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Obtaining accurate isotopic compositions with the double spike technique: practical considerations

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ABSTRACT

Ever-increasing precision in isotope ratio measurements requires a concomitant small bias and minimisation of inter-laboratory bias. The double spike technique is the most suitable method to obtain reliable isotope composition data that are accurately corrected for instrumental mass fractionation. Compared with other methods, such as sample-standard bracketing, only the double spike technique can correct for all sources of fractionation after equilibration of the sample with the double spike, such as that incurred during chemical separation and measurement. In addition, it is not dependent on *a priori* assumptions of perfect matrix matching of samples to reference materials or quantitative recovery of the sample through the chemical separation procedure to yield accurate results. In this review article, we present a detailed discussion of the merits of the double spike technique, how to design and calibrate a suitable double spike and analytical strategies. Our objective is to offer a step-by-step introduction to the use of the double spike technique in order to lower potential barriers that researchers new to the subject might face, such that double spiking will replace sample-standard bracketing as the measurement method of choice.

Keywords: double spike method; instrumental mass fractionation; mass-dependent isotope variation; spike calibration; measurement procedure optimisation

1. Introduction

Isotope geochemistry, the study of variation in the isotopic composition of elements, is a key aspect of the Earth Sciences. It has proven to be a crucial tool in establishing major concepts such as absolute dating of geological materials, the formation of the Earth in our solar system and the recycling of the Earth's crust into the mantle through plate tectonics. Traditionally, isotope geochemistry focused on isotopic anomalies arising from the decay of long-lived nuclides, such as the radiogenic ^{87}Rb-^{87}Sr and ^{238}U-^{206}Pb systems, and the mass-dependent isotopic fractionation of light elements (H, C, N, O, S) in the low-temperature geochemical realm. The latter, often but inappropriately called stable isotope fractionation, comprises fractionation of isotopes of an element through physicochemical processes as a function of the masses following a limited class of well-known functions (e.g., linear, power and exponential fractionation laws; Bigeleisen and Mayer 1947, Schauble 2004, Young *et al.* 2015). Elements heavier than S were traditionally regarded not to show isotopic fractionation in nature due to the small relative mass differences between their isotopes, but at present mass-dependent isotope fractionation has been detected for elements as heavy as Tl (Prytulak *et al.* 2013) and U (Andersen *et al.* 2015). The use of these "non-traditional stable isotopes" has taken flight to address a wide range of research questions across the Earth sciences. In particular, the advent of ICP-MS instruments heralded a new era of increasingly precise isotopic measurements that could, in principle, be applied to every non-monoisotopic, non-gaseous element in the periodic table. Improving the precision (repeatability) of isotopic measurements is relatively straightforward and relies for a large part on optimising counting statistics by longer measurements of higher-intensity ion beams (e.g., Albarede *et al.* 2004). The current levels of measurement precision, however, require a concomitant small bias, meaning the minimisation of (systematic) measurement errors both within and between laboratories, which has proven to be more of a challenge. A strict control on the accuracy of high-precision isotope ratio data is clearly required.

The double spike technique, where a tracer consisting of two artificially enriched isotopes is mixed with the sample, provides the most reliable method to obtain accurate isotopic compositions for elements with at least four isotopes (Albarède and Beard 2004, Rudge *et al.* 2009). Its fundamentals were proposed by Dodson (1963), but at first the double spike technique saw little use apart from the application to Pb (e.g., Compston and Oversby 1969, Cumming 1973, Hamelin *et al.* 1985, Galer and Abouchami 1998) and Ca isotope measurements (Russell *et al.* 1978). It took over three decades and a significant increase in measurement precision with new MC-ICP-MS instruments before the geochemical community became aware of the full potential of the double spike technique and the first doubly-spiked studies of mass-dependent fractionation of non-traditional isotopes appeared (e.g., Johnson and Beard 1999), thus vindicating Dodson's (1963) statement that, with the double spike technique, "*it would be possible in principle to measure precisely the natural isotopic fractionation of a large number of polyisotopic elements, for example Mg, Ca, Ti, Cr, Ni, Fe, Mo, Sn*".

Despite the clear advantages, Rudge *et al.* (2009) noted a general hesitation in the implementation of double spike measurement protocols, possibly related to the perceived difficulty of their practical use. Even though ready-to-use data reduction software and spreadsheets are available (e.g., Rudge *et al.* 2009, Creech and Paul 2015), designing, making and calibrating a double spike might present a significant inertia barrier. This article aims to lower this barrier by providing a practical guide to double spiking. The solutions to the double spike equations have been presented in various forms in the literature (e.g., Dodson 1963, Russell 1971, Hamelin *et al.* 1985, Galer 1999, Johnson and Beard 1999, Siebert *et al.* 2001, Albarède and Beard 2004). The most recent version by Rudge *et al.* (2009) is generally accepted by the geochemical community and we will follow their nomenclature and definitions throughout. As Rudge *et al.* (2009) have published the definitive approach for solving the double spike equation and its uncertainty propagation, and most researchers use publicly available data reduction programs such as the Double Spike Toolbox Matlab code (Rudge *et al.* 2009), we will not delve into a detailed discussion of the mathematics behind double spiking. Rather, we will focus on practical considerations when working with double spikes, aimed at researchers new to the subject. We aim to address questions arising when setting up a mass spectrometry protocol for a new element, including the advantages of double spiking over other corrections methods, how to choose a suitable double spike, ways to calibrate and validate a double spike, etc. To aid the discussion, we will often refer to the new Ni double spike that we recently implemented at the University of Bristol as an example.

2. Principles of the double spike technique

2.1. Instrumental mass fractionation

Mass spectrometric data require extensive correction for analytical artefacts and specifically the effects of instrumentally-induced mass-dependent fractionation (IMF). Non-quantitative transmission of a sample in the mass spectrometer gives rise to mass-dependent fractionation of isotope ratios just as physicochemical processes do in nature. In TIMS, preferential evaporation of the lighter isotopes in a sample leads to relatively small but variable IMF, whereas in ICP-MS, space charge effects in the interface cause strong but relatively constant IMF (e.g., Albarède and Beard 2004). Albeit the magnitude of IMF is variable, it closely follows the exponential mass fractionation law (Russell *et al.* 1978) that, for a given pair of isotopes (denoted *i*), can be written as

Eq. (1) $N_i = n_i e^{-\alpha P_i}$

where *N* is the true isotopic ratio of a sample, *n* is the measured isotopic ratio of a sample, α is the fractionation parameter and *P* is the natural logarithm of the exact mass ratio of the two isotopes (notation following (Rudge *et al.* 2009). The subscript *i* denotes the *i*th isotope ratio of the element in question, for example ^{60}Ni/^{58}Ni, ^{61}Ni/^{58}Ni, etc., corresponding to *i* = 1, 2, etc. The only free parameter in equation (1) is the mass fractionation parameter, α, whose value specifies the "degree of fractionation" with positive α being an IMF favouring detection of heavy isotopes over light. Note that α has no subscript and thus has the same value for all pairs of isotopes for a given element. Hence, to correct mass spectrometric data for IMF, it is necessary to determine α. Accurate correction is critical as the magnitude of the IMF often exceeds natural mass-dependent variations by orders of magnitude in ICP-MS measurements. There are several ways to approach this problem, the addition of a double spike tracer being one of them. We discuss the four most common IMF correction procedures below.

