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Double-spike inversion for three-isotope systems



Christopher D. Coath*, Tim Elliott, Remco C. Hin

School of Earth Sciences, University of Bristol, Queens Road, Bristol BS8 1RJ, UK

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ABSTRACT

Double spiking is conventionally used to make accurate determinations of natural mass-dependent isotopic fractionations for elements with four or more stable isotopes. Here we document a methodology which extends the effective application of double spiking to three isotope systems. This approach requires making a mixture with isotope ratios that lie on a 'critical curve' where the sample – double-spike mixing line and the tangent to the instrumental mass-bias curve are coincident. Inversion of the mixing equations for such a mixture leads to a solution for the sample fractionation which is independent (to first order) of the uncertainty in the instrumental mass-bias and, hence, independent of any mass-dependent artefacts in the measurement such as those produced by residual matrix not completely removed by prior chemical purification. In practice, mixtures can be made which yield an accuracy conservatively estimated to be $\sim 0.005\%$ /amu. The precision of the method is explored as a function of double-spike composition for Mg, Si and K isotope systems. We show that for Mg and Si measurement precision is not compromised by the compositions of viable critical mixtures nor by uncertainty magnification during inversion of the equations. Thus, double spiking provides a valuable means to obtain robust, high precision isotopic measurements of Mg and Si. For K, however, the low abundance of ^{40}K in the optimal critical mixture places a significant practical limitation on the application of double spiking to analyses of this element.

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1. Introduction

Multi-collector inductively coupled plasma mass-spectrometry (MC-ICPMS) has made more accessible the measurement of a wide range of isotopic systems and documentation of their variability. Two main approaches have been used for measuring mass-dependent isotopic fractionations by MC-ICPMS: double-spiking, as has previously been used for some elements amenable to thermal ionisation mass-spectrometry, and sample-standard bracketing, similar to the methodology traditionally used in gas source mass-spectrometers.

The sample – standard bracketing approach relies on 'external normalisation' by reference to standards measured in as similar a manner to the samples as possible, to correct the instrumental mass-bias of the sample measurement. This approach requires the assumption that samples and standards behave identically during analysis. Unpredictable deviations from this idealised situation add unknown uncertainty to external normalisation methodologies. The procedure of double-spiking involves the addition of a mixture of two calibrated, enriched isotopic 'spikes' to an unknown sample. This allows accurate correction of instrumental mass-bias by 'internal

normalisation' to the reference isotope ratio provided by the added double-spike (e.g. Dodson, 1963). Since the instrumental mass-bias is internally normalised, the double-spike method does not suffer the problems of sample – standard bracketing, offering a robust solution to isotope ratio measurement. Initially, double-spiking was most commonly applied to radiogenic isotope measurements by thermal ionisation mass-spectrometry (e.g. Krogh and Hurley, 1968; Compston and Oversby, 1969), but recently has seen more widespread application in measurements of mass-dependent isotopic variability using multi-collector plasma mass-spectrometry (e.g. Johnson et al., 2004; Rudge et al., 2009).

The traditional double-spike method of isotopic characterisation requires the measurement of four isotopes of the element of interest, i.e. three independent ratios (see Dodson, 1963). Inversion of the three mixing equations, one for each independent ratio, yields solutions for the three unknowns: the sample – double-spike mixing proportion, the instrumental mass-bias and the isotopic fractionation of the sample relative to a reference material. Clearly, for three-isotope systems, a unique solution for the unknowns is not possible as there are only two mixing equations. This problem seldom arises as there are rather few elements with three stable isotopes (Mg, Si, K, O, Ne, Ar) and only Mg, Si and K would likely be measured by double-spiking. Nonetheless, the elements Mg and Si represent $\sim 30\%$ of the Earth and K is a major heat-producing element. Although

* Corresponding author.

E-mail address: chris.coath@bristol.ac.uk (C. Coath).

small in number, the geological significance of these three-isotope elements is large.

A need for improved accuracy in the measurement of Mg and Si isotopic compositions has recently become evident, given the poorly understood scatter in published results of the same and similar samples (see discussions in [Teng et al., 2015](#) for Mg and [Fitoussi et al., 2009](#); [Armytage et al., 2011](#) for Si). These previous measurements of Mg and Si isotope ratios have used sample-standard bracketing techniques, which are inevitably prone to possible biases from residual matrix in sample relative to standard. Removing the influence of potentially variable instrumental mass-bias in the isotopic measurements of these elements would, therefore, be an important step in making these analyses more robust. To this end, we have explored a special case in which double-spiking can be used for elements with only three isotopes, following an ingenious method first reported by [Hofmann \(1971\)](#) for the accurate calibration of Sr spikes. Here we develop the theory of this ‘critical mixture double spiking’ more generally and discuss its specific application to Mg, Si and K isotopic measurements.

2. Previous work

The method described by [Hofmann \(1971\)](#) makes use of the fact that, ultimately, it is only the natural isotopic fractionation (hereafter, simply ‘fractionation’) of the sample that is of interest. The method relies on the making of a ‘critical mixture’ of sample and double-spike for which the other two unknowns (the instrumental mass-bias and mixing proportion) lose their individual identities and degenerate into a single composite variable. We shall describe the Hofmann method using nomenclature more in keeping with modern treatments of the traditional double-spike method, in particular [Rudge et al. \(2009\)](#). This treatment, therefore, differs markedly from that of Hofmann although the principles remain the same.

The degeneracy of the mass-bias and mixing proportion occurs when the effect of correcting the instrumental mass-bias on the measured isotope ratios of the mixture has a trajectory in three-isotope space, coincident with the mixing line between sample and double-spike. This coincidence is possible only for a linear mass-bias law, which we can write,

$$M_i = m_i(1 - \beta\Delta_i), \quad (1)$$

(see [Table 1](#) for the definition of most symbols used herein), where Δ_i is a constant, usually the mass difference between isotope i and the isotope used as the denominator for the ratios. For such a law the trajectory of the mass-bias in three-isotope ratio space is a straight line with slope $m_2\Delta_2/(m_1\Delta_1)$. Hence, the critical mixture must satisfy,

$$m_2\Delta_2/(m_1\Delta_1) = Q_2/Q_1, \quad (2)$$

since Q_2/Q_1 is the slope of the mixing line. To show how this leads to degeneracy of the mass-bias parameter, β , and the mixing proportion we proceed by writing down the mixing equation,

$$\begin{aligned} M_i &= \lambda T_i + (1 - \lambda)N_i \\ &= \lambda Q_i + N_i, \end{aligned} \quad (3)$$

and substituting for M_i from Eq. (1), thus,

$$\lambda Q_1 + N_1 = m_1(1 - \beta\Delta_1) \quad (4)$$

$$\lambda Q_2 + N_2 = m_2(1 - \beta\Delta_2). \quad (5)$$

Table 1

Main symbols. Vectors and matrices are in bold throughout. Subscripts $i, 1$ or 2 , refer to isotope abundance ratios of isotope i relative to the denominator isotope, the latter being the same for all ratios.

$\mathbf{N} = (N_1, N_2)$	Isotope ratios in sample.
$\mathbf{T} = (T_1, T_2)$	Isotope ratios in double-spike.
$\mathbf{M} = (M_1, M_2)$	Isotope ratios in sample-double-spike mixture.
$\mathbf{Q} = (Q_1, Q_2)$	$\mathbf{T} - \mathbf{N}$.
$\mathbf{n} = (n_1, n_2)$	Reference isotope ratios.
$\mathbf{m} = (m_1, m_2)$	Measured isotope ratios in sample – double-spike mixture.
P_i	Natural logarithm of the ratio of the mass of isotope i to that of the denominator isotope.
β	Instrumental mass-bias parameter.
α	Sample mass-fractionation parameter relative to reference.
λ	Sample – double-spike mixing parameter.
p	Molar proportion of double-spike in mixture.
D	Ratio of denominator isotope relative abundances in double-spike to sample.

Eliminating m_1 from Eq. (4) using Eq. (2) gives,

$$\begin{aligned} \Delta_1 Q_2(\lambda Q_1 + N_1) &= m_2 \Delta_2 Q_1(1 - \beta\Delta_1) \\ \Delta_1 Q_1(\lambda Q_2 + m_2 \Delta_2 \beta) + \Delta_1 Q_2 N_1 &= m_2 \Delta_2 Q_1. \end{aligned} \quad (6)$$

Multiplying Eq. (5) by $\Delta_1 Q_1$ and rearranging gives,

$$\Delta_1 Q_1(\lambda Q_2 + m_2 \beta \Delta_2) + \Delta_1 Q_1 N_2 = m_2 \Delta_1 Q_1. \quad (7)$$

Comparing Eqs. (6) and (7) shows that the term $\Delta_1 Q_1(\lambda Q_2 + m_2 \beta \Delta_2)$ is common to both and is the composite unknown referred to above. Subtracting one equation from the other eliminates both λ and β to give,

$$\Delta_1(Q_2 N_1 - Q_1 N_2) = m_2 Q_1(\Delta_2 - \Delta_1). \quad (8)$$

Finally, all that is required to find the sample fractionation is to choose a fractionation law describing the N_i in terms of a reference ratio and a fractionation parameter, e.g. the linear law: $N_i = n_i(1 - \alpha\Delta_i)$, substitute into Eq. (8) and solve for α .

