

A practical guide to the double-spike technique for calcium isotope measurements by thermal ionization mass spectrometry (TIMS)



Fang Liu, Zhaofeng Zhang*, Xin Li, Yajun An

State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

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ABSTRACT

The double spike technique is the most reliable method for calibrating instrumental and chemical mass-dependent fractionation, which has been widely applied in isotopic analysis of many elements such as Mo, Sn, Ru, Ca, etc. However, practical use of double spiking is possibly hindered by the perceived difficulties in proper double spike calibration, mathematical inversion and data reduction. In this study, we will refer to Ca double spike on how to yield excellent isotopic data on TIMS. A detailed description on how to choose and calibrate an optimal double spike is presented. Our main aim is to provide a practical guide when working with double spike, especially for researchers in new isotopic systems.

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1. Introduction

Metal stable isotope geochemistry is one of the research priorities in the Earth Sciences. It has been proven to be a crucial tool in elucidating many major scientific issues such as the origin of the Earth and the Moon in our solar system (e.g. Refs. [1,2]), the evolution of the continental crust (e.g. Refs. [3,4]), the extinction of life on the Earth (e.g. Refs. [5,6]), and the driving force of climatic changes (e.g. Ref. [7]), etc. Importantly, to perform accurate measurement of isotopic compositions is a prerequisite for all the applications. However, due to mass-dependent isotopic fractionation, matrixes and/or isobaric interferences during mass spectrometry, proper calibrations should be considered seriously to achieve the “true” isotopic compositions.

To correct for mass bias, many calibration procedures have been proposed, including element doping, standard-sample bracketing and double-spike technique. To be specific, (1) doping samples were added an element with a mass close to and interference-free on the target element, such as Zr or Ru in the case of Mo (e.g. Ref. [8]), while the instrument mass fractionation is corrected by assuming that the magnitude of fractionations are same between elements with close masses; (2) standard-sample bracketing is using the adjacent reference materials to correct the unknown samples with a prerequisite of performing same extent

fractionations during measurements between reference and sample (e.g. Refs. [9,10]); and (3) the double spike technique is applicable to an element that has four or more isotopes, two of which are enhanced by addition of artificially enriched spikes (e.g. Refs. [11–14]).

The double spike technique, which was firstly established by Dodson [15], provides a powerful calibration for both chemical and instrumental mass-dependent fractionation. In the early studies, the double spike technique was applied in Pb isotope (e.g. Refs. [16,17]), Ba isotope [18] and Ca isotope (e.g. Refs. [19,20]). With the development of mass spectrometry, it has been widely applied in isotopic analysis of many elements such as Fe (e.g. Ref. [21]), Hg (e.g. Ref. [22]), Mo (e.g. Ref. [23]), etc. However, practical adoption of double spiking could be hindered by the perceived difficulties such as double-spike calibration, mathematical inversion and data reduction. A ready-to-use data reduction program published by Rudge et al. [24], namely the Double Spike Toolbox Matlab code, making it available for researchers to calculate error propagation caused by the double spike. Recently, the Double Spike Toolbox has been widely applied to help researchers to build the double spike technique in metal stable geochemistry, such as Mo [25], Ru [26], Sn [27], etc.

In this study, we will follow the nomenclature and definitions proposed by Rudge et al. [24] to discuss how to choose the optimal double spikes, and then present a description of the double spike calibration. Theoretically, three factors, including the choice of spike pair, the composition of double spike and the ratio of double spike to sample, could have big impacts on the accuracy and

* Corresponding author.

E-mail address: zfzhang@gig.ac.cn (Z. Zhang).

precision of isotopic data (e.g. Refs. [24,28,29]). In practice, isotopic abundance, internal precision, optical effect and cost should also be taken into consideration when choosing the optimal isotope pair. Overall, to facilitate the adoption of the double-spike technique, we will refer to Ca double spike on how to yield excellent Ca isotopic compositions, aiming at providing a practical guide when working with double spikes. This will be helpful for researchers in new isotopic systems.

2. Principles of the double spike technique

The double spike technique is an effective method to calibrate mass fractionation during column chemistry and mass spectrometry. The basic principle of the technique is that mixture (sample + spike) is measured by mass spectrometry, and then sample-self information was extracted from the mixture by deducting the spike through proper fractionation calibration and iterative calculation (e.g., Refs. [24,30]). Fractionation law and data deduction are the two basic components to understand the principles of the double spike technique. In the following text, we will introduce them briefly.

2.1. Fractionation law

Due to the different zero-point energy in different isotopes, mass-dependent fractionation is ubiquitous in nature. During chemical purification, significant isotopic fractionation could be induced if recovery yield is bad, resulting into the apparent isotopic composition deviating from its "true" value, such as Ca [19,31], Fe [32], Zn [33], Nd [34], etc. Importantly, fractionation laws could be variable in different isotopic systems. For example, Zhu et al. [31] investigated that Ca isotope fractionation followed exponential law during the mass spectrometry, while Ranen and Jacobsen [35] thought that Ba isotope fractionation closed to equilibrium or Rayleigh fractionation.

