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Isobaric Spike Method for Absolute Isotopic Ratio Determination by MC-ICP-MS

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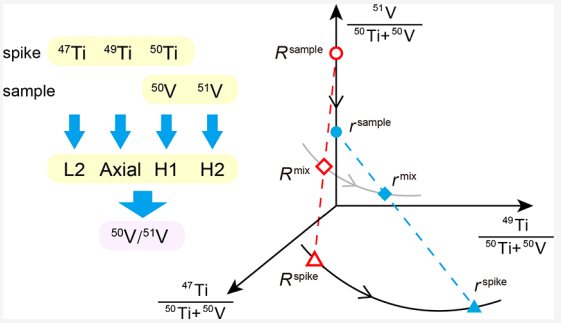
ABSTRACT: Absolute isotopic ratios are required for isobaric interference corrections, spike calibrations, and isotopic analysis by external normalization methods. However, high-precision natural isotopic abundance data are lacking for many elements, particularly those with less than four isotopes or having isobaric isotopes with other elements. In this study, we developed a method for absolute isotope ratio analysis, which integrates the concept of the double-spike method with isotopic analysis of element pairs that have isobaric isotopes. Using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), the isotopic composition of a sample can be derived by measuring a series of mixtures of the sample and a spike element that has an isobaric isotope with the element being analyzed. We applied this method to five pairs of elements (Ca−Ti, V−Ti, Cr−Ti, Ni−Zn, and In−Sn) and obtained the absolute isotopic ratios for Ca, V, Cr, Ni, and In, as well as the relative Ca isotopic composition. By simultaneous measurement of Ti and Ca isotopes, a quantitative relationship between the instrumental mass fractionation factors and element masses was developed. After correcting for the difference in instrumental mass fractionation factors, the obtained absolute ratios agree well with the literature data and have per mil level accuracy. This method has considerable potential in measuring the absolute isotopic ratios of elements that have isobaric isotope with other elements. Such precisely determined absolute isotopic ratios and the relationship between the instrumental mass fractionation factors and elemental masses will improve isobaric interference corrections, particularly when chemical purification is imperfect or during laser ablation analysis.



The development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has led to subtle variations in isotopic ratios of many elements in natural materials being resolved.[1] However, precise absolute isotopic ratios of specific elements are often required during high-precision isotopic analyses by MC-ICP-MS, especially for isobaric interference correction. When chemical procedures cannot completely remove the matrix elements from the element of interest or during laser ablation analysis, the absolute isotopic ratios of the interfering elements are required to correct for the interferences.[2−10] The isobaric interference correction is even more important during the measurement of isotopic anomalies in extraterrestrial samples, as improper correction will directly lead to inaccurate mass-independent isotopic results.[2,3,8−10] During spike calibrations and isotopic analysis by external normalization methods, absolute isotopic ratios are also required. However, many of the available natural isotopic abundances have poor precisions,[11] because the elements with high ionization potentials could not be precisely analyzed in early thermal ionization mass spectrometry (TIMS) studies. As such, published uncertainties on absolute isotopic ratios are considerably greater than the typical analytical uncertainties from a conventional MC-ICP-MS. For example, only two studies provided absolute V isotope abundances; however, their results are inconsistent with each other.[12,13] Furthermore, isobaric interference corrections using the Ca isotopic ratios recommended by IUPAC[11,14] have been found to introduce analytical artifacts on Ti isotopic anomalies,[3] which cannot be explained by the difference in fractionation factors between Ca and Ti, as the artifacts on ^{46}Ti and ^{48}Ti do not follow a mass fractionation law. Therefore, high-precision measurements by MC-ICP-MS require improved absolute isotopic ratio data.

There are several strategies for the correction of instrumental mass fractionation associated with MC-ICP-MS. The commonly used standard-sample bracketing (SSB) method is incapable of determining the absolute isotopic composition of unknowns, unless the isotopic composition of the standard is defined. The double-spike method is capable of robust correction of isotopic fractionation and precise measurement of absolute isotopic ratios.[15] By measuring a mixture of the sample and a synthetic isotopic spike that is

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composed of two or more enriched isotopes, the natural isotopic fractionation factor and absolute isotopic ratios of the sample can be obtained by solving three mixing equations of the isotope ratios. Although the double-spike method has been widely applied for isotopic analysis by MC-ICP-MS,[5,16−18] there are several shortcomings, including its restriction in applicability to elements with four or more isotopes and challenges in accurate calibration of the spike isotopic composition,[19] as well as knowledge of the precise reference isotopic ratios for natural samples.[5,20] Although a critical double-spike method has been developed for three-isotope systems,[19,21] its application is limited by the challenges in preparation of the optimal critical mixtures. Another common approach is external normalization that uses the isotopic composition of an elemental spike (dopant) to correct for mass-dependent instrumental fractionation of a different element.[22,23] The external normalization approach has been further developed (i.e., the combined standard-sample bracketing and internal normalization method[24−26] and the optimized regression method[23,27]) to overcome issues of mass-independent fractionation and inconsistent fractionation factors of different elements. For these methods, the ideal elemental spike should have a similar mass range as the element of interest but no isobaric interferences.

In this study, we combined the concepts of the double-spike and external normalization methods and applied this to mixtures of two elements that have isobaric interferences and can be analyzed by MC-ICP-MS. We further developed an algorithm of the double-spike inversion that can correct for the differences in masses and fractionation factors between the element of interest and spike element. We applied this isobaric spike method to analyze Ca, V, Cr, Ni, and In standards. The obtained $^{46}Ca/^{44}Ca$, $^{48}Ca/^{44}Ca$, $^{50}V/^{51}V$, $^{50}Cr/^{52}Cr$, $^{64}Ni/^{62}Ni$, and $^{113}In/^{115}In$ ratios are consistent with published values, which demonstrates the validity of the method for high-precision measurement of absolute isotopic ratios.