The method outlined above prompts a number of questions which are addressed in the following sections. These are as follows: (i) how can a more realistic mass-bias law be used, such as the exponential (kinetic) law ([Russell et al., 1978](#)); (ii) how do the measurement uncertainties propagate, i.e. what precision can be expected; (iii) what are the consequences for accuracy for failing to achieve a perfect critical mixture; (iv) how to make a critical mixture; (v) how best to calibrate the double-spike isotopic abundances and (vi) how is the accuracy dependent on the double-spike calibration? In the following sections we will address all of these questions.

3. Critical mixtures for the three-isotope double-spike method and the exponential mass-bias law

Assuming exponential mass-bias and sample fractionation laws, the mixing Eq. (3) becomes (see also [Rudge et al., 2009](#)),

$$\lambda Q_i + n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0, \quad (9)$$

where

$$N_i = n_i e^{-\alpha P_i}$$

and

$$M_i = m_i e^{-\beta P_i}. \quad (10)$$

The constant P_i is the natural logarithm of the ratio of the mass of isotope i to that of the denominator isotope.

In contrast to the case of a linear mass-bias law, a non-linear law cannot strictly be degenerate with respect to mixing proportion. We proceed by assuming we have some independent way of determining the mass-bias, β , which then allows us, in principle, to solve Eq. (9) for α and λ numerically. This assumption may appear to be cheating since, if we knew β , we would be able to calculate the sample's isotopic composition rather easily from measurements of un-spiked solutions by sample – standard bracketing. However, as we shall show in the sections that follow, by means of a critical mixture, defined as that which makes $d\alpha/d\beta = 0$, the accuracy of β has only a very small contribution to the accuracy with which we may determine α . This contrasts the case of the sample-standard bracketing method, where any inaccuracy in β propagates directly into inaccuracy in α .

Note that β is an input to the equations, an empirically determined variable, rather than a solution of the equations as is the case with the traditional four-isotope double-spike method.

Many of the mathematical methods used here are similar to those found in Albalat et al. (2012) and can be found in standard texts on calculus, such as Wrede and Spiegel (2010). Eq. (9) can be written,

$$F_i = \lambda T_i + (1 - \lambda)n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0. \quad (11)$$

Appendix A derives the differentials of λ and α with respect to β from Eq. (11) yielding,

$$\frac{d\alpha}{d\beta} = \frac{P_1 M_1 Q_2 - P_2 M_2 Q_1}{(1 - \lambda)(P_1 N_1 Q_2 - P_2 N_2 Q_1)}.$$

Solving for $d\alpha/d\beta = 0$ shows that the critical mixture, $\mathbf{M}^c = (M_1^c, M_2^c)$, must satisfy,

$$\frac{P_2 M_2^c}{P_1 M_1^c} = \frac{Q_2}{Q_1}, \quad (12)$$

the left-hand side being the slope of the tangent to the mass-bias curve at (M_1^c, M_2^c) and the right-hand side the slope of the sample – double-spike mixing line. Note the similarity with the critical mixture condition in the case of the linear mass-bias law: we have simply replaced the slope of the mass-bias line with the slope of the tangent to the mass-bias curve.

Eq. (12) enables us to define a locus of critical mixtures in 3-isotope space. Note that, as \mathbf{N} , \mathbf{M}^c and \mathbf{T} all lie on a line, we can replace Q_2/Q_1 with $(M_2^c - N_2)/(M_1^c - N_1)$ and Eq. (12) becomes,

$$P_2 M_2^c (M_1^c - N_1) = P_1 M_1^c (M_2^c - N_2)$$

or

$$\frac{N_1}{M_1^c} = 1 - \frac{P_1}{P_2} \left(1 - \frac{N_2}{M_2^c}\right). \quad (13)$$

Thus, the mixture is critical for mixture ratios, (M_1^c, M_2^c) , that lie on the curve defined by Eq. (13), which is shown in Fig. 1 for the case of magnesium isotopes. The critical mixture curve passes through (N_1, N_2) and asymptotically approaches $M_1^c = N_1/(1 - P_1/P_2)$ as $M_2^c \rightarrow \infty$ and $M_2^c = N_2/(1 - P_2/P_1)$ as $M_1^c \rightarrow \infty$. Note that both asymptotes are positive if we choose the middle-mass isotope for the denominator as this ensures that P_1 and P_2 have opposite signs and that the branch of the curve which is of interest lies entirely in the positive quadrant, simplifying the graphical presentation. The other branch, of no physical significance, is not shown

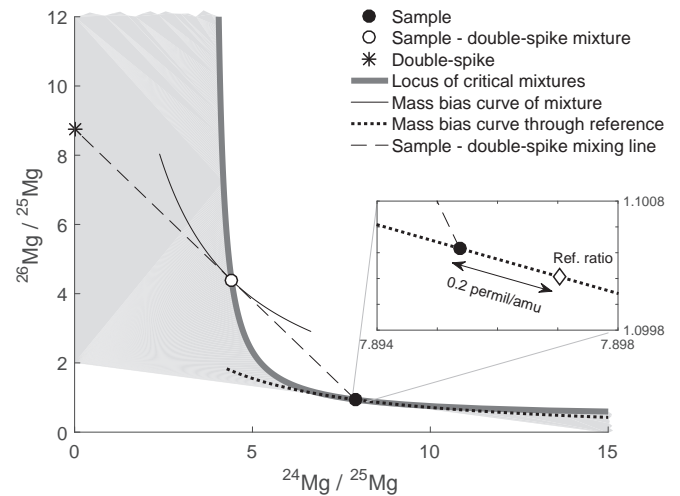


Fig. 1. Critical mixing in the case of magnesium isotopes. Note that the mixing line (dashed) is tangent to the exponential-law mass-bias curve (finer black solid curve) which, for clarity, is plotted over a range far greater than that found in practice. The grey area indicates viable double-spike compositions, i.e. those with sample – double-spike mixing lines intersecting the critical curve. A double-spike composition lying outside this area could not form a critical mixture with the sample. Inset shows a sample composition at the intersection of the mixing line and the instrumental mass-bias curve through the reference ratio (dotted). In this example, the isotopic composition of the sample is 0.2‰ per amu lighter than the reference. For clarity, the critical curve is not shown in the inset as it would appear indistinguishable from the mass-bias curve.

on the figure. Choosing the middle-mass isotope as the denominator, although unconventional in the geochemical community, has the added advantage that, because any viable double-spike must have non-zero abundance of this isotope (see Section 4), the double-spike composition can always be plotted in this space. Furthermore, the optimal double-spike composition has zero abundance of the light isotope (see Section 4) so following the conventional practice of using this isotope as the denominator would mean that the optimal double-spike composition could not be plotted and that some of the equations in the following sections would have to be re-cast to avoid T being infinite.

From Eq. (13) we appear to have one degree of freedom, e.g. a free choice of M_2^c , but, once the double-spike composition is chosen, the mixture must lie on the sample – double-spike mixing line providing another constraint and hence a unique solution for the critical mixture ratios (the open circle in Fig. 1). Substituting the mixing Eq. (3) into Eq. (13) yields the mixing parameter required for critical mixing, λ_c , as a function of the double-spike composition,

$$\lambda_c = \frac{P_1 N_1 Q_2 - P_2 N_2 Q_1}{Q_1 Q_2 (P_2 - P_1)}. \quad (14)$$

Note that the mixing parameter can be transformed to the molar mixture proportion of double-spike in the mixture, p , using,

$$\frac{1-p}{p} = \left(\frac{1-\lambda}{\lambda}\right) D, \quad (15)$$

where,

$$D = \frac{1 + \sum_i N_i}{1 + \sum_i T_i}, \quad (16)$$

the ratio of the relative isotopic abundances of the denominator isotope in the double-spike over that in the sample. See Rudge et al. (2009).

Inversion of Eq. (9) to yield the sample fractionation, α , is equivalent to determining the point, on a 3-isotope plot, found by drawing a line from the double-spike composition to the mass-bias corrected mixture measurement and extrapolating to intersect with the mass-bias curve passing through the reference ratio as shown in the inset of Fig. 1. Thus, the graphical visualisation of the inversion is similar to the four-isotope case, e.g. Fig. 2 in Siebert et al. (2001).

4. Precision

In this section we will consider the propagation of the analytical uncertainties on the measurements of a sample – double-spike critical mixture to the uncertainty in the sample fractionation, σ_α . We will leave to the following section considering the effect of the uncertainty of the instrumental fractionation and deviations of the mixture from critical.

The equation for the uncertainty propagation of the uncertainties in the measured ratios, σ_{m_1} and σ_{m_2} , and their covariance, $\sigma_{m_1 m_2}$, into σ_α is,

$$\sigma_\alpha^2 = \left(\frac{\partial \alpha}{\partial m_1} \right)^2 \sigma_{m_1}^2 + \left(\frac{\partial \alpha}{\partial m_2} \right)^2 \sigma_{m_2}^2 + 2 \left(\frac{\partial \alpha}{\partial m_1} \right) \left(\frac{\partial \alpha}{\partial m_2} \right) \sigma_{m_1 m_2}.$$

Substituting the partial differentials from Eqs. (B.3) and (B.4),

$$\sigma_\alpha^2 = J^{-2} \left(Q_2^2 e^{-2\beta P_1} \sigma_{m_1}^2 + Q_1^2 e^{-2\beta P_2} \sigma_{m_2}^2 - 2Q_1 Q_2 e^{-\beta(P_1 + P_2)} \sigma_{m_1 m_2} \right) \quad (17)$$

where J is given by Eq. (A.9).

