



## Double-spike inversion for three-isotope systems



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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  $^{40}\text{K}$  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

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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  $\Delta_i$  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,  $\beta$ , 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.
$\beta$	Instrumental mass-bias parameter.
$\alpha$	Sample mass-fractionation parameter relative to reference.
$\lambda$	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  $\lambda$  and  $\beta$  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  $\alpha$ .

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

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

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