ANALYTICAL BACKGROUND

Application of the Double-Spike Method to Two-Element Systems with Isobars. The basic ternary equations of the traditional double-spike method are based on mass conservation of sample−spike mixing, which geometrically defines a straight line in a three-dimensional plot of isotope ratios with a common demoninator.[21] This mixing line connects three points that represent the true compositions of the spike, mixture, and sample. In three-dimensional space, this line is unique because three independent equations can be constructed, which determine the three unknowns: the proportion of the reference isotope that is contributed by the spike to the mixture (φ), the instrumental fractionation factor (β), and the true isotopic ratio of the sample (R^{sample}) or the natural isotopic fractionation factor of the sample (α).

We now apply the double-spike method to a two-element system, with one or more isobaric isotopes on the element of interest. A spike element that has an entirely different isotopic composition acts as a double, triple, or multiple spike, assuming that the mixture is analyzed by MC-ICP-MS with a high ionization efficiency. This approach allows for simultaneous measurement of different elements. To establish a geometry similar to that of the traditional double-spike method, we selected the sum of the isobaric isotopes to be the denominator of the isotopic ratios, because the denominator needs to have a nonzero value. The isotopic composition of the two elements and their mixture can then be expressed in three-dimensional space using the other three isotopes (Figure 1). The equations are based on the spike−

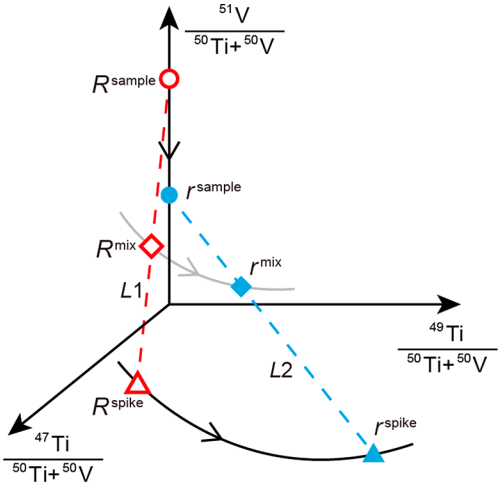

Figure 1. Schematic diagram of the isobaric spike method. The measurement of $^{50}V/^{51}V$ using ^{47}Ti, ^{49}Ti, and ^{50}Ti is presented as an example. The sample is a pure V solution and fractionates along the z-axis. The spike is a Ti standard that has a mass-bias curve that falls on the x−y plane (black curved line). The mass-bias curve of the mixture is the gray curved line. The mixture does not exactly fractionate along the theoretical mixing curve due to differences between the masses and the instrumental fractionation factors of the two elements. The red open symbols are the true ratios, and the blue solid symbols are the measured ratios. The mixing line for true ratios ($L1$; red dashed line) and measured ratios ($L2$; blue dashed line) intercept with the mass-bias curves at the isotopic compositions of the sample, spike, and mixture.

sample mixing line $L1$. For each isotope i, other than the chosen isobaric isotopes, we have

$$R_i^{mix} = \varphi R_i^{spike} + (1 - \varphi)R_i^{sample} \quad (1)$$

where φ is the proportion of the reference isotope of the mixture contributed by the spike (i.e., the ratio of the isobaric isotope of the spike element to the sum of the two isobars), R and r are the true and measured isotopic ratios of the spike, sample, or mixture, respectively, and M_{ref} and M_i are the masses of the isobaric isotopes for reference and the isotope i. We used the exponential mass fractionation law[16] to describe the instrumental mass fractionation process:

$$R_i^{mix} = r_i^{mix}\left(\frac{M_{ref}}{M_i}\right)^{\beta} \quad (2)$$

and the natural fractionation process:

$$R_i^{standard} = R_i^{sample}\left(\frac{M_{ref}}{M_i}\right)^{\alpha} \quad (3)$$

Consequently, if the isotopic ratios of the spike element (R^{spike}) are known, φ, α, and β can be solved based on these equations.

Improvement of the Algorithm. Shen et al.[28] sought to perform double-spike inversion that does not require the isotopic ratios of the spike as prerequisite. They proposed that if two sets of spike−sample mixtures were measured, the four mass-bias curves of the spike, sample, and two mixtures define

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Table 1. Instrumental Operating Conditions

Neptune Plus settings									
RF power	1200 W								
extraction voltage	−2000 V								
cool gas	∼15 L min^{-1}								
auxiliary gas	∼1.0 L min^{-1}								
sample gas	∼0.99 L min^{-1}								
mass resolution	high resolution ($m/\Delta m$ ∼ 10000) for Ca−Ti, V−Ti, and Cr−Ti; low resolution ($m/\Delta m$ ∼ 400) for Ni−Zn and In−Sn								
interface cones	Ni standard sampler cone, Ni H skimmer cone								
lens settings	optimized for maximum intensity								
typical sensitivity	15−20 V ppm^{-1} for ^{48}Ti ∼ 12 V ppm^{-1} for ^{64}Zn and ^{120}Sn								
measurement parameters									
	Sample uptake rate						100 μL min^{-1}		
	Sample measurement time						40 × 4.2 s		
	Background measurement time						10 × 4.2 s		
	Uptake time						100 s		
	Washout time						142 s		
cup configuration									
Faraday collector	L4	L3	L2	L1	axial	H1	H2	H3	H4
Ca−Ti				^{46}Ti	^{47}Ti	^{48}Ti	^{49}Ti	^{50}Ti	
		^{44}Ca		^{46}Ca		^{48}Ca			
V−Ti, Cr−Ti		^{46}Ti	^{47}Ti	^{48}Ti	^{49}Ti	^{50}Ti			
						$^{50}V/^{50}Cr$	^{51}V	^{52}Cr	
Ni−Zn				^{64}Zn		^{66}Zn	^{67}Zn	^{68}Zn	
		^{62}Ni		^{64}Ni					
In−Sn	^{112}Sn		^{114}Sn	^{115}Sn	^{116}Sn	^{117}Sn	^{118}Sn	^{119}Sn	^{120}Sn
		^{113}In		^{115}In					