The equation to transform the uncertainty of the fractionation parameter, σ_α , to the more familiar δ -value uncertainty, σ_δ is,

$$\sigma_\delta = \sigma_\alpha P_{h/l} e^{-\alpha P_{h/l}}, \quad (18)$$

where $P_{h/l}$ is the natural logarithm of the mass ratio of ${}^h X$ to ${}^l X$ where X is Mg, Si or K and h and l refer to the heaviest and lightest isotopes respectively.

To explore the behaviour of the δ -value uncertainty as a function of double-spike composition we adopt an error model for the measured critical mixture following Rudge et al. (2009), i.e. Poisson counting statistics and Johnson-Nyquist noise independently on each intensity and propagated to the ratios. Values of various constants relating to the measurement conditions in the error model are amplifier temperature 300 K, amplifier feedback resistor $10^{11} \Omega$, signal integration time 80 s, and total measured ion beam intensity 30 V (= 300 pA). We put $\alpha = 0$ and $\beta = 0$, as these make little practical difference if the fractionation and instrumental mass-bias are small. Combining Eqs. (17) and (18) the expression for the uncertainty now becomes,

$$\sigma_\delta^2 = P_{h/l}^2 J^{-2} \left(Q_2^2 \sigma_{m_1}^2 + Q_1^2 \sigma_{m_2}^2 - 2Q_1 Q_2 \sigma_{m_1 m_2} \right). \quad (19)$$

Mixtures are assumed to be critical, hence $M_i = \lambda_c Q_i + N_i$ with λ_c given in terms of the double-spike composition by Eq. (14) and J given by Eq. (A.9) with $\lambda = \lambda_c$.

Figs. 2–4 show contour plots of the uncertainty, σ_δ (in ‰), of $\delta^{26}\text{Mg}/^{24}\text{Mg}$, $\delta^{30}\text{Si}/^{28}\text{Si}$ and $\delta^{41}\text{K}/^{39}\text{K}$ respectively as a function of the composition of the double-spike on a 3-isotope ternary plot. The plots show that there are two local minima: one along the mixing line between the pure middle-mass and pure low-mass isotopes and another on the mixing line between the pure middle-mass and pure high-mass isotopes and that the lowest uncertainty, i.e. the global minimum, corresponds to a high-mass – middle-mass double-spike. These minima are shown more clearly in Figs. 5–7 which

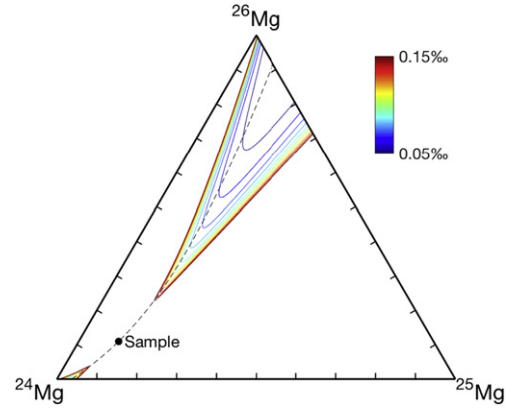


Fig. 2. Ternary plot for magnesium isotopes showing contour lines of constant analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the composition of the double-spike. Contours are the uncertainty in $\delta^{26}\text{Mg}/^{24}\text{Mg}$ (1σ) from 0.05‰ (dark blue) to 0.15‰ in intervals of 0.01‰. Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used. Dashed line indicates double-spike compositions for which equi-molar mixtures with the sample are critical.

plot the uncertainty along these mixing lines. Table 2 gives details of optimised double-spike mixtures, corresponding to the global minima, and the resulting precisions. Note that, for these and all figures and tables that follow, the reference ratios used are as follows: (${}^{25}\text{Mg}/^{24}\text{Mg}$, ${}^{26}\text{Mg}/^{24}\text{Mg}$) = (0.12663, 0.13932) (Catanzaro et al., 1966), (${}^{29}\text{Si}/^{28}\text{Si}$, ${}^{30}\text{Si}/^{28}\text{Si}$) = $(5.07446, 3.41465) \times 10^{-2}$ (Ding et al., 2005), and (${}^{39}\text{K}/^{41}\text{K}$, ${}^{40}\text{K}/^{41}\text{K}$) = (13.8566, 0.0017343) (Garner et al., 1975).

5. Accuracy

For an idealised model of the measurement, i.e. no instrumental artefacts other than mass-bias obeying the assumed law, the traditional method of double-spiking in four-isotope systems does not exhibit any inaccuracy, only uncertainty arising from the stochastic nature of the ion arrivals and thermal effects in the Faraday

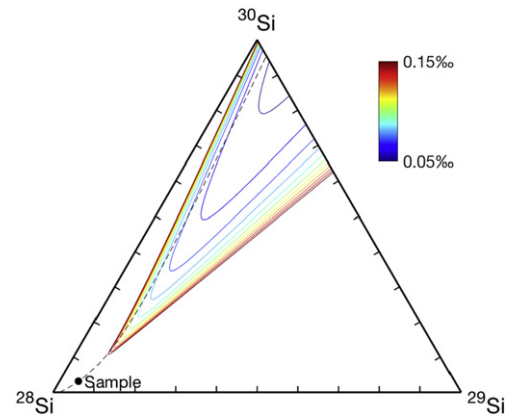


Fig. 3. Ternary plot for silicon isotopes showing contour lines of constant analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the composition of the double-spike. Contours are the uncertainty in $\delta^{30}\text{Si}/^{28}\text{Si}$ (1σ) from 0.05‰ (dark blue) to 0.15‰ in intervals of 0.01‰. Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used. Dashed line indicates double-spike compositions for which equi-molar mixtures with the sample are critical.

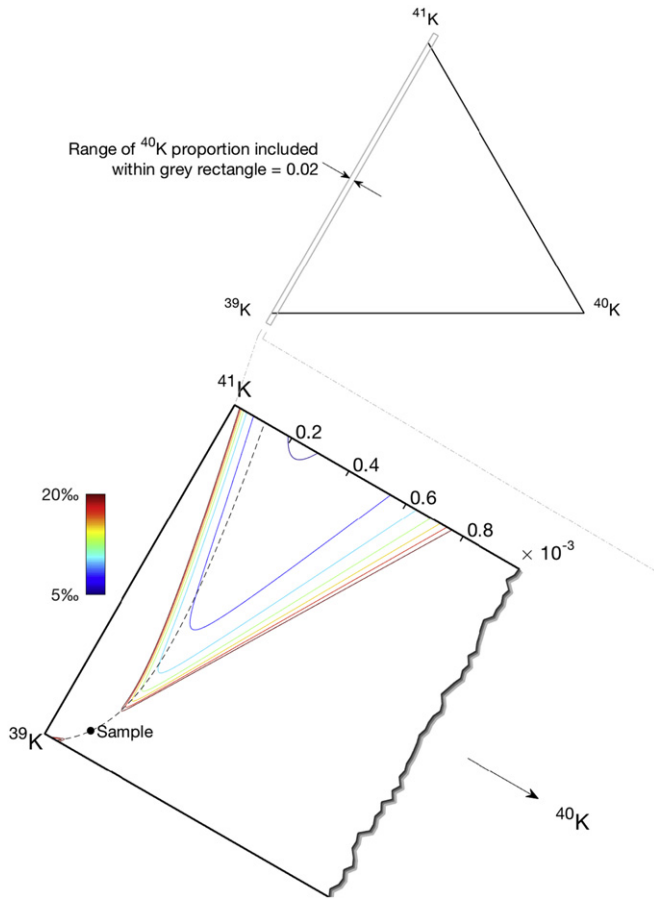


Fig. 4. Ternary plot for potassium isotopes showing contour lines of constant analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the composition of the double-spike. The region near the ^{39}K - ^{41}K tie-line has been expanded, the ^{40}K end-member lies off the plot as indicated by the arrow and the scale shows the ^{40}K abundance. Contours are the uncertainty in $\delta^{41}\text{K}/^{39}\text{K}$ (1σ) from 5‰ (dark blue) to 20‰ in intervals of 2.5‰. Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used. Dashed line indicates double-spike compositions for which equi-molar mixtures with the sample are critical.

cup amplifier electronics. The same is not true for three-isotope double-spiking, due to the reliance on making a critical mixture and on the estimation of instrumental mass-bias. The issue of accuracy discussed in this section, therefore, has no analogue in traditional double-spiking.

If the instrumental mass-bias were accurately estimated the measurement would not suffer any inaccuracy. Similarly, if the mixture were mixed to be accurately critical the result would also be accurate, to first order in terms of the mass-bias inaccuracy. However, as we will show, the product of the inaccuracies in the mass-bias and mixture *do* result in an inaccurate result and it is this product term that is likely to dominate in practice. We estimate the magnitude of the inaccuracy in a worst-case sense by taking upper limits of the inaccuracies in mass-bias (e.g. due to unknown matrix effects) and mixing and assume that they are perfectly correlated, i.e. the maximum inaccuracy in both apply simultaneously to a measurement. Therefore, we do not need to concern ourselves with propagating these inaccuracies as if they were random uncertainties.