For radiogenic isotope systems, such as Sr and Nd, internal normalisation eliminates all mass-dependent fractionation, both natural and IMF. In this case the sample is assumed to be fractionated (by a natural process) relative to some reference ratio for a non-radiogenic isotope pair to (e.g., ^{86}Sr/^{88}Sr = 0.1194; Nier 1938). During measurement, IMF further fractionates this ratio and the combined effect is rolled into a single value of α, the solution of equation (1), with N set equal to the reference ratio. Thus, the radiogenic isotope ratio (e.g., ^{87}Sr/^{86}Sr), devoid of all mass-dependent effects and leaving only the radiogenic excess or deficit, is readily determined from the measured ratio and the previously solved-for value of α.

When a non-radiogenic isotope pair is not available, notably for Pb, or the magnitude of natural mass-dependent fractionation is investigated, an external method is required to correct for IMF. The most commonly used method is sample-standard bracketing. Here, a reference material (standard) with a known composition is measured alongside the unknown samples and used to monitor IMF. A clear advantage of this approach is that the absolute composition of the reference material need not be known as long as results are expressed as the relative difference of an isotopic ratio (δ notation; Coplen 2011). By alternately measuring the reference material and unknown samples (“bracketing”) and using the mean isotope ratios of the adjacent reference materials to correct the unknown, drift in IMF during the measurement session can be corrected for (Albarede *et al.* 2004). A critical prerequisite for sample-standard bracketing is that samples and reference materials fractionate to the same extent during measurement, which is very difficult to validate as we will discuss below.

A third correction method involves doping samples with an element that has at least two interference-free isotopes and a mass close to that of the element of interest to monitor IMF, such as Tl in case of Pb (e.g., Longerich *et al.* 1987). The isotope composition of the dopant element is presumed to be known and, when one assumes that the magnitude of IMF is the same for elements of similar mass, can be used to correct the IMF of the element of interest. Whether IMF is indeed sufficiently similar for different elements is contentious and doping with another element can produce precise data that are nevertheless inaccurate (e.g., Thirlwall 2002, Waight *et al.* 2002, Taylor *et al.* 2015).

Finally, the double spike technique uses a well-calibrated artificial tracer enriched in two isotopes (the double spike) that is added to a sample. The addition of this exotic tracer allows an internal correction to be made to obtain the isotopic composition of a sample that is corrected for all mass-dependent isotope fractionation incurred after homogenisation with the tracer.

2.2. The double spike equation

The principles of the double spike technique are shown schematically in Figure 1. In four-isotope space, measurement of a natural sample *N* yields three independent isotope ratios that are affected by IMF so that the measured composition (*n*) is offset from the true value. The form of the IMF line is only dependent on the mass of the isotopes as given by equation (1) and is therefore known, but the displacement along the line, given by the mass fractionation parameter α, is not. Hence, the true composition *N* cannot be constrained other than to lie somewhere on the IMF line that passes through *n*. If an aliquot of the natural sample *N* is mixed with the double spike tracer (*T*), a mixture *M* will result with a composition that is dependent on the proportion (given by λ) in which the sample and double spike are mixed. The measurement of this mixture (*m*) will also be affected by IMF, again along a line of known form but with unknown displacement (β). It is now possible to construct one, and only one, mixing line that passes through the point *T* and intersects with the two IMF lines. The two intersection points are *N* and *M*; thus a solution for the sample composition (*N*) is found. The procedure can be described in algebraic terms as follows: the line *N*-*n* is given by equation (1); *M*-*m* and the mixing line *N*-*M*-*T* can be expressed as

Eq. (2) $M_i = m_i e^{-\beta P_i}$

Eq. (3) $M_i = \lambda T_i + (1 - \lambda) N_i$

Note that a linear mixing line, as described above, requires that the same denominator isotope is chosen for each of the three isotope ratios. Substituting equations (1) and (2) into equation (3) gives the exponential law double spike equation (Rudge *et al.* 2009):

Eq. (4) $$\lambda T_i + (1 - \lambda) n_i e^{-\alpha P_i} - m_i e^{-\beta P_i} = 0$$

Since the composition of the double spike is known and the ratios of n and m are measured, equation (4) has three unknowns: α, β and λ. Writing out equation (4) for $i = 1$, 2 and 3 provides three equations that can be solved numerically for the three unknowns (see Rudge *et al.* 2009), a procedure often referred to as inversion. Herein lies the main limitation of the double spike method: to solve the equations for three unknowns the isotope system requires at least four available isotopes (three ratios). We will refer to the four isotopes used in the double spike equation as the inversion isotopes. The true composition of the sample N can then be found by entering the value of α, obtained from the inversion, and the measured ratios for n in equation (1). As such, the isotope composition of a sample can be obtained through the measurement of a pure (n) and spiked (m) aliquot of the sample. This is used in the case of Pb isotopes where $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ are used as geochemical tracers (e.g., Thirlwall 2000, Klaver *et al.* 2016). Note that, although four isotopes are required for the double spike inversion, all isotopes of an element with five or more isotopes can be measured and corrected for IMF following Equation (1) so that the double spike technique can be used to obtain the absolute isotopic composition of an element.

2.3. Double spiking applied to natural mass-dependent fractionation

When one is interested in the natural mass-dependent (“stable”) isotope fractionation relative to a reference material, a simpler approach can be followed. Assuming IMF and natural fractionation both follow the exponential fractionation law, it follows that the isotopic composition of the sample and reference material satisfy equation (1) (i.e., they lie on the same mass-dependent fractionation line). In this case, the isotopic composition of the reference material in the double spike inversion (Eq. 4) can take the places of the measured ratios of the unspiked sample (n), thus obviating the need to measure the unspiked sample; a single measurement of the spiked sample (m) suffices to calculate α relative to the reference material. The value for α resulting from the double spike inversion represents the degree of natural fractionation (the displacement from reference material n to sample N), which can be directly expressed in the δ notation. Following the IUPAC convention (Coplen 2011) and taking Ni as an example:

Eq. (5) $$\delta\ {}^{i}Ni = e^{-\alpha P_i} - 1$$

where i again indicates a specific pair of isotopes of the element (e.g., $^{60}Ni/^{58}Ni$) and P is the natural logarithm of the ratio of the exact isotopic masses. Note that α is the quantity of interest and that the choice of isotope ratio in the δ notation is completely arbitrary; there is no advantage in choosing one ratio over another other than convention. Consequently, for double spike data, consistency between, for example, $\delta^{60/58}Ni$ and $\delta^{62/58}Ni$ cannot be used as an independent measure of data quality. This presents a marked contrast with other correction methods, such as sample-standard bracketing, where each isotope ratio is independently corrected for IMF through bracketing against the reference material.

2.4. Two special cases

The double spike technique is normally only applicable to elements with at least four stable isotopes but can be extended to 3-isotope elements using an ingenious adaptation (Hofmann 1971, Coath *et al.* 2017). This critical-mixture method employs the fact that β is an output parameter of the double spike equation but has little practical use. Thus, if β can be constrained through independent means, the number of unknowns decreases by one and only two independent isotope ratios are required to solve equation (4). Typically, any bias in estimating β, for instance through sample-standard bracketing, propagates directly into a bias in α and its associated uncertainty, the parameter of interest. In the special case where the IMF line *M*-*m* is tangential to the sample – double spike mixing line, however, a bias in estimating β has a marginal influence on α as the displacement of the presumed position of *M* is parallel to the mixing line. The IMF vector and mixing line only become parallel when sample and double spiked are precisely combined in a "critical mixture", typically requiring an iterative effort to optimise the sample – double spike proportion (Coath *et al.* 2017).