a unique mixing line that intercepts with all of these curves, and the intersect would be the true composition.[28] Following this concept, our isobaric spike method does not require to know the reference isotopic ratios of the spike element. However, the fractionated isotopic compositions of the spike, sample, and mixture also form a mixing line. Combined with eq 2, eq 1 can be rearranged as follows:

$$r_i^{\text{mix}} = \varphi R_i^{\text{spike}}\left(\frac{M_i}{M_{\text{ref}}}\right)^{\beta} + (1-\varphi)R_i^{\text{sample}}\left(\frac{M_i}{M_{\text{ref}}}\right)^{\beta} = \varphi r_i^{\text{spike}} + (1-\varphi)r_i^{\text{sample}} \quad (4)$$

This equation demonstrates that the points representing the three fractionated isotopic compositions are collinear and determine the fractionated mixing line (*L*2 in Figure 1). This means that the addition of a second mixture cannot reduce the number of variables, because there are an infinite number of fractionated mixing lines intercepting with all of the potential mass-bias curves of mixtures at any proportions, as well as the mass-bias curves of the spike and sample. Therefore, for the traditional double-spike method, the spike must be calibrated, and for the isobaric spike method, the reference ratio of the spike element is required.

Although eq 1 is sufficient to derive the isotopic composition of the element of interest, there are discrepancies between the masses of the isobaric isotopes and the instrumental fractionation factors of the two elements are not necessarily the same. This is addressed by using eq 4. The absence of isobaric isotopes in R^{spike} and R^{sample} makes it possible to use the parameters of the two elements separately. Using the masses and fractionation factors specific to each element, eq 4 can be represented as follows:

$$r_i^{\text{mix}} = \varphi_m R_i^{\text{spike}}\left(\frac{M_{i1}}{M_{\text{ref1}}}\right)^{\beta 1} + (1-\varphi_m)R_i^{\text{sample}}\left(\frac{M_{i2}}{M_{\text{ref2}}}\right)^{\beta 2} \quad (5)$$

where subscripts 1 and 2 refer to the spike element and the element of interest, respectively. The mixing proportion of the fractionated composition φ_m is different from the true mixing proportion φ. Consequently, using the double-spike inversion with eq 5 allows for accurate isotopic ratios of the element of interest to be calculated, which takes into account variable instrumental fractionation factors for different elements.

EXPERIMENTAL SECTION

Sample Preparation. We applied the isobaric spike method to five pairs of elements: Ca−Ti, V−Ti, Cr−Ti, Ni−Zn, and In−Sn. Both V and In have only two isotopes (^{50}V and ^{51}V; ^{113}In and ^{115}In). These isotopes can be interfered by isotopes of adjacent elements (^{50}Ti and ^{50}Cr to ^{50}V, ^{113}Cd to ^{113}In, and ^{115}Sn to ^{115}In), which hinder the employment of double-spike and external normalization methods. Therefore, only data from gravimetric isotope mixture method have been reported for V and In.[29] For Ca−Ti, V−Ti, and Cr−Ti pairs, all the stable isotopes of Ti have natural abundances higher than 5%, providing a considerable number of isobaric isotopes when Ti is added to Ca, V, or Cr. Because ^{46}Ca, ^{48}Ca, and ^{50}V are of very low abundance, the addition of the isobaric isotopes ensures precise measurement of the isotopic ratios. Therefore, we selected Ti as the spike to measure the absolute isotopic ratios of Ca, V, and Cr; for Ni and In, standard solutions of Zn and Sn were used as the spike, respectively.

For measurements of Ca−Ti, V−Ti, and Cr−Ti mixtures, we added a Ti standard to individual standard solutions of Ca,

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V, and Cr and measured the isotopic ratios of the three mixtures. The Ti, Ca V, and Cr standard solutions were purchased from SPEX CertiPrep, which are directly traceable to the NIST SRM standards. The standard solutions were diluted in 0.3 M HNO_3−0.0014 M HF, and the Ti concentrations were kept at 1 ppm. The trace HF was added to the solutions to prevent the hydrolysis and precipitation of Ti. For Ni−Zn experiments, a NIST SRM 986 Ni standard and a Zn solution from High-Purity Standards (HPS Zn), which has $\delta^{66/64}$Zn of −0.36‰[30] relative to IRMM-3702, were used. The Zn solution was diluted to 0.5 or 0.75 ppm in 0.05 M HNO_3 and doped with the Ni standard. For In−Sn experiments, a NIST SRM 3161a Sn standard solution was diluted to 0.2 or 0.5 ppm in 2% HNO_3 and doped with an In standard from Sigma-Aldrich. To investigate the effect of mixing proportions, we prepared mixtures of the sample and the spike with various mixing proportions (Table S1).