The measurement uncertainties on the mixture ratios will be ignored here as these were considered in the previous section.

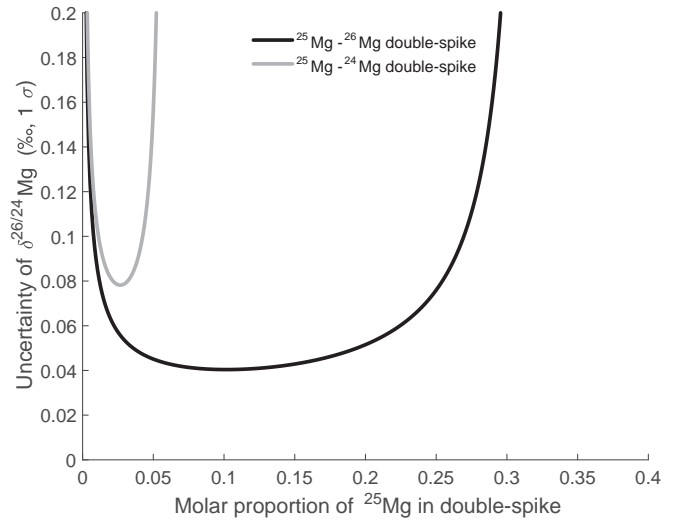


Fig. 5. Analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the proportion of ^{25}Mg in a ^{25}Mg - ^{26}Mg double-spike (black curve) and ^{25}Mg - ^{24}Mg double-spike (grey curve). Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used.

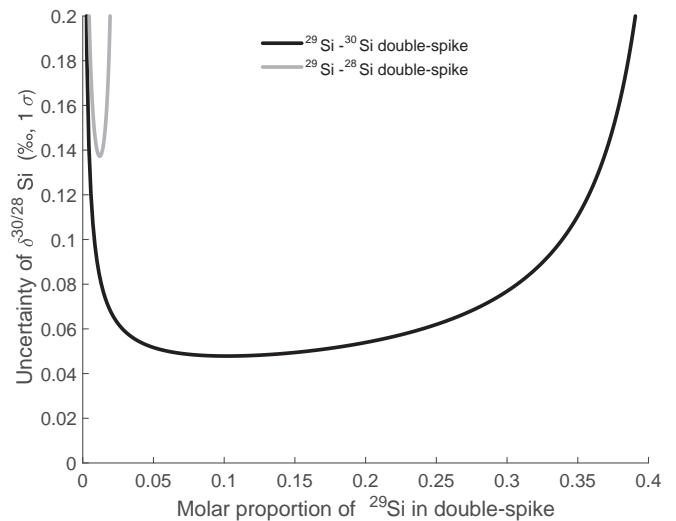


Fig. 6. Analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the proportion of ^{29}Si in a ^{29}Si - ^{30}Si double-spike (black curve) and ^{29}Si - ^{28}Si double-spike (grey curve). Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used.

Let β_0 be the true instrumental mass-bias and $\delta\beta = \beta - \beta_0$. Let λ' be the true mixing parameter to distinguish it from λ , the solution of Eq. (9).¹ Let $\delta\lambda' = \lambda' - \lambda_c$, the deviation of the mixing parameter from that corresponding to a critical mixture. Expanding α as a Taylor series about the point (β_0, λ_c) ,

$$\alpha(\beta, \lambda') = \alpha_0 + \frac{\partial\alpha}{\partial\beta} \delta\beta + \frac{\partial\alpha}{\partial\lambda'} \delta\lambda' + \frac{\partial^2\alpha}{\partial\beta\partial\lambda'} \delta\beta \delta\lambda' + \frac{1}{2} \frac{\partial^2\alpha}{\partial\beta^2} \delta\beta^2, \quad (20)$$

¹ In general, $\lambda = \lambda'$ only when $\beta = \beta_0$, i.e. when the mass-bias estimate is accurate.

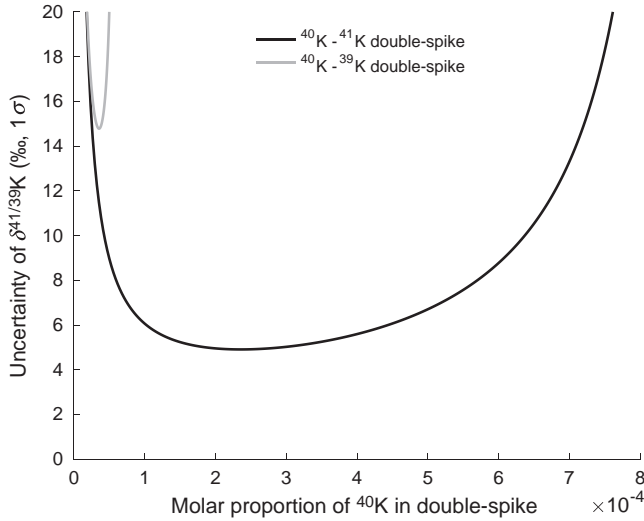


Fig. 7. Analytical uncertainty in isotopic fractionation calculated from measurements made on a critical mixture of sample and double-spike as a function of the proportion of ^{40}K in a ^{40}K - ^{41}K double-spike (black curve) and ^{40}K - ^{39}K double-spike (grey curve). Uncertainties are propagated from those on the measured mixture composition; see main text for details of the model used.

the partial differentials being evaluated at $(\beta, \lambda') = (\beta_0, \lambda_c)$ and where $\alpha_0 = \alpha(\beta_0, \lambda_c)$. Expressions for the partial differentials are derived in Appendix C and, substituting these into Eq. (20), yield,

$$\alpha(\beta, \lambda') = \alpha_0 - \frac{\delta\beta\delta\lambda'}{\lambda_c(1-\lambda_c)} + \left(\frac{P_2M_2^cQ_1(P_2-P_1)}{2J_c} \right) \delta\beta^2. \quad (21)$$

Note that the expression for $\partial\alpha/\partial\lambda'$, Eq. (C.4), has a numerator which is not a function of λ' and evaluates to zero at $\beta = \beta_0$. Therefore, all higher-order differentials with respect to λ' will also evaluate to zero and the coefficients of $\delta\lambda'^2, \delta\lambda'^3, \dots$ etc. in the Taylor expansion will be zero. The truncation error of Eq. (21) is, therefore, $O(\delta\beta^2\delta\lambda' + \delta\beta\delta\lambda'^2 + \delta\beta^3)$.

We can substitute λ' with the true molar mixing proportion, p' , in Eq. (21) using Eq. (C.9) to give,

$$\alpha(\beta, p') = \alpha_0 - \frac{\delta\beta\delta p'}{p_c(1-p_c)} + \left(\frac{P_2M_2^cQ_1(P_2-P_1)}{2J_c} \right) \delta\beta^2, \quad (22)$$

where p_c is the critical molar proportion of double-spike in the mixture.

Table 2

Double-spike compositions optimised for precision and accuracy for Mg, Si and K isotope systems. The critical molar mixing proportion of double-spike in the mixture, p_c , is shown for the case of a precision-optimised double-spike and is equal to 0.5 in case of accuracy-optimised (see main text).

	Optimised for precision				Optimised for accuracy	
	Double-spike comp. ^a	p_c	Precision ^b	Accuracy ^c $\delta\beta\delta p'$	Double-spike comp. ^a	Precision
Mg	0.102	0.438	0.0404‰	0.010‰	0.084	0.0408‰
Si	0.102	0.288	0.0478‰	0.012‰	0.045	0.0527‰
K	0.000241	0.266	4.91‰	0.013‰	0.000106	5.92‰

^a Proportion of middle-mass isotope, ^{25}Mg , ^{29}Si or ^{40}K , in the double-spike, the balance being provided by the heaviest mass isotope, ^{26}Mg , ^{30}Si or ^{41}K .

^b 1σ relative uncertainty in the fractionation between the heaviest and lightest isotopes, see Section 4 for error model.

^c Contribution from term in $\delta\beta\delta p'$ to the accuracy on the basis of a 0.5‰ inaccuracy in mass-bias and a 0.5% deviation of the sample – double-spike molar proportion from the critical mixture. The $\delta\beta\delta p'$ term contributes 0.01‰ in the case of the accuracy-optimised double-spike. The contribution to the accuracies from the term in $\delta\beta^2$ in Eq. (22) are (in ppm) 0.14, 0.14 and 0.15 for Mg, Si and K respectively for precision-optimised double-spike.