Basically, four mass-dependent fractionation laws have been proposed, including power law, exponential law, Rayleigh law and equilibrium law (e.g. Refs. [20,36,37]). The laws can be written in a general format:

$$\left(\frac{m_1 A / m_2 A}{m_1 A / m_2 A}\right)_M = b \left[\frac{(m_3 A / m_4 A)_M}{(m_3 A / m_4 A)_T}\right]^a \quad (1)$$

where A denotes one element, M and T refer to the measured and true isotope ratios, respectively. b and a are constants which are only related with masses. The superscripts, from m_1 to m_4 , are the mass numbers of isotopes. Conventionally, m_2 and m_4 are chosen the same value.

$$\text{Power law: } a = (m_3 - m_4) / (m_1 - m_2), \quad b = 1 \quad (2)$$

$$\text{Exponential law: } a = \ln(m_3 / m_4) / \ln(m_1 - m_2), \quad b = 1 \quad (3)$$

$$\text{Rayleigh law: } a = \left(1 - \sqrt{m_4/m_3}\right) / \left(1 - \sqrt{m_2/m_1}\right), \quad (4)$$

$$b = \left(\sqrt{m_4/m_3} / \sqrt{m_2/m_1}\right)^a$$

$$\text{Equilibrium law: } a = (1 / m_3 - 1 / m_4) / (1 / m_1 - 1 / m_2), \quad b = 1 \quad (5)$$

Take the natural logarithm of equation (1) in both sides, then:

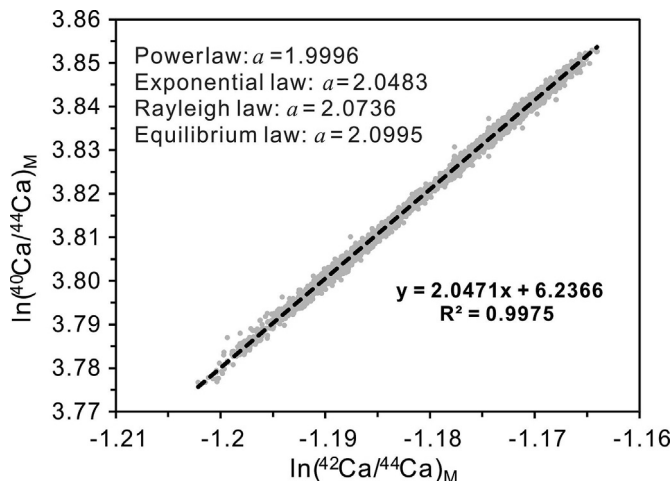


Fig. 1. $\ln(^{42}\text{Ca}/^{44}\text{Ca})_M$ vs. $\ln(^{40}\text{Ca}/^{44}\text{Ca})_M$ of the unspiked NIST SRM 915a of TIMS runs. Over 6000 raw data are plotted. The slope of given regression line (dashed one) indicates that the fractionation behavior follows the exponential law.

$$\ln\left(\frac{m_1 A / m_2 A}{m_1 A / m_2 A}\right)_M = a \ln\left(\frac{m_3 A / m_4 A}{m_3 A / m_4 A}\right)_M + \ln b \quad (6)$$

For a given isotopic inversion, such as Ca, if we choose $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{40}\text{Ca}/^{44}\text{Ca}$ ratios, then $m_1 = 42$, $m_2 = m_4 = 44$, $m_3 = 40$. Then the value of a can be calculated according to equation (2) ~ (5), which is 1.9996 for the power law, 2.0486 for the exponential law, 2.0736 for the Rayleigh law and 2.0995 for the equilibrium law. While equation (6) can be rewritten as:

$$\ln\left(\frac{^{42}\text{Ca}/^{44}\text{Ca}}{^{42}\text{Ca}/^{44}\text{Ca}}\right)_M = a \ln\left(\frac{^{40}\text{Ca}/^{44}\text{Ca}}{^{40}\text{Ca}/^{44}\text{Ca}}\right)_M - a \ln\left(\frac{^{40}\text{Ca}/^{44}\text{Ca}}{^{40}\text{Ca}/^{44}\text{Ca}}\right)_T + \ln b \quad (7)$$

In equation (7), the measured $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{40}\text{Ca}/^{44}\text{Ca}$ ratios are linearly correlated with a slope equals to a . As illustrated in Fig. 1, for TIMS measurements, raw Ca isotope data of the un-spiked NIST SRM 915a fall on a line with a slope of 2.0471, which appears to fit the exponential law fairly well ($a = 2.0483$), consistent with previous studies [19,31].

2.2. Data reduction

To correct mass-dependent fractionation induced during mass spectrometry, many mathematic algorithms behind the double spike technique have been proposed in previous studies (e.g. Refs. [21,30,38,39]). As shown in section 2.1, calcium isotopic fractionation during TIMS measurements follow the exponential mass fractionation law. Based on the exponential law, the principle to understand the process of data deduction is schematically shown in Fig. 2 [24,30].