An alternative option to extend the double spike technique is the use of one or two non-naturally occurring radioactive isotopes to make a double spike. This is commonly used for high-precision U-Pb and U-series measurements of small samples where well-calibrated ^{202}Pb-^{205}Pb and ^{233}U-^{236}U spikes allow direct correction for IMF as these isotopes do not naturally occur in samples (e.g., Todt *et al.* 1996). The main problem of upscaling this technique to mass-dependent fractionation studies of a greater variety of elements is the use of large quantities of costly radioactive spike material and the consequent radiological hazard. To our knowledge this has not yet been undertaken for elements other than U.

3. The advantages of double spiking

3.1. Matrix effects and variable mass fractionation

The main advantage of double spiking is that it provides accurate correction for IMF as long as the double spike is properly calibrated. It does not rely on an *a priori* assumption of identical IMF behaviour of samples and reference material – in clear contrast to sample-standard bracketing (SSB). To illustrate this point, we present a comparison between double spike and SSB-corrected $\delta^{60/58}$Ni data, obtained by MC-ICP-MS (see Appendix A), for the same measurements of a pure Ni solution in Figure 2. Because the double spike inversion yields a value for β (the magnitude of the IMF) for every measurement, double spike corrected data can be re-corrected assuming constant IMF between samples and the reference material as in SSB. Repeated double spike measurements of a pure Ni solution (our in-house CPI Ni solution) yield results with a high intermediate measurement precision. Correcting the same data through SSB leads to more scatter of the data points and introduces a bias compared to the double spike results. This is particularly evident in the case of CPI standards processed through the chemical separation procedure: whereas double spike-corrected results are indistinguishable from unprocessed CPI solutions, SSB-corrected data can yield over 1 ‰ lower $\delta^{60/58}$Ni values. This is a significant effect considering that natural variations in Ni isotopes are often <0.1 ‰. Clearly, the requirement of identical IMF of the reference material and processed CPI standards is not met. In this case, the likely cause is residual organic material (from the dimethylglyoxime used to elute Ni) in the processed Ni solutions. The presence of a small amount of matrix (any element or compound other than the one of interest) in samples can affect plasma conditions to such an extent that the IMF behaviour becomes significantly different compared to the matrix-free reference material. Such matrix effects are very common and very hard to systematically suppress (e.g., Barling and Weis 2008, Tipper *et al.* 2008, Shiel *et al.* 2009, van den Boorn *et al.* 2009, Nan *et al.* 2015, Peters *et al.* 2015), making it extremely difficult to obtain bias-free isotope data through sample-standard bracketing. Strikingly, the repeatability measurement precision (the 2 SE of the mean of 6-8 independent measurement results) is only a factor ~3 worse than for the DS-corrected data, indicating that SSB can induce a significant measurement bias yet yield relatively precise results, with the high precision potentially giving a false sense of security. The double spike method, on the other hand, has no trouble dealing with these matrix effects and produces accurate results.

3.2. Correcting for fractionation during chemical purification

As matrix effects can have a pronounced influence on IMF, care has to be taken to matrix-match samples to the elementally pure reference material, which typically involves the elimination of the sample matrix as much as possible. Purification of geological materials is mostly achieved through a single- or multistage ion-exchange chromatography ("column") procedure (e.g., Schönbächler and Fehr 2013). Although sample purification is essential, it can have negative side effects such as the introduction of organic species as in the case of Ni (Figure 2). A second major complication is that isotopic fractionation can occur during ion-exchange chromatography, implying that non-quantitative recovery of the analyte can lead to mass-dependent fractionation. This is particularly pertinent to lighter elements that are more readily fractionated due to the larger relative mass difference between their isotopes (e.g., Russell and Papanastassiou 1978, Oi *et al.* 1991, Chernonozhkin *et al.* 2015), but with increasing precision of isotope measurement results it should not be neglected for heavier elements either. Quantitative recovery of the analyte is thus required to avoid introducing a bias but is difficult to demonstrate on a sample-to-sample basis and any fractionation incurred during chemical purification cannot be corrected for using sample-standard bracketing. On the other hand, the double spike technique corrects for any mass-dependent fractionation after sample-spike equilibration. Hence, if a sample and double spike are mixed and equilibrated prior to ion-exchange purification, the double spike inversion will correct for the combined mass-dependent fractionation during purification and measurement. As such, the double spike technique is the only method that is not dependent on quantitative recovery through the separation procedure and can produce accurate results even if a significant fraction of the sample is lost during purification (e.g., <50 % yield).

4. Designing a double spike

The aim of the double spike technique is to produce isotope data with a small uncertainty. The accuracy of double spike data relies on the quality of the calibration of the double spike and reference material, which is discussed below, but the precision of the results depends greatly on the choice of double spike composition.

Obviously, one would prefer a double spike that produces the best possible precision, either in a ratio of interest (e.g., ^{207}Pb/^{204}Pb) or in α when natural mass-dependent fractionation is investigated. Rudge *et al.* (2009) included a model in their Double Spike Toolbox that can be used to calculate the theoretical precision in α or an isotope ratio for a wide range of variable parameters. Briefly, their precision model is based on linear propagation of the variance associated with the measurement of ion beam intensities: i) thermal noise of the resistors fitted in the amplifier feedback loop of the Faraday detectors (Johnson-Nyquist noise) and ii) counting statistics of the ion beam intensities (Poisson or shot noise; see e.g., Albarede *et al.* 2004). If the double spike is calibrated perfectly, the double spike inversion does not introduce a bias and only leads to magnification of the measurement precision. As such, the precision model provides a theoretical limit on the highest precision that can be achieved for a given total ion beam intensity and integration time.

A double spike that leads to minimal magnification of the measurement precision is considered optimal and a "cocktail list" of double spikes that yield the highest theoretical precision is provided by Rudge *et al.* (2009). We strongly prefer their approach of linear propagation of variances to assess the performance of a double spike over geometrical methods proposed by e.g., Galer (1999) and Johnson and Beard (1999). The latter predict that the precision of a double spike solution is dependent on the choice of denominator isotope in the ratios used in the double spike inversion. Because mixing and mass fractionation processes are coordinate-independent, there is no physical basis for the choice of denominator isotope to have any effect, as discussed by Rudge *et al.* (2009).

There are several factors that can influence the choice of the isotopes used in a double spike and, in the case of elements with five or more isotopes, the four isotopes used in the double spike inversion. Selecting the four inversion isotopes should be the first step in choosing an appropriate double spike: the same double spike can perform better or worse depending on the choice of inversion isotopes. The presence of isobaric interferences can make some isotopes less suitable as an inversion isotope. In the case of Ni, five stable isotopes are available: ^{58}Ni (68.08 % abundance), ^{60}Ni (26.22 %), ^{61}Ni (1.14 %), ^{62}Ni (3.63 %) and ^{64}Ni (0.93 %; Gramlich *et al.* 1989). We decided to avoid the use of ^{64}Ni as it suffers from isobaric interference by a major isotope of Zn (^{64}Zn has an abundance of 48.6 %; Rosman 1972), even though double spikes with ^{64}Ni yield the best possible precision. It is difficult to quantitatively remove Zn from samples as it is a common contaminant in labware and the environment. Correction for Zn interference is possible but undesirable as monitoring ^{66}Zn would require a magnet jump in the method and thus consume time and analyte. Hence, we have opted to exclude ^{64}Ni and use ^{58}Ni, ^{60}Ni, ^{61}Ni and ^{62}Ni as inversion isotopes. Isobaric interferences have also affected the choice of, for instance, Mo (Siebert *et al.* 2001) Cd (Ripperger and Rehkämper 2007) and Pt (Creech *et al.* 2013) inversion isotopes. In addition to isobaric interferences, the presence of nucleosynthetic anomalies in extra-terrestrial materials can also be taken into account when choosing the four inversion isotopes (e.g., Millet and Dauphas 2014).