Isotopic Analyses. The isotopic analyses were performed on a Thermo Fisher Scientific Neptune Plus MC-ICP-MS at the School of Earth Sciences and Engineering, Nanjing University. The operating conditions of the MC-ICP-MS and measurement parameters are listed in Table 1. During analyses for Ca−Ti, V−Ti, and Cr−Ti mixtures, the instrument was operated in high-resolution mode to resolve polyatomic interferences. An Aridus II desolvation system was used to enhance sensitivity and minimize molecular interferences, such as $^{28}Si^{19}F$ on ^{47}Ti, $^{29}Si^{19}F$ on ^{48}Ca and ^{48}Ti, and $^{30}Si^{19}F$ on ^{49}Ti. Due to the mass range of the MC-ICP-MS, only part of the isotopic spectra of Ca and Cr can be collected simultaneously with Ti isotopes. The Faraday collector configuration followed previous Ti isotopic studies.[8] For Ca−Ti measurements, the axial mass was set at 47, such that masses of ^{44}Ca to ^{50}Ti were collected. For V−Ti and Cr−Ti measurements, the axial mass was set at 49, allowing simultaneous collection of ^{46}Ti to ^{52}Cr (Table 1). Consequently, $^{46}Ca/^{44}Ca$, $^{48}Ca/^{44}Ca$, $^{50}V/^{51}V$, and $^{50}Cr/^{52}Cr$ ratios can be acquired using the isobaric spike method. Using the SSB method and the same instrumental operating conditions with Ca−Ti measurement, the relative isotopic composition of the SPEX Ti standard was measured against SRM 3162a on the MC-ICP-MS. In addition, a pure Ca standard was measured to assess the self-consistency of the obtained Ca isotopic ratios. The collectors were located at interference-free peak flat plateaus to avoid potential molecular interferences (e.g., $^{22}Ne_2$ on ^{44}Ca, $^{36}Ar^{14}N$ on ^{50}Ti, and $^{40}Ar^{12}C$ on ^{52}Cr). Analyses of Ni−Zn and In−Sn mixtures were also performed on the Neptune Plus MC-ICP-MS, which was on standard low-resolution, wet-plasma mode. During the Ni−Zn and In−Sn analyses, masses 62−68 and 112−120 were measured, and the cup configurations are shown in Table 1.

To improve the analytical precision, the measurements of sample−spike mixtures were bracketed by measurements of the Ti, Zn, or Sn standard, taking advantage of the continuous sample introduction of the MC-ICP-MS. The measured isotopic ratios of the Ti standard were normalized to $^{49}Ti/^{47}Ti = 0.749824$, which was calculated by the measured Ti isotope composition of SPEX Ti standard ($\delta^{49/47}$Ti = −0.92 ± 0.13‰) relative to SRM 3162a, which has a traceable absolute Ti isotope composition being reported in the literature ($^{49}Ti/^{47}Ti = 0.750517$[3,5]). Similarly, isotope ratios of the Zn standard was normalized to $^{68}Zn/^{66}Zn = 0.66516$ (calculated from $\delta^{66/64}$Zn = −0.36‰[30] of the HPS Zn and the reference ratio $^{68}Zn/^{66}Zn = 0.66540$[31] for IRMM-3702), and the Sn isotope ratios of the Sn standard were normalized to $^{118}Sn/^{120}Sn = 0.74295$.[32] Then, the normalized ratios were used for the isobaric spike calculation. After measurements, the isotopic ratios of the element of interest were first calculated using the same β factor as the spike elements, according to eq 5. The correction for different β factors is discussed in Section 4.3. Each absolute isotopic ratio was calculated with only one pair of isobars. For example, the absolute $^{46}Ca/^{44}Ca$ ratio was calculated using ^{44}Ca, ^{46}Ca, ^{46}Ti, ^{47}Ti, and ^{49}Ti data. On the contrary, relative Ca isotopic compositions were calculated relative to SRM 915a by assuming the Ca isotope ratios mass-dependently fractionated from the reference Ca isotope ratios $^{46}Ca/^{44}Ca = 0.0015125$ and $^{48}Ca/^{44}Ca = 0.0886516$.[33] In this case, the ^{44}Ca, ^{46}Ca, ^{46}Ti, ^{48}Ca, ^{48}Ti, and ^{47}Ti data were used and both ^{46}Ca and ^{48}Ca were spiked. The relative Ca isotopic compositions are expressed as $\delta^{48/44}$Ca:

$$\delta^{48/44}\mathrm{Ca} = \left[\frac{(^{48}\mathrm{Ca}/^{44}\mathrm{Ca})_{\mathrm{measured}}}{(^{48}\mathrm{Ca}/^{44}\mathrm{Ca})_{\mathrm{reference}}} - 1\right] \times 1000 \quad (6)$$

The isotope compositions of SPEX Ca and Cr standards relative to NIST standards (SRM 915a and SRM 3112a, respectively) were determined using well-established double-spike TIMS methods.[34,35] SPEX Ca has a $\delta^{44/40}$Ca = 1.14 ± 0.13‰ (2sd, n = 3) relative to SRM 915a, and SPEX Cr has a $\delta^{53/52}$Cr = 0.072 ± 0.033‰ (2sd, n = 2) relative to SRM 3112a. The measured absolute isotopic ratios of SPEX Ca and Cr standards were normalized to the SRM standards according to the relative isotopic compositions. For V and In, there are no international isotopic reference materials. However, compared to the relatively large uncertainties of the published reference ratios (i.e., 2.4‰ for $^{50}V/^{51}V$ and 4.2‰ for $^{113}In/^{115}In$),[13,29] the isotopic difference between different standards is expected to be insignificant.