As illustrated in Fig. 2a, the double spike (T) is mixed by two single spikes with a known proportion (given by λ). The double spike (T) is added into a natural sample (N) with a known proportion (given by p), and the resulting mixture (M) is measured as a different composition m . For a given pair of isotopes, natural variations in stable isotope ratios between a natural sample (N) and one standard (n) can be expressed as:

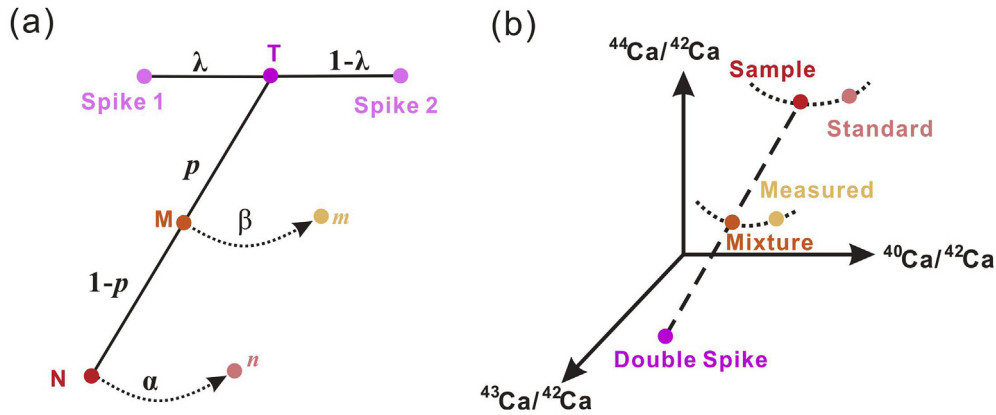


Fig. 2. Schematic diagrams of the double spike technique. (a) Theoretical principle showing the double spike technique, modified from Rudge et al. [24]. It is reproduced with permission from Rudge et al. [24]. Curves with arrows represent mass fractionation, and lines without arrows represent mixing. Spike 1 and Spike 2 are mixed in proportions λ to $1 - \lambda$ (per mole of element) to form the double spike (T). The mixture (M) consists of a proportion p (per mole of element) of double spike (T) to $1 - p$ of sample (N). During the mass spectrometry, the mixture (M) is measured as a different composition m with a fractionation factor β . Similarly, α is the natural fractionation factor between sample (N) and standard (n). (b) A geometric three-dimensional illustration of the Ca isotope composition of spike, sample and mixture, modified from Heuser et al. [30]. Geometrically, sample, double spike and mixture should fall on an ideal mixing line if there is no fractionation. In fact, the “measured” point will deviate from the mixing line due to instrumental fractionation.

$$N_i = n_i e^{-\alpha K_i} \tag{8}$$

Where N_i denotes the i th isotopic ratio of the sample ($i = 1, 2, 3$), e.g., $N_1 = ({}^{40}\text{Ca}/{}^{42}\text{Ca})_{\text{sample}}$. α is the natural fractionation factor between N and n . K_i is the natural log of the ratio of the atomic masses, e.g., $K_1 = \log(39.9626/41.9586)$ [24].

Similarly, a fractionation factor β between the mixture (M) and the measured m ,

$$M_i = m_i e^{-\beta K_i} \tag{9}$$

Based on the principle of mass conservation,

$$M_i = pT_i + (1 - p)N_i \tag{10}$$

Combined equations (8)–(10),

$$pT_i + (1 - p)n_i e^{-\alpha K_i} - m_i e^{-\beta K_i} = 0 \tag{11}$$

Equation (11) is non-linear with three unknowns, p , α , and β . To solve the three unknowns, at least three independent isotope ratios are required. For example, in a four-isotope inversion, ${}^{40}\text{Ca}$, ${}^{42}\text{Ca}$, ${}^{43}\text{Ca}$, and ${}^{44}\text{Ca}$, three available isotope ratios (${}^{40}\text{Ca}/{}^{42}\text{Ca}$, ${}^{43}\text{Ca}/{}^{42}\text{Ca}$, and ${}^{44}\text{Ca}/{}^{42}\text{Ca}$) can be generated. Once p , α , and β are solved, the true isotopic ratio of the sample (N) can also be achieved. Therefore, four or more isotopes are needed in this equation.

We noted that equation (11) is a transcendental one, therefore it is very difficult to solve it directly. To solve such a problem, three main iterative approaches have been proposed previously, including (i) Newton-Raphson iteration [24]; (ii) Monte Carlo-“nest” iteration [21,39,40]; and (iii) geometrical iteration [30,38,41]. Among these three approaches, geometrical iteration is relatively easy to understand. In the following study, it is thus introduced briefly and is visually shown in Fig. 2b. Theoretically, three points (including sample, double spike and mixture) should fall on an ideal mixing line if there is no fractionation. In fact, due to isotope fractionation during mass spectrometry, the measured ${}^{40}\text{Ca}/{}^{42}\text{Ca}$, ${}^{43}\text{Ca}/{}^{42}\text{Ca}$ and ${}^{44}\text{Ca}/{}^{42}\text{Ca}$ ratios deviated from the mixing line (Fig. 2b). In a three-dimensional space coordinates (Fig. 2b), the sample to spike ratio Q is defined as:

$$Q_{42} = {}^{42}\text{Ca}_{\text{sample}}/{}^{42}\text{Ca}_{\text{spike}} \tag{12}$$