Upon choosing the inversion isotopes, the precision model of Rudge *et al.* (2009) can be used to explore a wide parameter space to find the most suitable double spike. Simply choosing the one with highest theoretical precision might not always be the best choice. Taking Ni as an example again, we used the precision model of

Rudge *et al.* (2009) to generate contour diagrams of the precision in α as a function of double spike composition and the proportion of spike in the sample-spike mixture for two different double spikes (Figure 3). Excluding ^{64}Ni, a ^{60}Ni-^{62}Ni double spike yields the best possible precision, albeit only marginally better than a ^{61}Ni-^{62}Ni spike. The performance of the ^{60}Ni-^{62}Ni spike, however, is much more dependent on getting the sample-spike proportion exactly right: a small deviation from the optimal sample-spike proportion leads to a significant decrease in precision. If the double spike deviates from the optimal composition, this becomes even more pertinent. On the other hand, the ^{61}Ni-^{62}Ni spike has a broad precision minimum with very little deterioration in precision over a wide range in the sample-spike ratio. Versatility of a double spike in terms of sample-spike proportion is desirable, in particular when the concentration of the element in the double spike or, more likely, the sample is poorly known. As such, we preferred the use of a ^{61}Ni-^{62}Ni double spike.

The default precision model of the Double Spike Toolbox employs a total beam intensity for the four inversion isotopes of 100 pA (10 V), integration time of 8 s and a 10^{11} Ω amplifier feedback resistor. These measurement conditions are typical for MC-ICP-MS and TIMS measurements, but if the double spike method will be applied to much larger or smaller sample sizes it is worth investigating the effect of total beam intensity on the expected precision. Figure 4 shows the precision in α as a function of sample-spike proportion for two Ni double spikes at a total beam intensity that varies by three orders of magnitude. The broad precision minimum of the ^{61}Ni-^{62}Ni double spike, as seen in Figure 3, is maintained down to very low (0.1 V) beam intensities. In contrast, the deterioration in the precision when moving away from the optimal sample-spike proportion is more acute for the ^{60}Ni-^{62}Ni double spike although the best possible precision is always higher than for the ^{61}Ni-^{62}Ni double spike. Thus, use of a ^{60}Ni-^{62}Ni double spike would require more stringent control on mixing of sample and double spike in the optimal proportion, in particular for small sample sizes. If only a small amount of sample is available, one might not want to sacrifice an aliquot for concentration measurement prior to spiking and hence one would have to rely on published or estimated concentration data for the element of interest. In such a case, a versatile double spike with a wide precision minimum is preferable as it allows for significant deviation from the optimal sample-spike proportion without suffering a large decrease in precision. Another argument for choosing the ^{61}Ni-^{62}Ni spike is that it boosts the intensity of the minor ^{61}Ni isotope (1.14 % abundance). Although the precision model of Rudge *et al.* (2009) incorporates the Johnson-Nyquist noise that is the dominant source of predictable variance at low beam intensities, it does not take into account unpredictable, non-proportional effects, such as the variable effects of background and blank corrections on minor isotopes, which diminish at higher beam intensities.

A final consideration is the required purity of the single spikes and their cost. Optimal double spikes commonly include at least one minor (<5 % abundance) isotope of the element (Rudge *et al.* 2009) and the cost of single spikes is typically higher for isotopes with a low abundance in nature and increases with the enrichment factor of an isotope. Although the double spike technique does not critically rely on high purity single spikes as do isotope dilution methods (e.g., Stracke *et al.* 2014), the enrichment factor of the single spikes does have some influence on the versatility of a double spike and the precision that can be obtained. If reliable IMF correction is required but not the highest possible precision, it might be cost-efficient to opt for less-enriched single spikes of isotopes with a reasonably high natural abundance. Moreover, a double spike with a low proportion of spike in the optimal sample-spike mixture allows more measurements for a given quantity of double spike. The Double Spike Toolbox precision model allows the spike compositions to be varied so that the effects of single spike purity on the performance of double spikes can be investigated for a specific application.

5. Calibrating a double spike

5.1. Calibration relative to a reference material

The accuracy of data corrected for IMF using the double spike technique relies heavily on how well the composition of the double spike is known, although reporting data relative to a reference material that was spiked and measured together with the samples can correct a potential bias. Careful gravimetric mixing provides insufficient accuracy even in the rare case where the isotope composition of the single spikes is well known. The compositional certificate of single spikes provided by their distributor gives an indication only and cannot be trusted to be sufficiently accurate. Hence, proper calibration of the double spike composition is required. As it is extremely difficult to obtain an absolute isotope composition, double spikes are typically calibrated relative to a reference material: the $\delta = 0$ reference material for mass-dependent fractionation studies. For Pb double spikes, SRM 982 is commonly used as calibrant, leaving SRM 981 as an independent check of the quality of Pb isotope data (e.g., Thirlwall 2000, Klaver *et al.* 2016).

The calibration of a double spike relative to a reference material is shown in Figure 5; a schematic flowchart with a step-by-step approach is provided in Figure 6. As the calibration of the double spike is made relative to the reference material, the absolute isotope composition of the latter does not need to be known and it is sufficient to constrain the mass fractionation line on which the reference material lies (Rudge *et al.* 2009). The first step of the double spike calibration thus constitutes a precise measurement of the (unspiked) reference material. A first-order IMF correction can be applied by either an internal normalisation to a given ratio (e.g., Ni reference material SRM 986 corrected to $^{61}Ni/^{58}Ni = 0.016744$; Gramlich *et al.* 1989) or by doping with another element for an external estimate of the IMF. This ensures that the corrected composition of the reference material is close to its true value and only offset along the mass fractionation line, which does not introduce a bias in the double spike inversion (see Rudge *et al.* 2009 for a proof).

The next step is calibrating the composition of the double spike itself, which can be addressed in multiple ways but generally requires a measurement of the pure double spike. One can apply an external IMF correction to the pure double spike measurement by doping with another element (e.g., Pd for Mo or Cu for Ni; Siebert *et al.* 2001, Gall *et al.* 2012). The same caveat as for samples (section 2.1) applies here: an external estimate of IMF critically relies on the assumption of identical IMF behaviour between double spike and reference materials. In the absence of a geological matrix in these materials this could be justifiable and a small difference in IMF will not directly have a disastrous effect on the accuracy of double spike data, as discussed below. The second and our preferred approach entails the construction of the mixing line N-T between the double spike and a reference material through the measurement of one or more mixtures of the two (M_k; Figure 5). In theory, only a single mixture M_k is required (in addition to the measurement of the pure double spike) to solve Equation 5 for the composition of the double spike: simply substitute the composition of the reference material for the double spike (i.e., use the reference material as a "quadruple spike") and treat the pure double spike measurement as the unknown sample. A more accurate result can be obtained by measuring multiple mixtures with different proportions of sample to double spike. These mixtures serve to define the *N*-*T* mixing line in four-isotope space; the composition of the double spike lies at the intersection of this mixing line and the mass fractionation line defined by the measurement of the pure double spike (Figure 5). Two mixtures are required to constrain the direction of the *N*-*T* mixing line; the measurement of more mixtures leaves the system overdetermined and a least-squares approach can be used improve the precision with which the direction of the mixing line is determined (Rudge *et al.* 2009). Note that, in isotope systems where the total range of geological variation in mass-dependent isotope fractionation is small, the accuracy of the double spike inversion is largely dependent on how well the direction of the *N*-*T* mixing line is known, rather than the location of the double spike composition on this line (Rudge *et al.* 2009).