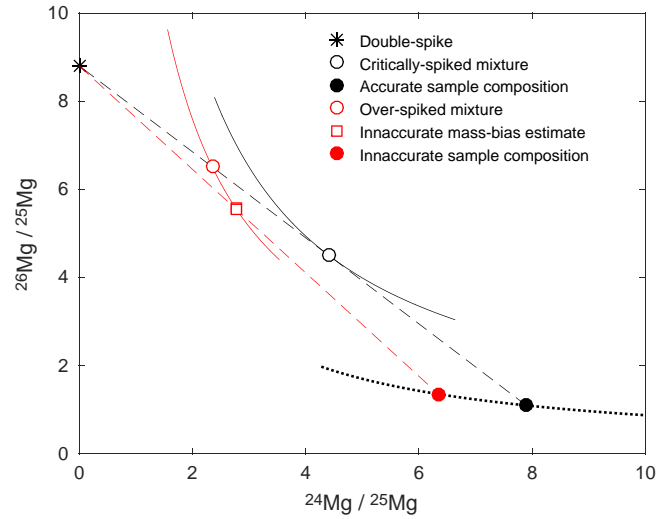


Fig. 8. Graphical demonstration of how the combination of non-critical spiking and poor mass-bias estimation leads to an inaccurate measurement of sample composition in the case of Mg isotopes. An over-spiked sample – double-spike mixture (open red circle) is analysed and ‘corrected’ for instrumental mass-bias. However, the correction is inaccurate: the open red square shows the apparent composition after applying the mass-bias correction. Note that the square lies far from the mixing line between double-spike and sample (black dashed line) because the mass-bias curve (solid red line) is not tangential to the mixing line. Drawing the red dashed line from the double-spike composition through the square and extrapolating to the intersection with the natural fractionation line (black dotted) gives a sample composition (solid red circle) which is isotopically heavier than the true value (solid black circle).

The coefficient of $\delta\beta\delta p'$ in Eq. (22) has a minimum absolute value of 4 at $p_c = 0.5$, i.e. an equi-molar mixture of sample and double-spike. It is a remarkably simple result that, regardless of the isotope system or measurement conditions, the accuracy cannot be better than $4\delta\beta\delta p'$. For example, if we think that the mass-bias estimate is accurate to 0.5‰ (for a given isotope ratio) and that the mixture deviates from critical by no more than 0.5% (by molar proportion) then the accuracy of the calculated mass-fractionation of the sample is limited to $4 \times 0.5\text{‰} \times 0.005 = 0.01\text{‰}$ (for the same isotope ratio). Fig. 8 shows graphically how inaccuracy results from the combination of non-critical mixing and poor mass-bias estimation.

Not shown in the table is the contribution to the inaccuracy from the term in $\delta\beta^2$ in Eq. (22). These are, for precision-optimised double-spike: 0.00014‰, 0.00014‰ and 0.00015‰ for Mg, Si and K respectively (heaviest over lightest isotopes), which are insignificant.

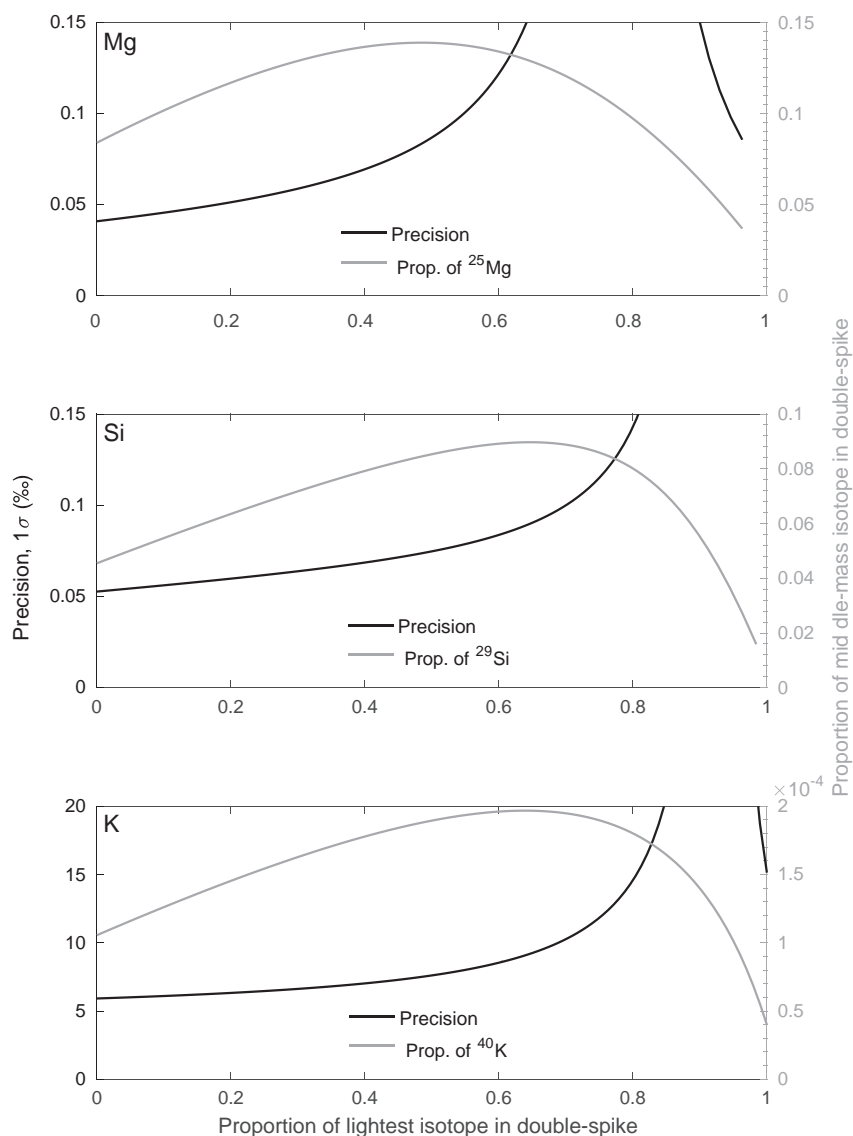


Fig. 9. The black line shows the measurement precision for critical mixtures for double-spike compositions constrained to lie on the locus of maximum accuracy, as a function of the proportion of the lightest isotope in the double-spike (x). For K, the plots extend almost to 1 in x because of the low abundance of ^{40}K in the double-spike. The best precision is obtained when there is none of the lightest isotope in the double-spike. For the error model used see Section 4. The grey line shows the proportion of the middle-mass isotope in the double-spike, the balance being made up by the heaviest isotope. Note the factor of 10^{-4} applied to the right-hand y-scale for K.

If the double-spike – sample mixture is constrained to be both critical and equi-molar (accuracy optimised), the composition of the double-spike has only one degree of freedom. Therefore, we are free to choose the abundance of only one isotope in the double-spike, over some range for which critical equi-molar solutions exist. The ternary plots in Figs. 2–4 show, as a dashed line, the locus double-spike compositions yielding equi-molar critical mixtures with the sample. Constrained to this locus, the best *precision* is achieved with a double-spike composition containing none of the lightest isotope, as is shown more clearly in Fig. 9.

In principle, therefore, we could choose i) to optimise the accuracy by setting $p_c = 0.5$ which, to achieve a critical mixture, constrains the double-spike composition and may not result in the best precision, or ii) solve the double-spike composition to optimise the precision (based on an error model) thereby constraining p_c and not achieving the best accuracy. Table 2 summarises these two scenarios for the Mg, Si and K isotope systems. Fortunately, for Mg and Si at least, the two optimisations are not so dissimilar so both accuracy and precision are close to optimal.

6. Preparing critical mixtures

Making a critical mixture of sample (or standard) and double-spike is an iterative procedure of mixing, isotope ratio measurement and adjustment of the mixture by adding sample or double-spike. In detail, this process would proceed as follows. Following an initial estimate of sample concentration based on, for example, ion beam intensities, one would mix double-spike and sample in molar proportion $p_c : 1 - p_c$ given by Eq. (14) and

$$p_c = \left(1 + \left(\frac{1 - \lambda_c}{\lambda_c} \right) D \right)^{-1} \quad (23)$$

from Eq. (15). The weights of double-spike (w_T) and sample (w_N) solutions mixed should be carefully recorded. Measurements of unspiked standard, to estimate the mass-bias, β , and the mixture yield an estimate of the mixture ratios, (M_1, M_2) , via Eq. (10). Either M_1 or

M_2 can now be used to calculate an accurate mixing parameter, for example using M_1 ,

$$p = \left(1 + \left(\frac{T_1 - M_1}{M_1 - N_1}\right)D\right)^{-1},$$

where we have combined Eqs. (9) and (15). The value of p can now be compared to p_c to determine how much the mixture is over-spiked ($p > p_c$) or under-spiked ($p < p_c$). Correction of the mixture for under-spiking is made by adding to the mixture a weight of spike given by,

$$w = w_T \left(\left(\frac{1-p}{p} \right) \left(\frac{p_c}{1-p_c} \right) - 1 \right),$$

and for over-spiking by adding a weight of sample given by,

$$w = w_N \left(\left(\frac{1-p_c}{p_c} \right) \left(\frac{p}{1-p} \right) - 1 \right).$$

For better accuracy, these amounts should be adjusted by a factor to allow for the amount of mixture that was consumed during the measurement used to determine p . The required factor is the ratio of the total number of moles of mixture remaining after measurement to that before the measurement. The above procedure can be repeated until the required mixture accuracy is obtained.