In the meanwhile, Q_{42} can also be calculated based on the measured (${}^{40}\text{Ca}/{}^{42}\text{Ca}$)_{measured} or (${}^{44}\text{Ca}/{}^{42}\text{Ca}$)_{measured}, namely

$$Q_{42(40)} = \frac{({}^{40}\text{Ca}/{}^{42}\text{Ca})_{\text{measured}} - ({}^{40}\text{Ca}/{}^{42}\text{Ca})_{\text{spike}}}{({}^{40}\text{Ca}/{}^{42}\text{Ca})_{\text{sample}} - ({}^{40}\text{Ca}/{}^{42}\text{Ca})_{\text{measured}}} \tag{13}$$

$$Q_{42(44)} = \frac{({}^{44}\text{Ca}/{}^{42}\text{Ca})_{\text{measured}} - ({}^{44}\text{Ca}/{}^{42}\text{Ca})_{\text{spike}}}{({}^{44}\text{Ca}/{}^{42}\text{Ca})_{\text{sample}} - ({}^{44}\text{Ca}/{}^{42}\text{Ca})_{\text{measured}}} \tag{14}$$

Note that $Q_{42(40)}$ equals to $Q_{42(44)}$ in geometry when mixture, sample and spike are in a line. If $Q_{42(40)} \neq Q_{42(44)}$, take $Q_{42} = (Q_{42(40)} + Q_{42(44)})/2$ for the first cycle of iteration algorithm. The flow chart of the numerical algorithm can be seen in Fig. 5 of Heuser et al. [30]. The isotopic compositions of a standard or un-spiked sample can be adopted as starting values. When $|Q_{42(40)} - Q_{42(44)}| < 10^{-6}$, the iteration can be terminated (usually 4–5 cycles). Then the Ca isotopic compositions of the sample can be achieved.

3. The optimal spike isotope pair

The main aim of double spiking is to get isotope data with high precision. A good double spike should produce low errors. Rudge et al. [24] suggested that the choice of the double spike could have a big impact on the precision of data, and they provided a Double Spike Toolbox to calculate the theoretical precision in α (natural fractionation factor). When choosing the spike pair, many factors should be taken into consideration, such as abundance, internal precision, and optical effect, etc.

In the case of elements with four or more isotopes, many possible choices of the double spike are available. Take Ca for example, six stable isotopes are available: ${}^{40}\text{Ca}$ (96.941%), ${}^{42}\text{Ca}$ (0.647%), ${}^{43}\text{Ca}$ (0.135%), ${}^{44}\text{Ca}$ (2.086%), ${}^{46}\text{Ca}$ (0.004%), and ${}^{48}\text{Ca}$ (0.187%). Since ${}^{40}\text{Ca}$ and ${}^{44}\text{Ca}$ have relatively higher abundance, they are not suitable to be candidates as spikes. With respect to ${}^{46}\text{Ca}$, it has extremely low abundance that is hard to be enriched, so it is seldom selected as a spike. In previous studies, ${}^{43}\text{Ca}$ – ${}^{46}\text{Ca}$ double spike was once adopted by Fletcher et al. [42] and Gopalan et al. [43]. Rudge et al. [24] suggested ${}^{43}\text{Ca}$ – ${}^{46}\text{Ca}$ double spike can produce the lowest error in theory within ${}^{42}\text{Ca}$, ${}^{43}\text{Ca}$, ${}^{46}\text{Ca}$, and ${}^{48}\text{Ca}$

isotopes inversion. However, the enrichment level of ^{46}Ca is less than 25% (<https://www.isoflex.com/>), which is not appropriate as one spike. Thus, only ^{42}Ca , ^{43}Ca and ^{48}Ca are suitable candidates as spikes. Apart from considering the abundance of isotopes, sometimes isobaric interference is also an important factor. For example, in the case of Ni, ^{64}Ni is avoided because it suffers from isobaric interference by ^{64}Zn (with an abundance of 48.6%) [28], whereas it is not the case for Ca isotopes. Therefore, three isotope pairs are available in Ca isotopic system, namely ^{42}Ca – ^{43}Ca , ^{42}Ca – ^{48}Ca and ^{43}Ca – ^{48}Ca .

Among these three spike pairs, the internal precision and error propagation model of Rudge et al. [24] are used to determine the most suitable spike pair. The contour diagrams of the precision in α are displayed in Fig. 3. The performance of ^{42}Ca – ^{43}Ca , ^{42}Ca – ^{48}Ca and ^{43}Ca – ^{48}Ca are both dependent on the double spike composition and the proportion of spike in the sample-spike mixture. Based on theoretical calculations, the optimal compositions of ^{42}Ca – ^{43}Ca , ^{42}Ca – ^{48}Ca and ^{43}Ca – ^{48}Ca spikes are ^{42}Ca : ^{43}Ca = 1:1, ^{42}Ca : ^{48}Ca = 5:8, ^{43}Ca : ^{48}Ca = 1:2, respectively [24,44]. As shown in Fig. 3d, with optimal spike compositions, ^{42}Ca – ^{43}Ca spike produces a lowest error with 2.6‰ in α , which is bigger than errors that generated by ^{42}Ca – ^{48}Ca (~1.5‰) and ^{43}Ca – ^{48}Ca (~1.6‰) [11,44]. The relationship between the error (1SD) in α and the internal precision (2SE) in $\delta^{44/40}\text{Ca}$ can be expressed as: $\delta^{44/40}\text{Ca} = \alpha \times 1000 \times \ln(43.95549/39.96259) \times 2/\sqrt{100}$. Considering that the external precision of $\delta^{44/40}\text{Ca}$ in literature is about $\pm 0.12\text{‰}$ (which corresponds to the error of ~6.3‰ in α), all these three spike pairs can satisfy the current scientific demands. However, it should