RESULTS AND DISCUSSION

Isotopic Compositions Uncorrected for Instrumental Mass Fractionation Factors. For mixtures with different mixing proportions, the absolute isotopic ratios of $^{46}Ca/^{44}Ca$, $^{48}Ca/^{44}Ca$, $^{50}V/^{51}V$, $^{50}Cr/^{52}Cr$, $^{64}Ni/^{62}Ni$, and $^{113}In/^{115}In$ that were calculated using the same β as the spike (Ti, Zn, or Sn) are shown in Figure 2 and listed in Table S1. In the calculation, the uncertainties in isotopic ratios of the spike elements propagated to the combined standard uncertainties of the results (Table S1). The measured absolute isotopic ratios do not show any systematic correlations with the mixing proportions and are close to the literature values (Figure 2). Exponential mass fractionation law was applied for the calculation as it is the most widely used[36] and has proven successful describing the mass fractionation of Ca, Ti, Cr, Ni, Zn, and Sn isotopes.[5,16,23,33,37−39] Other fractionation laws (i.e., power, Rayleigh) have been applied to derive the absolute ratios of the elements of interest for comparison (Table S2). In general, the ratios calculated by different laws for the same sample are comparable within the combined standard uncertainties. However, for $^{50}Cr/^{52}Cr$ ratios, the discrepancy between different laws is significant.

Although the difference between the instrumental fractionation factors of the element pair was not corrected, the measured isotope ratios of samples with the highest concentrations (D-Ca-5, D-V-5, D-Cr-5, and InSn-5), which have the smallest uncertainties, generally agree with previously published reference ratios (Figure 2). D-Ca-5 has $^{46}Ca/^{44}Ca$ =

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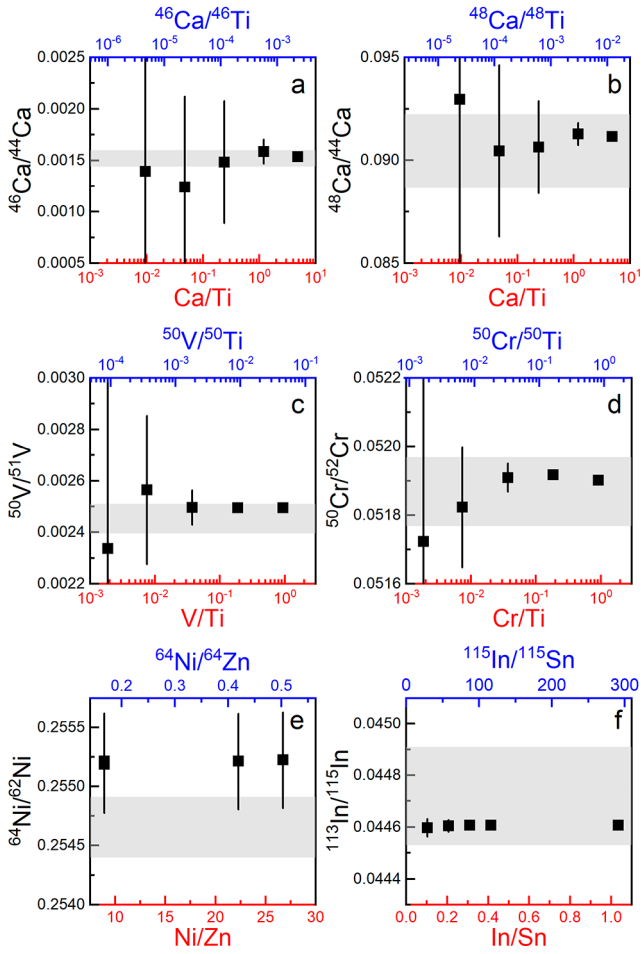

Figure 2. Absolute isotopic ratios of (a) $^{46}Ca/^{44}Ca$, (b) $^{48}Ca/^{44}Ca$, (c) $^{50}V/^{51}V$, (d) $^{50}Cr/^{52}Cr$, (e) $^{64}Ni/^{62}Ni$, and (f) $^{113}In/^{115}In$ uncorrected for instrumental mass fractionation factors. The gray bands represent the range of previously published ratios and their uncertainties. The error bars present the combined uncertainties. The literature data and reference sources are listed in Table S4.

0.001535(24) and $^{48}Ca/^{44}Ca$ = 0.091152(175) (the combined standard uncertainties are given in parentheses as a concise notation), with much smaller uncertainties as compared with the previously published ranges of 0.001439−0.001599 and 0.088649−0.092231 for $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$, respectively. The measured $^{50}V/^{51}V$ of D-V-5 is 0.002495(4), which is within the previously published range of 0.002395−0.002509. D-Cr-5 yielded $^{50}Cr/^{52}Cr$ = 0.051902(6), which is also within the previously published range of 0.051768−0.051968. InSn-5 yielded $^{113}In/^{115}In$ = 0.044607(13), which is consistent with the reference ratio 0.04472(19).[29] Therefore, even without correction for differences in interelement mass bias, the derived absolute isotopic ratios for Ca, V, Cr, and In appear to be accurate. Only the measured $^{64}Ni/^{62}Ni$ ratios (~0.2552) deviate from the literature ratio of 0.25465(26), which may be due to the difference in β factors between Ni and Zn.

The relative Ca isotopic compositions are provided in Table S3 and Figure 3. For comparison, we obtained the Ca isotopic composition with and without the bracketing standard. In the case of using a bracketing standard, the normalized Ti isotope ratios of the bracketing standard were used and the precision is much better than that for the results obtained using reference

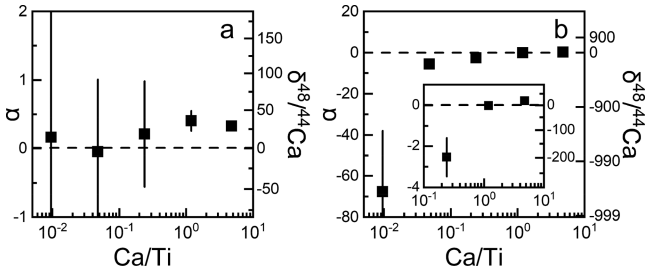

Figure 3. Relative Ca isotopic compositions measured using both ^{46}Ti and ^{48}Ti as the spike. (a) Results obtained using normalized Ti isotope ratios of the bracketing standard as the spike ratios. (b) Results obtained without a bracketing standard but using reference ratios as the spike ratios. The bracketing standards considerably improved the precisions. The absolute Ca isotope composition obtained by double-spiked TIMS is presented as the dashed lines for comparison.