5.2. Validation of the calibration and possible biases

Upon calibration of the double spike, it is important to validate the quality of the calibration. Any bias in the double spike calibration should become apparent when a series of mixtures of a quality control material ("secondary standard") is measured at various sample-spike proportions (Figure 6). If the calibration is accurate, the quality control material mixtures should yield the correct value and not show any systematic variation with sample-spike proportion. A constant offset or deviations at high or low double spike proportions in the mixtures flag an issue with the double spike calibration. We will explore the effects of two common sources of uncertainty in the double spike calibration: the effect of blank correction on the pure double spike and reference material measurements and variable IMF between reference material and double spike when applying an external IMF correction. Again, we will use our Ni double spike as an example. This double spike was calibrated relative to reference material SRM 986 using multiple SRM 986-double spike mixtures as described above. The accuracy of the calibration was checked by measuring multiple spiked aliquots of a quality control material (our in-house CPI Ni solution); the results are shown in Figure 7.

Systematic errors in the measurement of the pure double spike are the most likely source of inaccuracies in the double spike calibration. Due to its extremely non-natural isotopic composition and generally low abundance of all but the spike isotopes, correction for the contribution of instrumental background has a pronounced effect on the measured isotopic composition of the double spike. Making blank corrections without introducing a bias can be problematic for isotopic measurement by MC-ICP-MS. Blanks corrections are usually made by subtracting the on-peak intensity measured in the pure solvent, the same as that used for dissolution and dilution of the analyte. The intensities so measured will include: i) trace levels of the analyte and other elements present in the solvent, ii) plasma-generated molecular species and iii) instrument "memory" of previously analysed solutions. In particular, memory effects (iii) are of special concern in the case of double spike measurements because of the variable isotopic composition of the double-spike sample mixtures in combination with a mass-fractionation of the instrumental memory, which is often distinct from the IMF of the analyte. We have modelled, therefore, the effect of over- and under-correcting a) the double-spike composition with an IMF-affected reference material composition and b) the reference material isotopic composition with an IMF-affected double-spike composition. Figure 7 shows that an increasingly inaccurate double-spike inversion results as the proportion of double-spike in the mixture increases and decreases for cases (a) and (b) respectively. The sign and magnitude of the bias are a function of the composition of this blank and the error in correcting for it, but the overall form of the bias, as shown in Figure 7, is independent of these parameters. The magnitude of the bias at a given sample-spike proportion is constant and does not scale with α, meaning that samples spiked in exactly the same proportion will yield results that are correct relative to one another, but will be wrong in an absolute sense; any difference in sample-spike proportion will lead to bias between samples.

For a double-spike calibrated by direct measurement of the pure double-spike and corrected for IMF by sample-standard bracketing, or by internal normalisation by addition of another element, such as Cu in the case of Ni (Gall *et al.* 2012) or Pd for a Mo double spike (Siebert *et al.* 2001), it is likely that the IMF correction will not be accurate. From the mixing equation (4) it is easily shown that the effect of this inaccuracy on the calibration is to offset the apparent sample fractionation α by the same magnitude but with the opposite sign. This effect is independent of the proportion of double-spike in the mixture: all samples and all mixtures are offset the same. Therefore, an external correction may be applied, based on measurements of double-spiked reference materials, or, equivalently, the double-spike calibration can be adjusted.

The measured Ni CPI data in Figure 7 are identical within uncertainty of the mean for sample-spike proportions between ~0.15 and ~0.75. The measurement at p ~0.8 is marginally higher, potentially reflecting a small blank correction-induced inaccuracy in the double spike calibration, but these results give confidence that samples measured at sample-spike proportions <0.7 should yield results with a small uncertainty. Demonstrating constant results for a quality control material over a wide range in sample-spike proportions is vital in validating a double spike method.

5.3. Improving a double spike calibration?

From the discussion above it is evident that the measurement of the pure double spike is likely the weak spot of the calibration. Blank correction has a significant effect on the measured composition and it is questionable to what degree a blank or background correction can be bias-free. In particular for ICP-MS instruments, memory effects can be pronounced and such a background can have a distinctly non-natural composition due to complex mass fractionation effects (e.g., Albarede *et al.* 2004). Bias introduced by the blank correction on the sample-spike mixtures are less of an issue because it induces a translation largely along the sample-spike mixing line, thus hardly influencing the obtained direction of the mixing line. A way to circumvent the need to measure the pure double spike involves a second mixing line between the double spike and a secondary standard with a very different isotopic composition to the primary reference material (Rudge *et al.* 2009). This is illustrated in Figure 5. Multiple mixtures EM_k between the secondary, exotic standard E and the double spike will allow the construction of the secondary mixing line; the double spike composition lies at the intersection between the mixing lines N-T and E-T. This approach requires the use of a secondary standard with a sufficiently exotic composition, potentially by doping with an isotopic spike that is not used in the double spike. Its composition need not be known as long as at least four mixtures (including an unspiked exotic standard) are measured. In theory, this method might yield a more precise double spike calibration as it does not rely on accurately blank-correcting a pure double spike measurement. Practical impedances include the availability of a suitable exotic secondary standard, introducing such a material in the mass spectrometer in the light of possible memory effects and the complicated mathematics required to solve for the intersection of the two mixing lines.

6. Double spike measurement strategies

6.1. General considerations

As long as the isotopic compositions of the double spike and reference material are properly calibrated and any spectral interferences are resolved or corrected for, the double spike method should yield data with a low uncertainty. In practice, however, there might be significant long- and short-term drift caused by external factors such as Faraday cup degradation, magnet instability and tailing from interfering species, clipping of the ion beam and other mass-independent effects (e.g., Albarede *et al.* 2004, Carlson 2014). These effects can be transient in time but, particularly in ICP-MS instruments, surprisingly straightforward to address by adopting sample-standard bracketing as a secondary correction. Bracketing spiked samples with the spiked reference material typically improves the reproducibility of data and counteracts long- and short-term drift: the double spike method accurately corrects for mass fractionation while bracketing resolves additional analytical artefacts. In addition, bracketing with a reference material spiked in a similar fashion as the samples will eliminate some of the potential biases introduced by inaccuracies in the double spike calibration and is hence recommended. The precision of double spike data can be enhanced by improving counting statistics by measuring more intense ion beams (higher analyte concentration) for a longer time. In order to offer the best correction for transient instrument drift, it might be preferable to measure the same sample multiple times bracketed by the spiked reference material, potentially in different measurement sessions, and pool the data of these measurements. In this case, there is a trade-off between analyte and time loss during sample uptake and washout and the improvement in precision.

There is no time-penalty in the use of double spiking as a correction method for IMF in the case of mass-dependent isotope fractionation studies. Once the double spike is calibrated, total integration time per sample need not be different to other correction methods (sample-standard bracketing, doping). Hence, the number of samples that can be measured per day is the same if bracketing is adopted as a secondary correction; if such a secondary correction is not deemed necessary, more samples can be measured per session by double spike than by sample-standard bracketing. In addition, the use of a double spike obviates the need to verify column yields and absence of matrix in the analyte on a sample-by-sample basis, which are clear prerequisites for sample-standard bracketing, and as such presents a significant decrease in analytical time and effort.