be noted that errors produced by ^{42}Ca – ^{43}Ca spike fluctuate small at a wide range of sample/spike ratio, which will be beneficial to researchers in practice (Fig. 3d) [44].

When choosing proper spike pair, ion optic effects and stability of signal are also needed to be considered. Since the mass dispersion of Ca isotopes is 20%, exceeding the capacity of most modern TIMS instruments (17%–18%), usually it is difficult to measure all isotopes simultaneously. To resolve such problem, dynamic measurement with two sequences in cup configuration was used to measure all isotopes (e.g. Refs. [30,45]), which can be called “peak jump” method. The biggest disadvantage of this approach is that “time difference” exists in the reception of signals in different cycles, possibly resulting into a bad precision due to instability of signal if the instrument is not stable. He et al. [46] allowed static measurement of masses from 40 to 48 on Triton Plus TIMS with a customized cup configuration, avoiding the effect of “time difference”. However, in this case, ion optical effects caused by poor focusing of ion beams that placed into the edge Faraday cups (e.g. Refs. [39,47]) should be taken seriously. If ion beams are pushed too far off-axis, the optical effect can make a big difference. For example, Fletcher et al. [42] attributed the peak asymmetry to ion optic effect that resulted into poor precisions. Among the three spike pairs, only one single sequence is needed to measure $^{44}\text{Ca}/^{40}\text{Ca}$ ratio when using ^{42}Ca – ^{43}Ca spike, which can largely reduce the effect of “time difference” and ion optical effect. Therefore, we preferred the use of ^{42}Ca – ^{43}Ca double spike.

A final consideration is their cost and purity of the single spike. The cost of single spike is typically higher for isotope with lower