The most significant source of inaccuracy, which could compromise the above procedure, is in the estimate of the instrumental mass-bias. It is important, therefore, to know how the accuracy of the mass-bias affects the accuracy of the critical mixture. By differentiation of the exponential mass-bias law, Eq. (10), we can write

$$\delta M_i = -M_i P_i \delta \beta, \quad (24)$$

which expresses the change in the corrected ratio, δM_i , due to a change in the mass-bias parameter, $\delta \beta$. From Eq. (3) we have the corresponding change in the mixing parameter,

$$\begin{aligned} \delta \lambda &= \delta M_i / Q_i \\ &= -(M_i P_i / Q_i) \delta \beta \end{aligned} \quad (25)$$

and likewise by rearrangement and differentiation of Eq. (15),

$$\begin{aligned} \delta p &= \delta \lambda (1 - p + pD) / D \\ &= -\frac{M_i P_i (1 - p + pD)^2}{Q_i D} \delta \beta. \end{aligned}$$

We can replace $P_i \delta \beta$ with the change in the relative fractionation of ratio i , δf_i , to give

$$\delta p = -\frac{M_i (1 - p + pD)^2}{Q_i D} \delta f_i.$$

Taking i to be the ratio of the heaviest to the lightest isotopes, the factor $M_i (1 - p + pD)^2 / (Q_i D)$ evaluates to 0.72, 1.09 and 1.07 for Mg, Si and K respectively, where the precision-optimised double-spikes of Table 2 have been assumed. That is, for a 0.5‰ inaccuracy in the measured mass-bias, the corresponding inaccuracy in the measured molar mixing proportion is 0.4‰ for Mg and 0.5‰ for Si and K. Therefore, the ability to produce sufficiently accurate critical mixtures, say within 0.5%, is not limited by our ability to determine the instrumental mass-bias and, at this level of accuracy, the iterative method of making critical mixtures is robust.

7. Double-spike calibration

Using a standard of known isotopic composition, the double-spike composition may be determined by interchanging the roles of sample and double-spike in the inversion of the mixing equations: the double-spike is now the unknown and the standard the known composition. The only additional complications are i) starting from poor knowledge of the double-spike composition, it requires some iterations to make a critical mixture; and ii) a reference point on the instrumental mass-bias curve, passing through the double-spike composition, must be established. For the latter it is necessary to make a measurement of pure double-spike, which is analogous to making a measurement of an un-spiked sample in the conventional Pb double-spike method.

Let \mathbf{t} be the measured pure double-spike composition and let β_t be the estimated mass-bias of the measurement, which can be made by bracketing the double-spike measurements with those of an un-spiked standard. Our initial estimated double-spike composition is, therefore, $T_i = t_i e^{-\beta_t P_i}$.

1. From \mathbf{T} and the standard composition, \mathbf{N} , calculate p_c from Eqs. (14), (16) and (23).
2. Make a critical mixture from weights of standard (w_N) and double-spike (w_T) in proportion $w_T/w_N \approx p_c/(r(1-p_c))$. If this is the first iteration, the double-spike to standard concentration ratio, r , must be estimated. Note that concentrations in this section are in units of moles per unit weight of solution.
3. Measure the mixture composition, m_i , and un-spiked standards, to estimate the mass-bias, β , and solve the mixing equation, $m_i e^{-\beta P_i} = \lambda t e^{-\beta_t P_i} + (1-\lambda)N_i$, for λ and β_t . We now have a new estimate of the double-spike composition, $T_i = t_i e^{-\beta_t P_i}$.
4. Using the λ and \mathbf{T} from the previous step, calculate p from Eqs. (15) and (16) and calculate a new concentration ratio, $r = p w_N / (w_T (1-p))$. Start the next iteration from step 1 and continue iterating until the double-spike composition does not change to an acceptable tolerance.

Modelling shows that only two iterations should be required assuming the second iteration achieves a mixture sufficiently close to critical, which largely depends on the care taken by the analyst. Note that, because of the symmetry of the equations with respect to the interchange of sample and double-spike and $\lambda \iff (1-\lambda)$, the same accuracy and precision considerations apply here as do for the case of sample measurement discussed in Sections 4 and 5. The only additional uncertainty that applies in this case arises from the reproducibility of the mass-bias curve through the measured pure double-spike. Several measurements of pure double-spike should be made and an exponential-law curve fitted to the data to establish it precisely. Any point on the curve may be chosen as the reference, \mathbf{t} .

8. Sensitivity to double-spike calibration

In all the above we have assumed we accurately know the double-spike composition. Here we will show how variations in the assumed double-spike composition propagate into the measured sample fractionation.

Let \mathbf{T}' be the true double-spike composition and let \mathbf{T} be the composition assumed in the inversion of the double-spike mixing equations. We parameterise the displacement of \mathbf{T} from \mathbf{T}' thus,

$$\mathbf{T} = \mathbf{T}'(1 + \gamma \mathbf{v}).$$

The vector $\mathbf{v} = (v_1, v_2)$ is in the direction of this displacement in relative ratio space with \mathbf{T}' as the reference point. The magnitude of

the displacement is $\gamma|\mathbf{v}|$, where $|\mathbf{v}|$ is the magnitude of \mathbf{v} . We choose to keep $|\mathbf{v}|$ constant and equal to $(P_1^2 + P_2^2)^{\frac{1}{2}}$. Consequently, a mass-dependent displacement is given by $\mathbf{v} = \mathbf{P}$ and, in this special case, $1 + \gamma v_i \approx e^{\gamma P_i}$ to first order terms in γ , i.e. γ behaves like a mass-bias parameter.

In Appendix D we derive an expression for $d\alpha/d\gamma$ (Eq. (D.5)),

$$\frac{d\alpha}{d\gamma} = \frac{-\sin(\theta - \phi)}{\sin(\theta_0 - \phi)}. \quad (26)$$

In relative ratio space, θ is the direction of \mathbf{v} , θ_0 the direction of instrumental mass-bias and ϕ is the direction of the mixing line. From this equation we can make the following observations: a) $d\alpha/d\gamma = -1$ if $\theta = \theta_0$, i.e. an inaccuracy of the double-spike calibration in a mass-dependent sense results in an inaccuracy in the sample fractionation of equal magnitude but opposite in sign; b) $d\alpha/d\gamma = 0$ if $\theta = \phi$, i.e. an inaccuracy in the direction of the sample – double-spike mixing line has no effect (to first order); and c) $d\alpha/d\gamma$ has a maximum in magnitude at $\theta = 90^\circ + \phi$, i.e. when \mathbf{v} is perpendicular to the mixing line.

As instrumental mass-bias is typically the most challenging measurement artefact to control and correct for it follows that the inaccuracy in the calibration of the double-spike is typically in a mass-dependent sense. The observation (a) above shows that such an inaccuracy propagates directly to the sample fractionation.

9. Discussion and summary

The double-spike method requires all three isotopes to be precisely determined, in contrast to sample – standard bracketing, where only two isotopes need to be measured. Critical mixtures of Mg and Si have higher abundances of the lowest abundance isotope, 10% and 6.3% for ^{25}Mg and ^{30}Si respectively, than the second-highest abundance isotope in un-spiked samples. Thus, critical double spiking seems likely of useful application to Mg and Si isotopic measurements.

In contrast, K is ill-suited to double spiking because the precision-optimised critical mixture has a very low abundance, 0.015%, of ^{40}K leading to poor measurement precision of this isotope. In addition, ^{40}K cannot be measured by MC-ICPMS because of the presence of the isobar, ^{40}Ar , in the mass spectrum so application of the double-spike method would have to use another measurement technique, such as thermal-ionisation mass spectrometry (TIMS). In multi-collector TIMS the low ^{40}K could be mitigated by analysing larger sample loads to give higher ion beam currents for longer measurement times and a high-gain Faraday cup amplifier for the $^{40}\text{K}^+$ beam can be used to reduce the relative Johnson-Nyquist noise. For example, a total K^+ ion beam of 3 nA with ^{40}K measured using an amplifier equipped with a $10^{12}\Omega$ feedback resistor, $10^{10}\Omega$ resistors elsewhere and a measurement time of 30 min gives a precision of 0.07‰ (1σ) on the $^{41}\text{K}/^{39}\text{K}$ fractionation. These measurement conditions may approach the limit of what is practical with current mass spectrometry methods.

The only other three isotope systems (O, Ne and Ar) are all typically measured by gas source mass-spectrometry where the influence of residual sample matrix in biasing instrumental fractionation has not been highlighted as a limiting problem for accuracy of measurement. A double spiking approach is therefore unlikely to be of value in these determinations, even in the unlikely scenario that problems of instrumental sample memory could be addressed.

The accuracy of the method is potentially compromised by the product of the accuracy of critical mixing and the accuracy of the instrumental mass-bias estimate. For the latter, we have used a figure of 0.5‰, which represents a generously conservative estimate

of what can be determined by measurements of bracketing standards. We have used literature data on geological reference samples to obtain an estimate of the potential inaccuracy of using pure standards to estimate the instrumental mass-bias of bracketed samples. We have taken the full range of published values as a conservative bound on uncertainty as summarised in the introduction to Teng et al. (2015) for USGS rock standards BCR-1, BCR-2 as well as San Carlos Olivine.