Ti isotope ratios without a bracketing standard. However, even for D-Ca-5 that has the best precision, the measured relative Ca isotopic compositions correspond to large natural fractionation factors (α) of 0.33 ± 0.03, irrespective of whether the bracketing standard was used. This equals a $\delta^{48/44}Ca$ value of 29.4 ± 2.5‰, which is remarkably higher than the TIMS results ($\delta^{48}/^{44}Ca$ = 1.04 ± 0.12‰).

Testing the Self-Consistency of the Isobaric Spike Method Using Ca Isotope Results. First, we checked the validity of the isobaric spike method by comparing the absolute Ca isotopic ratios determined in this study with those reported in the literature, given that Ca isotopes have been extensively studied. Although the ratios that were calculated with the same instrumental mass fractionation factors (β) for Ca and Ti fall within the range of literature ratios, when taking into account analytical uncertainties, the calculated absolute $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios are significantly higher than the accepted reference ratios measured by Russell et al.[16] and several recent Ca isotope studies.[34,40−44] This suggests that the $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios calculated without correction for variable β could be inaccurate. As each of the absolute Ca isotopic ratios was obtained with only one pair of isobars, the absolute $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios were independently obtained. Thus, we can test if the uncorrected ratios are mass-dependently fractionated from the reference ratios and raw measured ratios of the Ca standard. Then differences in the fractionation factors for Ca and Ti are significant. In Figure 4, the uncorrected $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios fall on a fractionation line defined by the reference ratios and raw measured ratios of the Ca standard, and thus the discrepancy between the measured and literature ratios is consistent with the mass fractionation law, which indicates that the isobaric spike method is self-consistent. Therefore, the large "natural" fractionation of the relative Ca isotopic compositions can be accounted for by differences in β factors between Ca and Ti.

Correction for Different Instrumental Mass Fractionation Factors. Albarède et al.[45] reported two linear relationships between the weighted average mass (m) and ion transmission rate (τ) under the same MC-ICP-MS conditions, which were for elements with m < 40 and m > 40. However, no quantitative relationship between m and τ was established because the measured τ has large uncertainties (<20%) and is dependent on analytical conditions.[45] Nevertheless, based on their results, it is reasonable to assume that a linear relationship exists between m and τ, with two parameters

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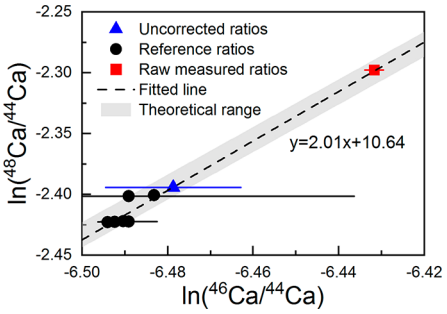

Figure 4. Test of the self-consistency of the Ca isotopic data. The best-fit line $y = 2.01x + 10.64$ (dashed line) to the reference ratios (black circles) and raw measured ratios (red square) of the Ca standard is a mass fractionation line. Using the reference ratios, the theoretical fractionation line was calculated from the exponential mass fractionation law, yielding a common slope of 1.96 and intercepts of 10.28 to 10.30 (gray band), which include the fitted line. The uncorrected ratios (blue triangle) fall on the fitted mass fractionation line, indicating that the results are self-consistent.

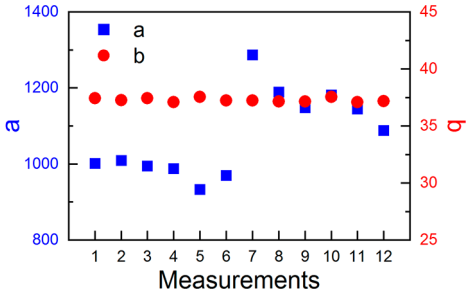

Figure 5. *a* and *b* values calculated using the measured Ca isotope ratios of D-Ca-5. The variation of *a* is significantly larger than that of *b*, which is highlighted by the similar scaling of the ordinates for *a* and *b*.

a and *b* for a certain experimental condition, formularized as follows:

$$m = a\tau + b \tag{7}$$

Albarède et al.[45] showed that different analytical conditions yielded similar correlations between m and τ, suggesting that the intercept b is constant and slope a varies with the conditions. For τ and β, the authors obtained the following:

$$\beta = -0.24 \ln \tau \tag{8}$$

Combining eqs 7 and 8, it follows that

$$\beta = -0.24 \ln(m/a - b/a) \tag{9}$$

Thus, the two parameters can be solved by two sets of β and m. In our study, analyses of different elements were performed under the same conditions in each analytical session and the different elements have a common relationship between m and β (i.e., the same a and b in eq 7). Consequently, for each measurement, parameters a and b can be solved using the reference ratios (Table S5). We calculated a and b based on the $^{48}Ca/^{44}Ca$ data, as there are many recently published ratios that are consistent with each other and have high precision (Table S4). For D-Ca-5, which has the most precise Ca isotope data, the intercept b has an average of 37.28. The variation in b between different analytical sessions is small ($2\sigma = 0.34$), which is consistent with the prediction that b is constant for different analytical conditions.[45] However, the slope a of D-Ca-5 is 1084 ± 222 and varies with analytical conditions (Figure 5). Using $b = 37.28$ and the β obtained from the spike element, the β for the element of interest can be calculated in each measurement. It is then possible for the absolute isotopic ratios to be calculated using specific β factors for Ca, V, Cr, Ni, and In (Figure 6; Table 2). Using this approach, the corrected $^{46}Ca/^{44}Ca$ and $^{64}Ni/^{62}Ni$ ratios are consistent with the literature ratios (Table S4). The relative Ca isotopic composition was corrected to $\delta^{48}/^{44}Ca = 1.2 \pm 2.5‰$, which is consistent with the TIMS result ($\delta^{48}/^{44}Ca = 1.04 \pm 0.12‰$), a dramatic improvement compared to the β-uncorrected $\delta^{48}/^{44}Ca$ value of 29.4 ± 2.5‰ (Figure 3). Only the corrected $^{50}Cr/^{52}Cr$ ratio moderately deviates from the literature data by −0.5‰, which may reflect an artifact from inappropriate mass fractionation law. Therefore, after correcting for different β factors, the isobaric spike method yields absolute and relative isotopic ratios with an accuracy at the per mil level.