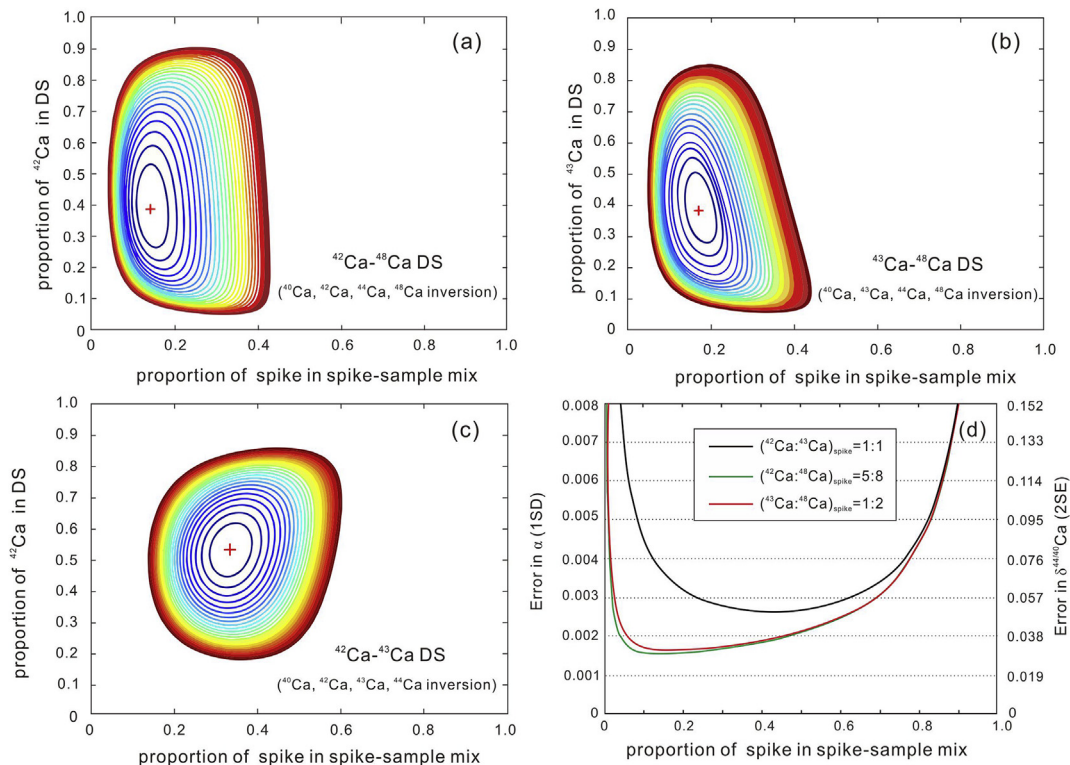


Fig. 3. Contour plot of error in α for (a) ^{42}Ca – ^{48}Ca spike using ^{40}Ca , ^{42}Ca , ^{44}Ca , and ^{48}Ca inversion, (b) ^{43}Ca – ^{48}Ca spike using ^{40}Ca , ^{43}Ca , ^{44}Ca , and ^{48}Ca inversion and (c) ^{42}Ca – ^{43}Ca spike using ^{40}Ca , ^{42}Ca , ^{43}Ca , and ^{44}Ca inversion [24,44]. (d) Plot of error in α and $\delta^{44/40}\text{Ca}$ against proportion p of double spike in mixture with the optimal Ca double spikes [11,44]. It should be noted that it is reproduced with permission from Rudge et al. [24] and Liu et al. [44]. For (a), (b) and (c), the vertical axis gives the proportion λ of single spike in the double spike, and the horizontal axis represents the proportion p of double spike in mixture. The optimum is marked by a cross. Only contours within 25% of the optimal error are shown and the interval is 1%. For (d), the left hand y-axis is the precision in α (1SD, standard deviation), and the right hand y-axis is the precision in $\delta^{44/40}\text{Ca}$ (2SE, standard deviation of the mean). They can be transformed by $\delta^{44/40}\text{Ca} = \alpha \times 1000 \times \ln(43.95549/39.96259) \times 2/\sqrt{100}$. The spike compositions are ^{42}Ca spike = (2.56%, 96.8%, 0.11%, 0.51%, 0.01%, 0.02%), ^{43}Ca spike = (5.30%, 0.18%, 90.0%, 4.44%, 0.01%, 0.08%), and ^{48}Ca spike = (2.10%, 0.02%, 0.01%, 0.07%, 0.01%, 97.78%). The ^{48}Ca spike composition was taken from Oak Ridge National Laboratory, USA, while ^{42}Ca and ^{43}Ca spike compositions were from Isoflex Company [11,44].

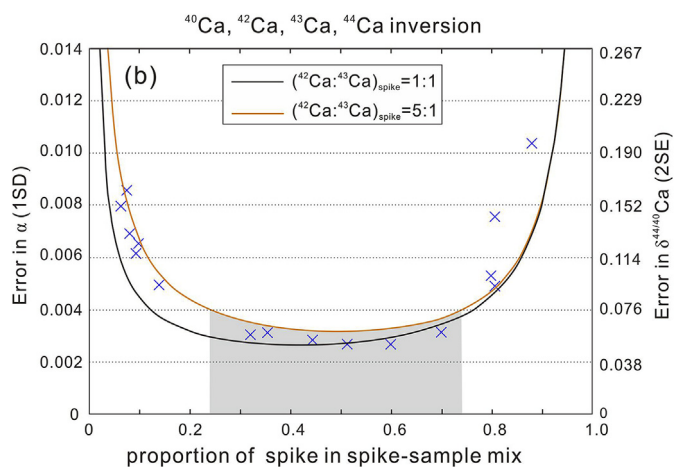


Fig. 4. Comparison of theoretical curves with TIMS data for Ca. The solid lines are theoretical curves for a total beam intensity of $\sim 15V$ with 4s integrations according to Rudge et al. [24]. The black line is the optimal composition of 50% ^{42}Ca and 50% ^{43}Ca spike; while the orange line represents a double spike $^{42}\text{Ca}/^{43}\text{Ca}$ ratio of 5:1. Blue crosses are experimental results based on a $^{42}\text{Ca}/^{43}\text{Ca}$ ratio of 5:1. The experiment data are generally in agreement with theory. The shadow area represents the range of optimal molar ratio of sample to spike when the internal precision in $\delta^{44/40}\text{Ca}$ is lower than 0.076‰. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

abundance, so it could be cost-efficient to choose a spike with a reasonably high natural abundance. As shown in Fig. 4, the theoretical lowest error in α is $\sim 3.2\text{‰}$ when the $^{42}\text{Ca}/^{43}\text{Ca}$ ratio is set as 5:1, which is only slightly higher than the error with optimal $^{42}\text{Ca}/^{43}\text{Ca}$ ratio of 1:1. Considering that the price of ^{42}Ca spike is one order of magnitude lower than ^{43}Ca spike, raising the proportion of ^{42}Ca in the double spike can largely reduce the cost. In practice, the error estimated from the Double Spike toolbox [24] can be tested experimentally. For instance, a $^{42}\text{Ca}-^{43}\text{Ca}$ double spike with a ratio of 5:1 was added to NIST SRM 915a in a range of various proportions. The resulting mixtures were measured by TIMS, and internal error in $\delta^{44/40}\text{Ca}$ can be calculated. When the errors were plotted in Fig. 4, they were fairly close to the theoretical curves, suggesting some good validation for the error model proposed by Rudge et al. [24].

4. Calibrating a double spike and spike/sample ratio

The accuracy of data corrected for mass fractionation relies heavily on the composition of the double spike. Recalibrating the isotopic composition of the double spike because (1) the compositions certificate of single spikes provided by their producer are

typically within 4 significant digits and thus cannot be 100% accurate and (2) gravimetric mixing of two single spikes is also not sufficient accuracy. Since obtaining an absolute isotope composition is extremely difficult, double spike is generally calibrated relative to a reference material.