A hypothetical example comparing the method described here to sample – standard bracketing for the measurement of Mg isotopes would serve to highlight the important differences. For a fair comparison we shall keep constant the sample Mg consumed for an analysis. Critical mixture double spiking, optimised for precision, has sample:double-spike in proportion 0.56:0.44. If such a mixture has a total Mg beam of 300 pA then the sample contribution to the beam is 168 pA. We will assume 80 s integration times for one analysis of sample or standard, a $10^{11}\Omega$ feedback resistor at a temperature of 300 K and that the only sources of random noise are Poisson statistics and Johnson-Nyquist noise. For the bracketing method, the bracketing standards will also be assumed to have a total Mg beam of 168 pA and that the mean of two bracketing standard measurements will be used to correct for the mass-bias of the sample measurement. The expected measurement precision (1σ) by sample – standard bracketing under these conditions is 0.014‰ compared to 0.040‰ (Table 2) by the double-spike method. These precisions can be further improved by taking the mean of repeated measurements of the sample but, if the precision is to be representative of the true uncertainty of the result, it is vital to have confidence in the accuracy of the method since systematic errors become increasingly important as the random uncertainties are reduced. Herein lies the strength of using a double-spike tracer, that is, the method is robust with respect to matrix-induced instrumental mass-bias giving confidence in the accuracy of the result and in the quoted uncertainty being a reliable measure of the range within which the true composition lies.

Samples containing radiogenic ^{26}Mg would be expected to affect the calculated sample fractionation. To determine the size of this effect let N_1 and N_2 be, respectively, the $^{24}\text{Mg}/^{25}\text{Mg}$ and $^{26}\text{Mg}/^{25}\text{Mg}$ ratios in a sample with $\alpha = 0$ and let the isotopic anomaly due to radiogenic ^{26}Mg be ϵ , i.e.

$$N_1 = n_1,$$

$$N_2 = n_2(1 + \epsilon).$$

As usual, for simplicity we shall put $\beta = 0$; the instrumental mass-bias having a negligible effect. We proceed to derive the sensitivity of α to ϵ as follows. The mixing equation for m_2 is,

$$m_2 = \lambda T_2 + (1 - \lambda)n_2(1 + \epsilon)$$

$$\frac{\partial m_2}{\partial \epsilon} = (1 - \lambda)n_2.$$

Combining with Eq. (B.4) gives,

$$\begin{aligned} \frac{\partial \alpha}{\partial \epsilon} &= (1 - \lambda)n_2 f^{-1} Q_1 \\ &= \frac{n_2 Q_1}{P_1 n_1 Q_2 - P_2 n_2 Q_1}. \end{aligned}$$

Substituting the values for a precision-optimised double-spike composition gives the result,

$$\frac{\partial \alpha}{\partial \epsilon} = 4.0.$$

To put this in more familiar terms, we multiply this result by negative the natural logarithm of the ratio of the ^{26}Mg and ^{24}Mg masses to yield the sensitivity of the apparent fractionation of $^{26}\text{Mg}/^{24}\text{Mg}$ to ϵ , which evaluates to -0.32 . Therefore, a sample with a $+0.1\%$ radiogenic excess on ^{26}Mg would, if unaccounted for, result in an offset of the $^{26}\text{Mg}/^{24}\text{Mg}$ fractionation by -0.032% . To correct for this artefact it is only necessary to use reference ratios with the same radiogenic excess when performing the inversion of the equations, thus, a measurement of unspiked samples must be made to establish the excess in addition to the double-spike measurement to determine the mass-dependent fractionation.

In summary, by using a double-spike tracer it is possible to measure Mg and Si isotopic abundances that are precise and accurate to around 0.01% . In order to realise this possibility, it is necessary to prepare sample – double-spike mixtures that are critical to better than 0.5% . This ought to be readily achieved by an iterative process of measurement and mixture adjustment. Owing to the very low natural abundance of ^{40}K , K isotope measurements are less well suited to this method.

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Data Access Statement

All underlying data to support the conclusions are provided within this paper.

Appendix A. Derivatives with respect to the estimated instrumental mass-bias

The double-spike mixing equation, Eq. (11), is,

$$F_i = \lambda T_i + (1 - \lambda)n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0.$$

The total differential, dF_i , is given by,

$$dF_i = (\partial F_i / \partial \lambda) d\lambda + (\partial F_i / \partial \alpha) d\alpha + (\partial F_i / \partial m_i) dm_i + (\partial F_i / \partial \beta) d\beta. \quad (\text{A.1})$$

Hence, implicit differentiation with respect to β (at constant m_i), and writing out explicitly for $i = 1, 2$ gives,

$$(\partial F_1 / \partial \lambda)(d\lambda / d\beta) + (\partial F_1 / \partial \alpha)(d\alpha / d\beta) + \partial F_1 / \partial \beta = 0 \quad (\text{A.2})$$

$$(\partial F_2 / \partial \lambda)(d\lambda / d\beta) + (\partial F_2 / \partial \alpha)(d\alpha / d\beta) + \partial F_2 / \partial \beta = 0. \quad (\text{A.3})$$

Eqs. (A.2) and (A.3) are linear in $d\lambda / d\beta$ and $d\alpha / d\beta$ and are, therefore, readily inverted to give,

$$\begin{pmatrix} d\lambda / d\beta \\ d\alpha / d\beta \end{pmatrix} = -\mathbf{J}^{-1} \begin{pmatrix} \partial F_1 / \partial \beta \\ \partial F_2 / \partial \beta \end{pmatrix} \quad (\text{A.4})$$

where the 2×2 matrix \mathbf{J} is given by

$$\mathbf{J} = \begin{pmatrix} \partial F_1 / \partial \lambda & \partial F_1 / \partial \alpha \\ \partial F_2 / \partial \lambda & \partial F_2 / \partial \alpha \end{pmatrix}.$$

Explicitly, from Eq. (11),

$$\partial F_i / \partial \lambda = T_i - N_i, \quad (\text{A.5})$$

$$\partial F_i / \partial \alpha = -P_i(1 - \lambda)N_i \quad (\text{A.6})$$

and

$$\partial F_i / \partial \beta = P_i M_i. \quad (\text{A.7})$$

Hence, the inverse of matrix \mathbf{J} is,

$$\begin{aligned} \mathbf{J}^{-1} &= \mathbf{J}^{-1} \begin{pmatrix} -P_2(1 - \lambda)N_2 & P_1(1 - \lambda)N_1 \\ -(T_2 - N_2) & T_1 - N_1 \end{pmatrix} \\ &= \mathbf{J}^{-1} \begin{pmatrix} -P_2(1 - \lambda)N_2 & P_1(1 - \lambda)N_1 \\ -Q_2 & Q_1 \end{pmatrix}, \end{aligned} \quad (\text{A.8})$$

where

$$J = (1 - \lambda)(P_1 N_1 Q_2 - P_2 N_2 Q_1). \quad (\text{A.9})$$

Substituting Eqs. (A.7) and (A.8), into Eq. (A.4) gives,

$$\frac{d\alpha}{d\beta} = \frac{P_1 M_1 Q_2 - P_2 M_2 Q_1}{(1 - \lambda)(P_1 N_1 Q_2 - P_2 N_2 Q_1)}. \quad (\text{A.10})$$

Appendix B. Derivatives with respect to the measured mixture ratios

From Eq. (A.1), at constant β , we have the explicit differentiation,

$$(\partial F_1 / \partial \lambda)(\partial \lambda / \partial m_1) + (\partial F_1 / \partial \alpha)(\partial \alpha / \partial m_1) + \partial F_1 / \partial m_1 = 0$$

$$(\partial F_2 / \partial \lambda)(\partial \lambda / \partial m_2) + (\partial F_2 / \partial \alpha)(\partial \alpha / \partial m_2) + \partial F_2 / \partial m_2 = 0.$$

As we did in the previous section, these linear equations in $\partial \lambda / \partial m_i$ and $\partial \alpha / \partial m_i$ can be inverted, thus,

$$\begin{pmatrix} \partial \lambda / \partial m_1 & \partial \lambda / \partial m_2 \\ \partial \alpha / \partial m_1 & \partial \alpha / \partial m_2 \end{pmatrix} = -\mathbf{J}^{-1} \begin{pmatrix} \partial F_1 / \partial m_1 & \partial F_1 / \partial m_2 \\ \partial F_2 / \partial m_1 & \partial F_2 / \partial m_2 \end{pmatrix}. \quad (\text{B.1})$$

Explicitly,

$$\partial F_i / \partial m_j = \begin{cases} 0 & ; (i \neq j) \\ -e^{-\beta P_i} & ; (i = j) \end{cases}. \quad (\text{B.2})$$

Substituting these and \mathbf{J}^{-1} from Eq. (A.8) into Eq. (B.1) gives,

$$\partial \alpha / \partial m_1 = -J^{-1} Q_2 e^{-\beta P_1} \quad (\text{B.3})$$

$$\partial \alpha / \partial m_2 = J^{-1} Q_1 e^{-\beta P_2}. \quad (\text{B.4})$$

Appendix C. Derivatives and second derivatives with respect to the true mixing parameter and instrumental mass-bias

Let the true mixture parameter be λ' and the true instrumental mass-bias be β_0 . Hence,

$$m_i = (\lambda' T_i + (1 - \lambda') N_i) e^{\beta_0 P_i}$$

and

$$\begin{aligned} \frac{dm_i}{d\lambda'} &= (T_i - N_i) e^{\beta_0 P_i} \\ &= Q_i e^{\beta_0 P_i}. \end{aligned} \quad (\text{C.1})$$