Similar to single spikes used in isotope dilution techniques, a double spike measurement can be used to obtain the concentration of the element of interest in a sample. As the sample – double spike mixing parameter (λ) is computed as part of the double spike inversion, it can be used to calculate the amount of the natural element present in the mixture; see Rudge *et al.* (2009) regarding how to convert λ to a molar proportion. This requires that the double spike is calibrated for concentration and careful weighing of the sample and spike contributions to the mixture; the former is easily achieved using a gravimetric solution of the reference material for the double spike calibration.

6.2. Data reduction

Solutions to the double spike equation have been presented in various forms in the literature. The earliest forms are based on a linear mass fractionation law (e.g., Dodson 1963, Hamelin *et al.* 1985) for which the double spike equations can be solved algebraically. Natural and instrumental mass fractionation, however, most closely follow an exponential mass fractionation law (Russell *et al.* 1978). A geometric approach to approximate an exponential law solution was commonly used (e.g., Johnson and Beard 1999) until Albarède and Beard (2004) and Rudge *et al.* (2009) promoted numerical methods to solve the exponential law double spike equation (Equation 4). Rudge *et al.* (2009) presented a detailed guide on how to numerically solve Equation 4 using matrix algebra and a Newton-Raphson iteration, which, following their equations, is easily implemented into a spreadsheet program. Alternatively, the Double Spike Toolbox Matlab code or the Iolite add-in IsoSpike (Creech and Paul 2015) can be used for data reduction.

A mass spectrometric measurement is typically divided into multiple cycles with a discrete integration time (e.g., 50 cycles of 4.2 s integration time yielding a total measurement duration of 210 s). This means that there are two ways to approach data reduction: the double spike inversion can be carried out on a cycle-by-cycle basis after which an average can be calculated for the results of the individual cycles, or the average of the measured cycles can be used in the inversion. In other words, the difference lies in taking an average before or after performing the double spike inversion. If the input data are identical (i.e., no cycles are rejected at any stage), the results of the two approaches should be almost identical and thus we assert no preference for either one. Treating the data on a cycle-by-cycle basis has the advantage that it provides an easy way to assess the uncertainty of a single measurement by taking the standard error of the results for all cycles (Creech and Paul 2015) rather than having to rely on complex linear uncertainty propagation (formulated by Rudge *et al.* 2009) or Monte Carlo approaches.

In the case of our Ni method, we perform all data reduction in an automated offline spreadsheet. Data are corrected for isobaric interference of ^{58}Fe on a cycle-by-cycle basis after which the corrected ratios are screened for outliers (>4 interquartile ranges from the median), which typical originate from memory effects of the introduction system (see Appendix A). We then use the average ratios for the double spike inversion and apply no uncertainty propagation or estimate for individual measurements. Rather, we analyse every sample 6-10 times, bracketed by the spiked SRM 986 reference material, in at least two different measurement sessions and report the average and standard error for these repeat measurements.

6.3. Mass-independent anomalies and double spiking

So far, we have largely focused on the use of the double spike technique to derive the magnitude of natural mass-dependent isotope fractionation relative to a reference material. We reiterate that for this purpose a single measurement of the spiked sample is required; the calibrated reference material is used as the unspiked composition in the double spike inversion. The fundamental assumption of this approach is that the sample and reference material are distinct through mass-dependent fractionation *only* (i.e., they lie on the same mass fractionation line). The presence of mass-independent anomalies, i.e. any isotopic effects that do not obey the assumed fractionation law, will cause a bias in the calculated value of α unless explicitly corrected for (e.g., Hu and Dauphas 2017). In practically all terrestrial applications this condition is met, and a single measurement of the spiked sample is required to solve the double spike equation. Mass-independent anomalies can, however, be present in various forms and particularly so in extra-terrestrial samples (e.g., Dauphas and Schauble 2016). Regardless of the origin of the mass-independent anomalies, however, measuring both a spiked and an unspiked aliquot will always yield the true isotopic composition of a sample. It must be noted that because the double spike is calibrated relative to a reference material, the true isotopic composition so measured is known only as a relative difference from the reference material, but without the restriction of a purely mass-dependent relationship between the two.

The most commonly encountered type of mass-independent anomaly results from the radiogenic ingrowth due to the decay of a long- or a short-lived radioactive parent and affects, for instance, ^{40}Ca, ^{87}Sr and ^{182}W. The magnitude of these radiogenic anomalies can be orders of magnitude larger than natural mass-dependent fractionation of these elements. If it is not possible to exclude the radiogenic isotope as an inversion isotope, separate measurements of the unspiked and spiked sample are required. This allows one to obtain the true isotopic composition and a non-radiogenic isotope pair can subsequently be expressed as a deviation from the reference material (e.g., $\delta^{88/86}$Sr; Krabbenhöft *et al.* 2009, Lewis *et al.* 2017). In the case of Pb where three out of four stable isotopes are radiogenic, two measurements are also required but it is impossible to disentangle the contribution of mass-dependent fractionation from radiogenic anomalies.

Other sources of deviation from mass-dependent fractionation include the nuclear field shift effect, cosmogenic or spallation effects and nucleosynthetic anomalies. Nuclear field shift anomalies result from variations in the shape and size of nuclei as a function of the number of neutrons and are commonly manifested as an odd-even isotope effect. It predominantly affects heavier elements and has been demonstrated for Hg, Tl and U in natural samples (e.g., Dauphas and Schauble 2016). In addition, it can occur during ion-exchange chemistry or measurement (e.g., Fujii *et al.* 2009). For instance, nuclear field shift effects have been invoked to explain the anomalous behaviour of ^{207}Pb above certain filament temperatures in TIMS measurements (e.g., Thirlwall 2000, Amelin *et al.* 2005, Klaver *et al.* 2016). As nuclear field shift effects remain poorly understood, there is no straightforward way to correct potential fractionation during sample processing.

Extra-terrestrial materials often display mass-independent anomalies as a result of cosmogenic and/or nucleosynthetic effects. Meteorites display systematic mass-independent variations resulting from the heterogeneous distribution of the products of stellar nucleosynthesis in the Solar System, roughly as a function of heliocentric distance (e.g., Dauphas 2017, Kruijer *et al.* 2017). In addition, materials exposed in space undergo neutron-capture reactions induced by interactions with cosmic rays, thus producing cosmogenic anomalies. Again, the simplest way to deal with these mass-independent anomalies is to perform a spiked and an unspiked measurement for a sample, but this might not be possible when the amount of sample is limited, such as in the case of precious meteoritic samples, or when contamination of the unspiked sample with double spike during sample preparation or measurement is an issue. In this case, it is still possible to perform some corrections to account for the mass-independent anomalies if additional data are available. For instance, measurements of another element have been successfully used as neutron dosimeter to correct cosmogenic anomalies in the element of interest (e.g., Kruijer *et al.* 2013). When internally-normalised mass-independent data are reported in the literature, ideally for the same meteorite/sample or at least the same meteorite class, these data can be used to correct for nucleosynthetic anomalies given that the these are expressed relative to the same reference material. The most direct approach is to impose the nucleosynthetic anomaly of the sample on the composition of the reference material; this is equivalent to making an unspiked measurement and, in other words, synthesising an unspiked measurement from the reference ratios and mass-independent anomalies. The obtained alternative reference material is related to the sample only by mass-dependent fractionation and can then be used as an input parameter in the double spike inversion to solve for the natural mass-dependent fractionation. Alternatively, one can apply an *a posteriori* correction to double spike data given that the magnitude of the mass-independent anomalies is known (Burkhardt *et al.* 2014, Hu and Dauphas 2017). The latter is likely easier to implement and we found no significant difference between the two methods correcting our mass-dependent Ni data.