For Ca double spike calibration, NIST SRM 915a is commonly used as a calibrant. The first step is to measure the un-spiked NIST SRM 915a repeatedly on TIMS. The instrumental fractionation is corrected by an internal normalization to a given ratio ($^{42}\text{Ca}/^{44}\text{Ca} = 0.31221$ [48]) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences. After normalization, the un-spiked NIST SRM 915a yields 47.162 ± 0.012 (2SD, $n = 85$) for $^{40}\text{Ca}/^{44}\text{Ca}$, 0.06486 ± 0.00003 (2SD) for $^{43}\text{Ca}/^{44}\text{Ca}$, 0.00151 ± 0.00004 (2SD) for $^{46}\text{Ca}/^{44}\text{Ca}$, and 0.08869 ± 0.00005 (2SD) for $^{48}\text{Ca}/^{44}\text{Ca}$, respectively. Note that the absolute $^{40}\text{Ca}/^{44}\text{Ca}$ ratio is variable between laboratories. For instance, Huang et al. [49] reported $^{40}\text{Ca}/^{44}\text{Ca}$ ratio of un-spiked NIST SRM 915a of 47.134 ± 0.002 ($2\sigma_m$) at the Harvard University. Therefore, it is meaningless to compare the absolute ratios, but the isotope ratio difference ($\delta^{44/40}\text{Ca}$) is comparable between laboratories. Generally, Ca isotope ratio is commonly reported relative to standards, such as NIST SRM 915a: $\delta^{44/40}\text{Ca} = [(^{40}\text{Ca}/^{44}\text{Ca})_{\text{sample}} / (^{40}\text{Ca}/^{44}\text{Ca})_{\text{SRM 915a}} - 1] \times 1000$. In this equation, the $^{40}\text{Ca}/^{44}\text{Ca}$ value of un-spiked NIST SRM 915a is used as a basic value for internal isotope normalization.

The second step is to measure the double spike itself. Since the instrumental fractionation is inevitable during measurement, a fractionation factor is needed to correct the raw data. If $^{43}\text{Ca}-^{42}\text{Ca}$ double spike is adopted, an initial $^{43}\text{Ca}/^{42}\text{Ca}$ ratio can be calculated by gravimetric method and it is assumed to be close to its true value. This is because the abundances of ^{43}Ca and ^{42}Ca in double spike are relatively high and small errors can be caused by gravimetric analysis compared with other isotopes. By using the so-called “true value” as an internal normalization, a fractionation factor can be calculated, and then other isotopic ratios (including $^{40}\text{Ca}/^{42}\text{Ca}$, $^{44}\text{Ca}/^{42}\text{Ca}$, $^{46}\text{Ca}/^{42}\text{Ca}$ and $^{48}\text{Ca}/^{42}\text{Ca}$) can be calculated using an exponential law. After that, the initial isotopic compositions of the double spike are achieved. It should be noted that all the ratios are not the final because the initial $^{43}\text{Ca}/^{42}\text{Ca}$ ratio is not precise and might be revised. When $^{43}\text{Ca}/^{42}\text{Ca}$ ratio is revised, all the ratios are required to be recalibrated.

The third step is to measure spiked NIST SRM 915a to check that the accuracy of the composition of the double spike. A good calibration should satisfy one important condition: $\delta^{44/40}\text{Ca}$ values are not correlated with $^{40}\text{Ca}/^{42}\text{Ca}$ ratios of the sample-spike mixture (e.g. Ref. [28]). This can be proved from a geometrical scenario: in a three-dimensional space (Fig. 2), the mixture lies between the double spike and sample, and the sample refers to an unknown but

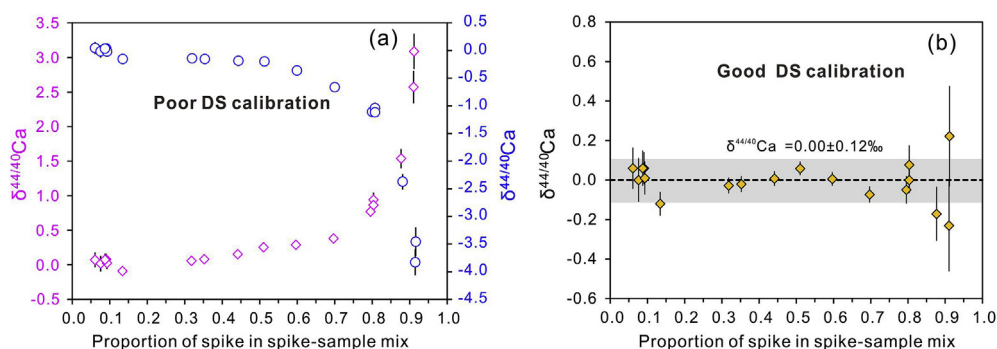


Fig. 5. The effects of isotopic compositions of the double spike on a batch of raw data. (a) Poor calibration of double spike and (b) good calibration of double spike. NIST SRM 915a with different amounts of $^{42}\text{Ca}-^{43}\text{Ca}$ spikes were measured on TIMS.