Analogously to Eq. (A.4) we can write,

$$\left(\frac{\partial \lambda / d\lambda'}{\partial \alpha / d\lambda'} \right) = -\mathbf{J}^{-1} \left(\frac{\partial F_1 / \partial \lambda'}{\partial F_2 / \partial \lambda'} \right), \quad (\text{C.2})$$

where the partial differentials on the left-hand side are at constant β . Explicitly,

$$\begin{aligned} \frac{\partial F_i}{\partial \lambda'} &= \frac{\partial F_i}{\partial m_i} \frac{dm_i}{d\lambda'} \\ &= -Q_i e^{(\beta_0 - \beta)P_i}, \end{aligned} \quad (\text{C.3})$$

where we have combined Eqs. (B.2) and (C.1). Substituting for \mathbf{J} in Eq. (C.2) from Eqs. (A.8) and (A.9) gives,

$$\begin{aligned} \frac{\partial \lambda}{\partial \lambda'} &= \frac{-P_2(1-\lambda)N_2Q_1 e^{(\beta_0 - \beta)P_1} + P_1(1-\lambda)N_1Q_2 e^{(\beta_0 - \beta)P_2}}{(1-\lambda)(P_1N_1Q_2 - P_2N_2Q_1)} \\ &= \frac{-P_2N_2Q_1 e^{(\beta_0 - \beta)P_1} + P_1N_1Q_2 e^{(\beta_0 - \beta)P_2}}{(P_1N_1Q_2 - P_2N_2Q_1)} \end{aligned}$$

and

$$\frac{\partial \alpha}{\partial \lambda'} = \frac{-Q_1Q_2 e^{(\beta_0 - \beta)P_1} + Q_1Q_2 e^{(\beta_0 - \beta)P_2}}{(1-\lambda)(P_1N_1Q_2 - P_2N_2Q_1)}. \quad (\text{C.4})$$

Differentiating with respect to β ,

$$\begin{aligned} \frac{\partial^2 \alpha}{\partial \beta \partial \lambda'} &= \left(\frac{Q_1Q_2}{P_1N_1Q_2 - P_2N_2Q_1} \right) \left(\frac{P_1 e^{(\beta_0 - \beta)P_1} - P_2 e^{(\beta_0 - \beta)P_2}}{(1-\lambda)} \right. \\ &\quad \left. + \frac{-e^{(\beta_0 - \beta)P_1} + e^{(\beta_0 - \beta)P_2}}{(1-\lambda)^2} \frac{d\lambda}{d\beta} \right) \\ &= \left(\frac{Q_1Q_2}{J} \right) \left\{ P_1 e^{(\beta_0 - \beta)P_1} - P_2 e^{(\beta_0 - \beta)P_2} \right. \\ &\quad \left. + \left(\frac{-e^{(\beta_0 - \beta)P_1} + e^{(\beta_0 - \beta)P_2}}{(1-\lambda)} \right) \left(\frac{P_2N_2M_1 - P_1N_1M_2}{P_1N_1Q_2 - P_2N_2Q_1} \right) \right\} \\ &= \left(\frac{Q_1Q_2}{J} \right) \left\{ P_1 e^{(\beta_0 - \beta)P_1} - P_2 e^{(\beta_0 - \beta)P_2} \right. \\ &\quad \left. + \left(\frac{-e^{(\beta_0 - \beta)P_1} + e^{(\beta_0 - \beta)P_2}}{J} \right) (P_2N_2M_1 - P_1N_1M_2) \right\} \quad (\text{C.5}) \end{aligned}$$

Finally, we use Eq. (A.10) but now with *partial* differentiation with respect to β at constant λ' . Differentiating this equation with respect to β again gives,

$$\begin{aligned} \frac{\partial^2 \alpha}{\partial \beta^2} &= \frac{-P_1^2M_1Q_2 + P_2^2M_2Q_1}{J} + \left(\frac{-P_1M_1Q_2 + P_2M_2Q_1}{(1-\lambda)J} \right) \\ &\quad \times \left(\frac{P_2N_2M_1 - P_1N_1M_2}{P_1N_1Q_2 - P_2N_2Q_1} \right) \\ &= \frac{-P_1^2M_1Q_2 + P_2^2M_2Q_1}{J} + \left(\frac{-P_1M_1Q_2 + P_2M_2Q_1}{J^2} \right) \\ &\quad \times (P_2N_2M_1 - P_1N_1M_2). \end{aligned} \quad (\text{C.6})$$

Evaluating the partial differentials given by Eqs. (A.10) and (C.4)–(C.6) at $(\beta, \lambda') = (\beta_0, \lambda_c)$ yields,

$$\begin{aligned} \left. \frac{d\alpha}{d\beta} \right|_{(\beta_0, \lambda_c)} &= 0, \\ \left. \frac{\partial \alpha}{\partial \lambda'} \right|_{(\beta_0, \lambda_c)} &= 0, \\ \left. \frac{\partial^2 \alpha}{\partial \beta \partial \lambda'} \right|_{(\beta_0, \lambda_c)} &= \frac{Q_1Q_2(P_1 - P_2)}{J_c} \\ &= \frac{-1}{\lambda_c(1 - \lambda_c)}, \end{aligned} \quad (\text{C.7})$$

where we have used Eq. (14) and,

$$J_c = (1 - \lambda_c)(P_1N_1Q_2 - P_2N_2Q_1).$$

Lastly,

$$\begin{aligned} \left. \frac{\partial^2 \alpha}{\partial \beta^2} \right|_{(\beta_0, \lambda_c)} &= \frac{-P_1^2M_1^cQ_2 + P_2^2M_2^cQ_1}{J_c} \\ &= \frac{P_2M_2^cQ_1(P_2 - P_1)}{J_c}, \end{aligned}$$

where we have used Eq. (12).

Let p' be the true molar mixing proportion. In terms of λ' ,

$$\frac{1 - p'}{p'} = \left(\frac{1 - \lambda'}{\lambda'} \right) D. \quad (\text{C.8})$$

Differentiating,

$$\frac{dp'}{d\lambda'} \left(\frac{1}{p'^2} \right) = \frac{D}{\lambda'^2}.$$

Dividing both sides by the corresponding sides of Eq. (C.8),

$$\frac{dp'}{d\lambda'} \left(\frac{1}{p'(1 - p')} \right) = \frac{1}{\lambda'(1 - \lambda')}. \quad (\text{C.9})$$

Hence Eq. (C.7) can be written,

$$\left. \frac{\partial^2 \alpha}{\partial \beta \alpha \lambda'} \right|_{(\beta_0, \lambda_c)} = -\frac{dp'}{d\lambda'} \left(\frac{1}{p_c(1 - p_c)} \right).$$

Appendix D. Derivatives with respect to double-spike composition

Using the parameterisation described in Section 8,

$$\mathbf{T} = \mathbf{T}'(1 + \gamma\mathbf{v}),$$

where \mathbf{T} and \mathbf{T}' are the assumed and true double-spike compositions respectively and $|\mathbf{v}| = (P_1^2 + P_2^2)^{\frac{1}{2}}$, we will derive an expression for $d\alpha/d\gamma$ at $\gamma = 0$ for a critical mixture.

Similarly to Eq. (A.4), we may write,

$$\left(\frac{d\lambda/d\gamma}{d\alpha/d\gamma} \right) = -\mathbf{J}^{-1} \left(\frac{\partial F_1/\partial \gamma}{\partial F_2/\partial \gamma} \right). \quad (\text{D.1})$$

Explicitly,

$$\left. \frac{\partial F_i}{\partial \gamma} \right|_{\gamma=0} = \lambda_c T_i v_i, \quad (\text{D.2})$$

hence,

$$\left. \frac{d\alpha}{d\gamma} \right|_{\gamma=0} = \frac{\lambda_c(Q_2 T_1 v_1 - Q_1 T_2 v_2)}{(1 - \lambda_c)(P_1 N_1 Q_2 - P_2 N_2 Q_1)}. \quad (\text{D.3})$$

Substituting from Eq. (14) and using $\mathbf{T} = \mathbf{N} + \mathbf{Q}$,

$$\left. \frac{d\alpha}{d\gamma} \right|_{\gamma=0} = -\frac{v_2 Q_1 / T_1 - v_1 Q_2 / T_2}{P_2 Q_1 / T_1 - P_1 Q_2 / T_2}. \quad (\text{D.4})$$

Let

$$\theta = \tan^{-1}(v_2, v_1); \quad (\text{the direction of } \mathbf{v})$$

$$\theta_0 = \tan^{-1}(P_2, P_1); \quad (\text{the direction of the mass-bias})$$

$$\phi = \tan^{-1}(Q_2/T_2, Q_1/T_1); \quad (\text{the direction of the mixing line})$$

where $\tan^{-1}(y, x)$ returns the inverse tangent of y/x and the sign of (x, y) gives the quadrant of the angle returned with zero being the positive x -axis and $\pi/2(90^\circ)$ the positive y -axis. Eq. (D.4) may now be written

$$\left. \frac{d\alpha}{d\gamma} \right|_{\gamma=0} = \frac{-\sin(\theta - \phi)}{\sin(\theta_0 - \phi)}, \quad (\text{D.5})$$

which can be readily verified by substitution and using $|\mathbf{v}|^2 = v_1^2 + v_2^2 = P_1^2 + P_2^2$.

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