6.4. Optimising measurements when sample is limited

In our arguments for choosing an appropriate double spike above, we assumed that an unlimited amount of sample material is available, i.e. one can always hold the total beam intensity constant regardless of the double spike contribution. This is rarely the case and the amount of analyte available for measurement can be relatively small, thus restricting the presumed flexibility in choosing sample-spike proportions. John (2012) suggested that increasing the amount of double spike in excess of the optimum proportion can improve the precision, which might be beneficial when sample-limited. There is some merit to this argument: a higher total beam intensity leads to an improvement in counting statistics, which might exceed the decrease in precision caused by a suboptimal sample-spike proportion. That this is, however, not always the case is illustrated in Figure 8. We modelled the theoretical precision in α as a function of sample-double spike proportion with the Double Spike Toolbox, but instead of adopting a constant total beam intensity we fixed the amount of natural Ni to 0.5 V and varied the amount of double spike added. For our ^{61}Ni-^{62}Ni double spike, precision indeed improves marginally when double spike was added in excess of the optimal proportion (denoted by a star in Figure 8), as found by John (2012), but this is not the case for a hypothetical ^{60}Ni-^{62}Ni spike (the optimal composition based on Oak Ridge single spikes). This makes sense when comparing the behaviour of these spikes at a constant total beam intensity (Figure 4): the ^{60}Ni-^{62}Ni double spike is characterised by a steeper decrease in precision away from the optimum that is not balanced by the improvement in counting statistics obtained through over-spiking. Note that, for a ^{60}Ni-^{62}Ni double spike, over-spiking holds no benefit even when prepared from isotopically pure single spikes. Another important constraint is the trade-off with a potential decrease in accuracy at higher sample-spike proportions as a result of a bias in the double spike calibration (Figure 7). We argue that the marginal gain in precision at high sample-spike proportions is not sufficient to potentially jeopardize the robustness of the data. Hence, we are wary of over-spiking to improve precision unless the accuracy of the double spike data at high sample-spike proportions is explicitly demonstrated.

7. Summary and outlook

The aim of this review article was to demonstrate the usefulness of the double spike method in obtaining reliable mass-dependent isotope data and lowering potential inertia barriers in working with double spikes through a step-by-step discussion. We emphasize that the double spike technique is the only way to eliminate the effects of potential mass-dependent fractionation during sample processing and measurement, given that the double spike is added beforehand. In addition, it is superior to other methods, including sample-standard bracketing, in correcting for fractionation during measurement as it is not susceptible to matrix effects. An external normalisation to spiked reference materials measured alongside the samples can eliminate the effects of long- and short-term instrumental drift and potential inaccuracies in the double spike calibration. With the double spike technique, it has been proven to be possible to measure natural mass-dependent fractionation to an uncertainty better than 20 ppm for elements with at least four isotopes. In the light of the rapid increase in the application of the “non-traditional stable isotopes” in the high-temperature geochemical realm, the use of the double spikes will continue to grow. We envisage that double spiking will rapidly replace sample-standard bracketing as the method of choice for obtaining reliable mass-dependent isotope data.

Although the basics of the double spike technique are well established, there is still room for innovation and potential improvements. With ongoing developments in amplifier technology, measurements of low intensity ion beams will become increasingly precise. This might open possibilities for the use of radioactive spikes that is currently restricted by their cost and/or activity. Elements that are outside the reach of the regular double spike technique might have a radioactive isotope with a sufficiently long half live to allow its use as a spike. In addition, the regular double spike inversion requires three independent isotope ratios. For elements with five or more isotopes, additional independent isotope ratios are available for data reduction but in the present form of the inversion these are not used. There is no theoretical restriction to a 3-dimensional solution of the double spike equation; including more independent isotope ratios will leave the system overdetermined. Although difficult to visualise, a least-squares regression solution in a higher number of dimensions can potentially increase the precision and accuracy of the double spike method. Moreover, in three dimensions no triple spike has been found to be advantageous over a double spike (e.g., Rudge *et al.* 2009), but whether this holds in a higher number of dimensions remains to be investigated.

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Appendix A – Analytical details

All Ni isotope data shown in the figures were collected using a Thermo-Finnigan Neptune multi-collector ICP-MS and a CETAC Aridus introduction system at the University of Bristol. When applicable, samples were spiked prior to ion-exchange purification. All measurements were carried out in medium resolution (m/Δm >6000, 5-95% peak edge definition) to resolve isobaric interferences, notably $^{40}Ar^{18}O^+$ on $^{58}Ni^+$ and trace argide and oxide interference on the other masses. Isobaric interference of ^{58}Fe on ^{58}Ni could not be resolved but was corrected by monitoring $^{56}Fe^+$ and $^{57}Fe^+$ and subtracting IMF-corrected $^{58}Fe^+$ from $^{58}Ni^+$; this correction was found to be robust to at least $^{56}Fe/^{60}Ni \geq 0.6$ while samples had $^{56}Fe/^{60}Ni < 0.15$. Samples were measured at a concentration of total Ni (sample plus double spike) of ~1 µg ml^{-1} in 0.3 mol L^{-1} HNO_3, yielding a total Ni ion beam intensity of 50-85 V on 10^{11} Ω amplifiers compared to a background of <20 mV. Each sample was measured 6-8 times (50 cycles of 4.2 s integration time) in at least two measurement sessions, always bracketed by measurements of double spiked SRM 986 reference material. Results are expressed as $\delta^{60/58}Ni$ relative to this reference material (Equation 5) with a quoted precision that is 2 standard error of the mean of the replicate measurements.

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FIGURE CAPTIONS

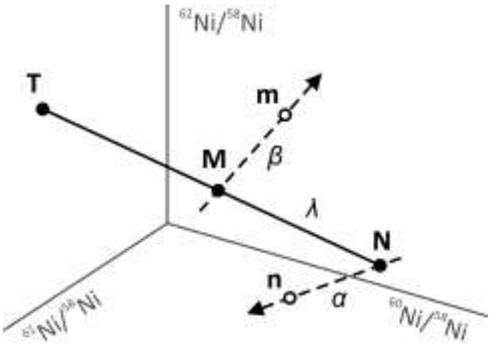

Figure 1. Schematic diagram showing the principle of the double spike technique. In 4-isotope space, using Ni as an example, a natural sample (*N*) and double spike (*T*) have very different compositions. A mixture between the two (*M*) lies on the *N*-*M*-*T* mixing line (mixing parameter λ), but the measured composition of the mixture (*m*) and natural sample (*n*) are displaced along instrumental mass fractionation (IMF) lines *M*-*m* and *N*-*n*, respectively. The form of these IMF lines is known, but the degree of fractionation (mass fractionation parameters α and β) is not. As the composition of the double spike is known, measurement of *n* and *m* is needed to solve the double spike equation to yield α, β and λ, where α can subsequently be used to calculate the true composition *N* of the sample.