fixed point, if the composition of the double spike is well constrained, the composition of sample can be precisely calculated based on the proportion of sample to spike. In other words, if the composition of the double spike is well calibrated, only one $\delta^{44/40}\text{Ca}$ value of the sample can be achieved regardless of various proportion of spike in spike-sample mixture. A case study was shown in Fig. 5, where spike-sample mixtures with various proportions were measured on TIMS to check the accuracy of double spike. When the composition of the double spike is poorly calibrated, $\delta^{44/40}\text{Ca}$ are either negatively or positively with the proportion of spike in spike-sample mixture (Fig. 5a). Instead, if the composition of the double spike is well calibrated, $\delta^{44/40}\text{Ca}$ values are relatively constant (Fig. 5b). Therefore, if negative or positive relationships are observed between $\delta^{44/40}\text{Ca}$ values and proportion of spike in mixtures, suggesting that the composition of double spike is not correct. If this is the case, we need to go back to the second step, manually trim the so-called “true value” of $^{43}\text{Ca}/^{42}\text{Ca}$ ratio till no relevance is observed anymore. Once $\delta^{44/40}\text{Ca}$ values of NIST SRM 915a are close to 0.00 and independent on the proportion of spike in mixture, the calibration of the composition of double spike can be terminated.

After the isotopic compositions of the double spike are properly calibrated, the optimal ratio of spike to sample can also be predicted. As shown in Fig. 4, a spike/sample ratio between 0.23 and 0.73 yielded relatively good internal precisions. The underspiked (lower than 0.23) or overspiked (greater than 0.73) samples resulted in large internal precisions. This is also further constrained by analyzing NIST SRM 915a in a wide range of spike/sample ratios in Fig. 5b. Therefore, we suggested that the optimal molar ratio of spike to sample is 0.23–0.73.

5. The advantages and limitations of double spiking

The application of double spike has greatly promoted the development of Earth science. Once the double spike is properly calibrated, it can provide accurate correction of mass-dependent fractionation. The double spike should be mixed well with samples prior to ion exchange chemistry. The biggest advantage of double spiking is that the isotopic fractionation can be corrected simultaneously during both column chemistry and mass spectrometry. If this is the case, recovery yield cannot be so strict. For example, to eliminate isobaric interferences, Cenki-Tok et al. [50] truncated the elution curve and the yield was diminished to 70%. Zhu et al. [51] suggested that even though the yield was as low as 20%, accurate isotopic compositions can also be achieved.

Double spiking also has some limitations or disadvantages that should be noted. Firstly, double spiking is normally applicable to elements with 4 or more stable isotopes since three independent isotopes ratios are required in the double spike inversion [24,52]. In some special cases, double spike technique can be extended to three-isotope elements, such as Si, Mg and K [53,54]. However, this approach is only feasible when the sample-double spike mixing line is tangent to the exponential-law mass-bias curve [53]. Secondly, isotopic ratios of the two isotopes used as spikes cannot be directly calculated through data reduction. For instance, if ^{42}Ca – ^{43}Ca double spike is used, $^{43}\text{Ca}/^{42}\text{Ca}$ ratio of sample cannot be achieved through iterative calculation, while it can be transformed by multiplying a mass-dependent factor (e.g. Refs. [36,37]).

One thing should be noted that the composition of the double spike will change over time based on our practical observation over a period of 6 years. Calcium concentration of the double spike is relatively low with ~35 ppm in our laboratory. It is therefore systematic errors can be caused if the composition of the double spike is not recalibrated after one year. Young et al. [55] suggested that storing solutions with Mg concentrations larger than 40 ppm

in Teflon bottles cannot result in drift for years, while systematic $\delta^{26}\text{Mg}$ drift is observed for CAM-1 solutions with 5 ppm in a few months. The cause of the drift is unknown, possibly related with the adsorption of heavy isotopes by the bottle itself or impurities released from the bottle. Therefore, we highly recommend that double spikes should be stored with a high concentration (at least a few hundred ppm) in Teflon bottles.

6. Summary

Taking Ca isotope as an example, this study aims at providing a practical view on the use of double spiking, making it easier for researchers when working with double spikes in variable isotopic systems. The fractionation laws and data deduction approaches are briefly summarized to help us to understand the principles of the double spike technique. The choice of spike pair, the composition of double spike and the ratio of spike to sample are important factors that can affect the accuracy and precision of isotopic data. A Double Spike Toolbox was used to calculate the theoretical precision in α (natural fractionation factor). When choosing the spike pair, many factors should be taken into consideration, such as abundance, internal precision, and optical effect, cost etc. The isotopic compositions of double spike are calibrated relative to the reference standards. A good calibration should yield same δ -values regardless of different proportions of sample to spike. Theoretically, the optimal sample to spike ratio will yield the lowest error, which can be also calculated based on the error model.

Declaration of competing interest

The authors declare that no conflict of interest.

CRediT authorship contribution statement

Fang Liu: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Funding acquisition, Writing - original draft. **Zhaofeng Zhang:** Conceptualization, Supervision, Project administration, Funding acquisition, Writing - review & editing. **Xin Li:** Writing - review & editing. **Yajun An:** Writing - review & editing.

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