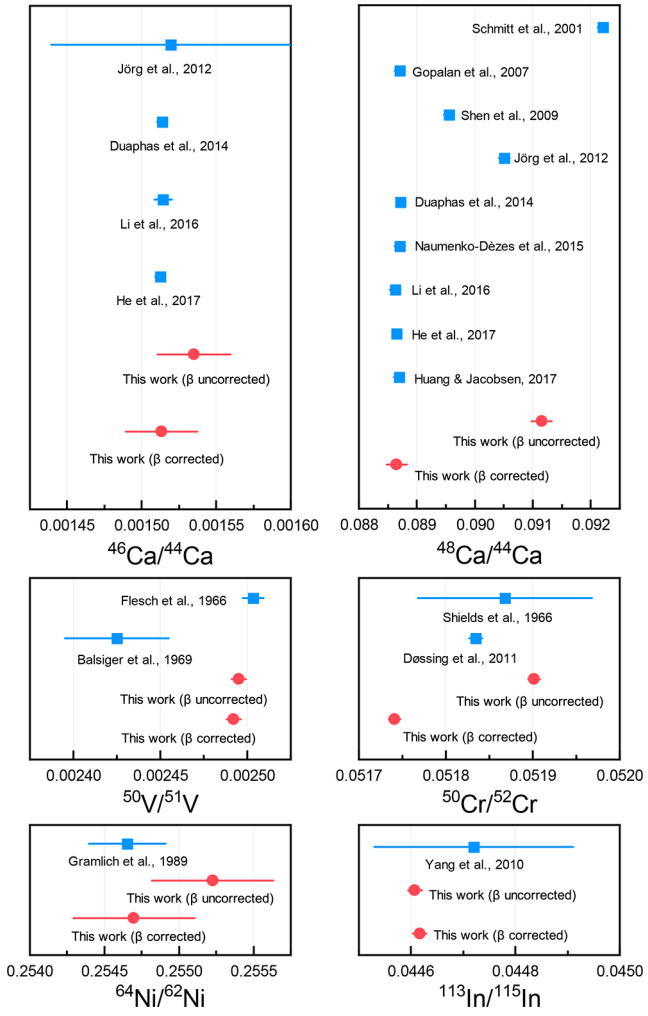

Figure 6. Comparison of published reference Ca, V, and Cr isotopic ratios, our uncorrected ratios, and those corrected for different instrumental mass fractionation factors. The literature data and reference sources are listed in Table S4.

Advantages and Applications of the Isobaric Spike Method. Many of the reference natural isotopic abundances have large uncertainties and variations.[11] For example, $^{46}Ca/^{44}Ca$ and $^{48}Ca/^{44}Ca$ ratios in the literature show percent-level variations (14‰ for $^{46}Ca/^{44}Ca$ and 42‰ for $^{48}Ca/^{44}Ca$; Figure 6), which are much larger than the natural

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Table 2. Summary of Measured Absolute Isotopic Ratios

	β uncorrected ratios	β corrected ratios	2sd	combined uncertainty	range of previously published ratios[a]
$^{46}Ca/^{44}Ca$	0.001535	0.001514	0.000024	0.000024	0.001439−0.001599
$^{48}Ca/^{44}Ca$	0.091152	0.088655	0.000175	0.000175	0.088649−0.092231
$^{50}V/^{51}V$	0.002495	0.002492	0.000004	0.000004	0.002395−0.002509
$^{50}Cr/^{52}Cr$	0.051902	0.051741	0.000004	0.000006	0.051768−0.051968
$^{64}Ni/^{62}Ni$	0.255226	0.254698	0.000032	0.000406	0.254398−0.254910
$^{113}In/^{115}In$	0.044607	0.044617	0.000002	0.000013	0.044530−0.044910

[a]The range of previously published ratios include the reported uncertainties. The detailed literature data are listed in Table S4.

variations of ~6‰.[46] The isobaric spike method is capable of obtaining precise absolute isotopic ratios for elements that have isobaric isotopes with another element. This method is particularly useful in the cases where other methods are not applicable, such as elements with only two or three isotopes. For example, V and In both have only two isotopes, thus their isotope ratios cannot be measured by the traditional double-spike method, and the isobaric isotopes of ^{50}V (^{50}Ti and ^{50}Cr), ^{113}In (^{113}Cd), and ^{115}In (^{115}Sn) hinder the use of the external normalization method. However, the isobaric spike method has considerable potential in measuring the V and In isotopic composition, as mass bias can be corrected by using a Ti (Cr) and Sn (Cd) standard as the spike.

