr error magnification factors obtained from simulation and actual measurement. Dotted, bold and solid profiles are the error magnification factors of ^{84}Sr/^{86}Sr, ^{87}Sr/^{86}Sr and ^{88}Sr/^{86}Sr, respectively simulated for the actual double spike isotopic composition shown in table 3. Gray diamond and white circle represents the error magnification factors of ^{84}Sr/^{86}Sr and ^{87}Sr/^{86}Sr obtained in the analysis of NBS 987.

are estimated by simulating the error propagation through double spike data analysis. The simulation shows that choice of spiked masses in the double spike, isotopic composition of the combined-spikes, combination of the three isotope ratios used in the double spike calculation and the sample-spike mixing factor Q all affect the degree of error magnification throughout the analysis. The best double spike isotopic compositions that give the smallest error magnification for each element are ^{84}Sr/^{86}Sr$_{double\ spike}$ ~ 2.5, ^{134}Ba/^{136}Ba$_{double\ spike}$ ~ 2.5, ^{150}Nd/^{145}Nd$_{double\ spike}$ ~ 1.0 and ^{150}Sm/^{154}Sm$_{double\ spike}$ ~ 0.47 for Sr, Ba, Nd and Sm, respectively. Optimal conditions of the mixing factor Q corresponding to each of the best double spike isotopic compositions are 0.47, 0.60, 0.04 and 0.90 for Sr, Ba, Nd and Sm, respectively. The optimal combinations of isotopes used in the double spike calculation are C_{Ba2} (^{134}Ba/^{136}Ba, ^{135}Ba/^{136}Ba and ^{138}Ba/^{136}Ba), C_{Nd4} (^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd) and C_{Sm21} (^{147}Sm/^{150}Sm, ^{152}Sm/^{150}Sm and ^{154}Sm/^{150}Sm) for Ba, Nd and Sm, respectively. Small error magnification factors are obtained in the case where the reference isotope was spiked.

7. REFERENCES

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8. ACKNOWLEDGEMENTS