This method is an alternative way to measure ratios of some isotopes that have very low abundances. For example, ^{46}Ca has an extremely low natural abundance, and thus obtaining the precise measurement of $^{46}Ca/^{44}Ca$ is difficult and requires an additional data collection sequence,[16,47] variable amplifiers,[40,47,48] or customized Faraday collectors.[33] However, given that ^{46}Ti has a relatively high natural abundance, the addition of Ti standard makes it possible to measure $^{46}Ca/^{44}Ca$ without adding an expensive synthetic double-spike or using variable amplifiers. Although no systematic optimization of the mixing proportions has been carried out, the isobaric spike method yields isotopic ratios to a precision of the per mil level. Despite the additional uncertainties induced from the isotopic ratios of the spike elements (Table S1), the measured $^{50}V/^{51}V$ and $^{113}In/^{115}In$ still have the highest precision among the published ratios (Table S4; Figure 6), indicating that this isobaric spike method is particularly suitable for such isotopic systems. For Ca, Cr, and Ni, our results are precise enough to be compared with the literature data and could be further improved after optimizing the mixing proportions of sample and spike.

This method also provides a way to cross-calibrate the reference isotopic ratios of different elements that have isobaric isotopes, making the spike calibration of the double-spike method more rigorous. For the traditional double-spike method, a widely used approach to calibrate the spike is by mixtures of the spike and a standard that already has reference isotopic ratios.[5,15,17,20] However, given that the isotopic composition of the spike is derived from the reference ratios, any errors on the reference ratios propagate to the spike composition and ultimately the sample measurements. For example, most Ca isotopic studies use $^{42}Ca/^{44}Ca = 0.31221$[16] as a standard value to internally normalize standard compositions.[16,20,33,41,47,48] However, some other groups measure the absolute Ca isotope ratios independently and have obtained $^{42}Ca/^{44}Ca$ ratios of 0.30592[49] and 0.30898[50] (normalized to SRM 915a), which are significantly lower than 0.31221. These studies also obtained $^{48}Ca/^{44}Ca$ ratios of 0.09221[49] and 0.090505[50], which are higher than the ratios reported elsewhere (~0.0887[16,33,47,48]). For the $^{50}V/^{51}V$ ratio, the literature data were measured in the 1960s and have large uncertainties;[12,13] thus, new measurements are required. In this study, the absolute isotopic ratios of Ca, V, and Cr measured using reference Ti isotope ratios are consistent with published reference ratios, indicating that the isobaric spike method is a robust approach for mutually calibrating these isotope ratios.

Moreover, according to our simultaneous measurements of Ca and Ti under the same analytical conditions, a useful equation that quantitatively describes the relationship between m and β for different elements can be presented as follows:

$$\beta = -0.24 \ln(m/a - 37.28/a) \quad (10)$$

This equation makes it possible to calculate β for an element by measuring the isotope ratio of another element. Although different b can be derived using different isotopic systems, the consistency of the results with the literature data demonstrates the validity of mass fractionation factor correction using b = 37.28. We note that further study is needed to better constrain the b value in the eq 10 under different conditions, but it appears b = 37.28 is an optimized parameter for the systems investigated in this study. This relationship is particularly useful for the correction of isobaric interferences. Currently, accurate correction is hindered by using a β factor for the interfering element that is the same as the β factor of the element of interest.[3,9] Although several approaches have been proposed to deal with this issue, such as an arbitrary instrumental mass fractionation factor[4] or empirical corrections,[3,9] these methods do not have a solid theoretical basis. Other studies have undertaken additional measurements to obtain the β factors of the interfering elements,[6,7] but the variations in analytical conditions mean it is not ideal to use fixed β factors. In this study, we present a new method to correct for the difference in β factors on the basis of eq 10. By measuring the isotopes with no isobaric interferences of the element of interest, the β factor for this element can be obtained. Then, using eq 10, the β factor of the interfering elements can be calculated, allowing for a more accurate correction for interfering isotopes, independent of the concentration of the interfering elements. This is particularly useful for isotopic measurements with imperfect chemical purification procedures or laser ablation analyses.

CONCLUSIONS

The isobaric spike method is a combination of the traditional double-spike and external normalization methods, which provides rigorous mass bias corrections and precise measurement of β-uncorrected absolute isotopic ratios by MC-ICP-MS. By adding a spike element, the absolute isotopic ratio of the element of interest can be obtained. The high ICP

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ionization efficiency allows simultaneous measurement of the element of interest and the spike element. We improved the algorithm for the traditional double-spike inversion to correct for the slight differences in the masses of the isobaric isotopes and differences in the fractionation factors of the element of interest and the spike element. This method was applied to Ca, V, Cr, Ni, and In isotopes. The absolute isotopic ratios of Ca, V, Cr, Ni, and In, as well as the relative Ca isotopic composition, were obtained. The measurements of the sample−spike mixtures were bracketed by measurements of pure solutions of the spike element, and the normalized isotope ratio of the bracketing standards significantly enhanced the precision. Through simultaneous measurement of Ca and Ti isotopes, we developed a quantitative relationship between mass and the instrumental mass fractionation factors of different elements. After correction for different instrumental mass fractionation factors, the resultant absolute isotope ratios are consistent with published reference values with accuracy at the per mil level. This method has considerable potential for measuring the isotopic composition of elements that have less than four isotopes, without the need for a synthetic double-spike and spike calibration. It also provides a method to cross-calibrate the absolute isotopic ratios of elements that have isobaric isotopes. In addition, the determination of precise absolute isotopic ratios and relationship between mass and instrumental mass fractionation factors can improve isobaric interference corrections. This is particularly important for laser ablation MC-ICP-MS studies. However, the method has not yet been optimized to minimize uncertainties, and further research is needed to improve the method by optimizing the sample−spike mixing proportions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.9b04160.

Tables of absolute isotopic ratios, relative Ca isotopic compositions, comparisons of measured absolute isotopic ratios with ratios in literature, and parameters for instrumental mass fractionation factor correction (PDF)

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Notes

The authors declare no competing financial interest.

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