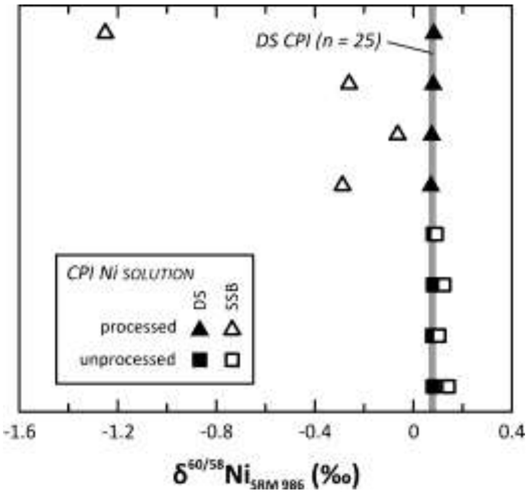

Figure 2. Comparison of double spike (DS) versus sample-standard bracketing (SSB) corrected data for our in-house CPI Ni solution. Data points are the average of 6-8 repeats of the same solution measured in at least two measurement sessions; repeatability precision (2 SE of 6-8 independent measurement results per sample) is smaller than symbol size. The CPI Ni solution is elementally pure and should hence be expected to behave the same as the SRM 986 Ni reference material. The CPI solution was measured without processing, but spiked aliquots were also processed along with samples through the chemical purification protocol. Double spike-reduced data are highly reproducible ($\delta^{60/58}Ni_{SRM\ 986}$ = 0.078 ± 0.015 ‰, 2s, n = 25; grey bar). The double spike inversion yields a value for β (see section 2.2) for every measurement, allowing a correction to be made assuming that IMF is identical for the CPI standard and SRM 986. These pseudo-corrected data (shown as open symbols) therefore show the composition of the CPI standard as if they were corrected through sample-standard bracketing. See text for discussion.

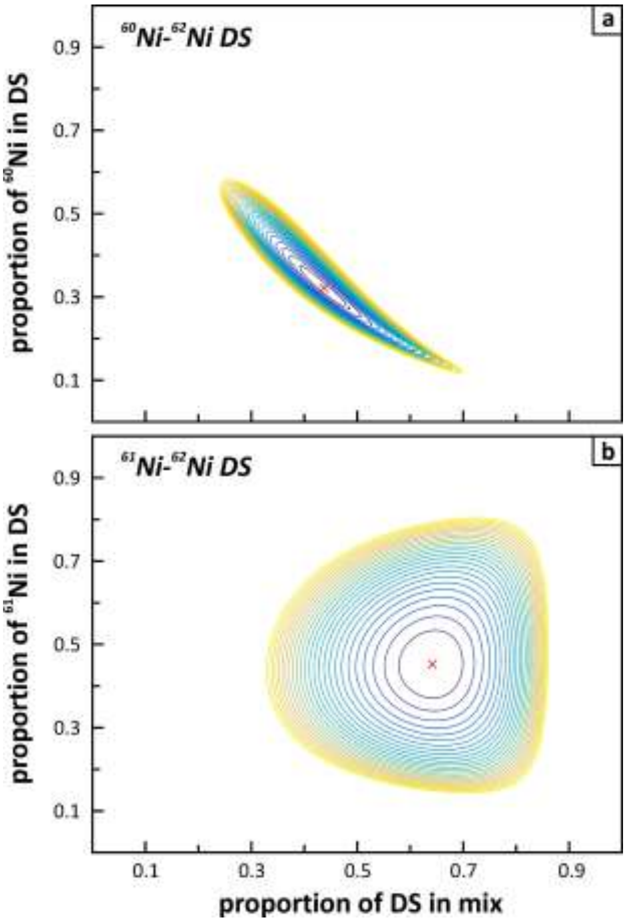

Figure 3. Contour diagram of the theoretical precision in α (see Figure 1) as a function of double spike composition and sample-spike ratio for two different Ni double spikes, generated using the default settings of the precision model in the Double Spike Toolbox (Rudge et al. 2009) and ^{58}Ni, ^{60}Ni, ^{61}Ni and ^{62}Ni as inversion isotopes. The precision decreases from blue to yellow; the optimal composition of the double spike is denoted by the cross. Although a ^{60}Ni-^{62}Ni double spike will yield a slightly higher absolute precision in α at the optimal sample-spike proportion (see Figure 4), its magnification of measurement precision is much more dependent on the sample-spike ratio than for a ^{61}Ni-^{62}Ni double spike.

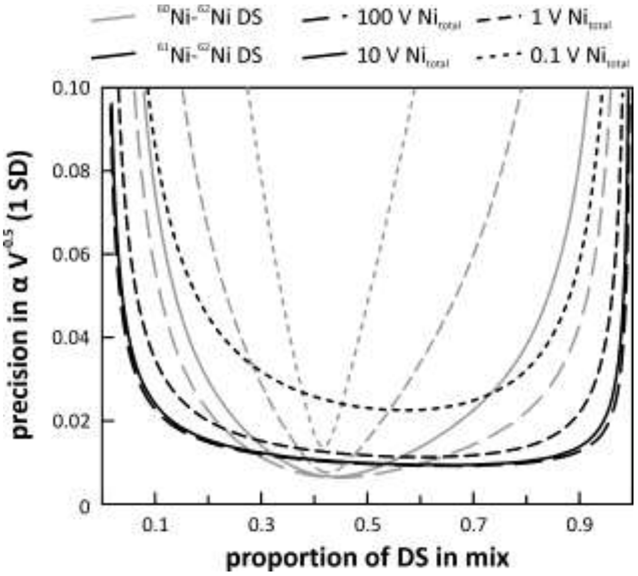

Figure 4. The theoretical precision in α as a function of sample-spike ratio and total beam intensity (in V for 10^{11} Ω amplifier feedback resistors) for the two Ni double spikes (the optimal double spike composition shown in Figure 3), generated using the precision model in the Double Spike Toolbox (Rudge et al. 2009) and ^{58}Ni, ^{60}Ni, ^{61}Ni and ^{62}Ni as inversion isotopes; the default setting of the Toolbox is a 100 pA (10 V) total ion beam intensity, 8 s integration time and 10^{11} Ω amplifier feedback resistors. The precision in α is divided by the square root of the beam intensity to eliminate the effect of shot noise and facilitate comparison of the two double spikes. A ^{61}Ni-^{62}Ni double spike has a broad precision minimum at any total ion beam intensity and hence, near this minimum, the precision in α is not very sensitive to the proportion in which the sample and double spike are mixed, which is ideal if the concentration of either is not well known. A ^{60}Ni-^{62}Ni double spike on the other hand can produce a higher absolute precision for α if double spike and sample are mixed accurately but suffers a lower precision when the sample-spike proportion is suboptimal. This behaviour is compounded at lower beam intensities.

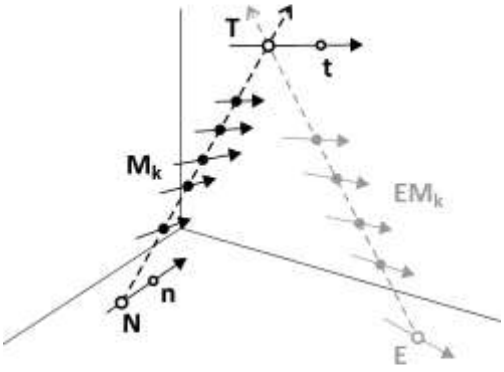

Figure 5. Schematic four-isotope diagram illustrating the calibration of a double spike. Solid arrows indicate mass fractionation lines; dashed arrows mixing lines. The measured composition of a reference material (*n*) and double spike (*t*) is offset from the true values *N* and *T* by IMF. A first-order IMF correction will yield the composition *N*. Multiple mixtures *M*$_k$ (k = 1, 2, …) between *N* and *T* will constrain the direction of the mixing

line *N*-*T*; the calibrated double spike composition is the intersection between the mixing line and the mass fractionation line *t*-*T*. Alternatively, a reference material with an exotic composition (*E*) and mixtures EM_k (k = 1, 2, …) can be used to construct a secondary mixing line *E*-*T* such that the calibrated double spike composition lies at the intersection of mixing lines *N*-*T* and *E*-*T*, thus obviating the need of a pure double spike measurement.

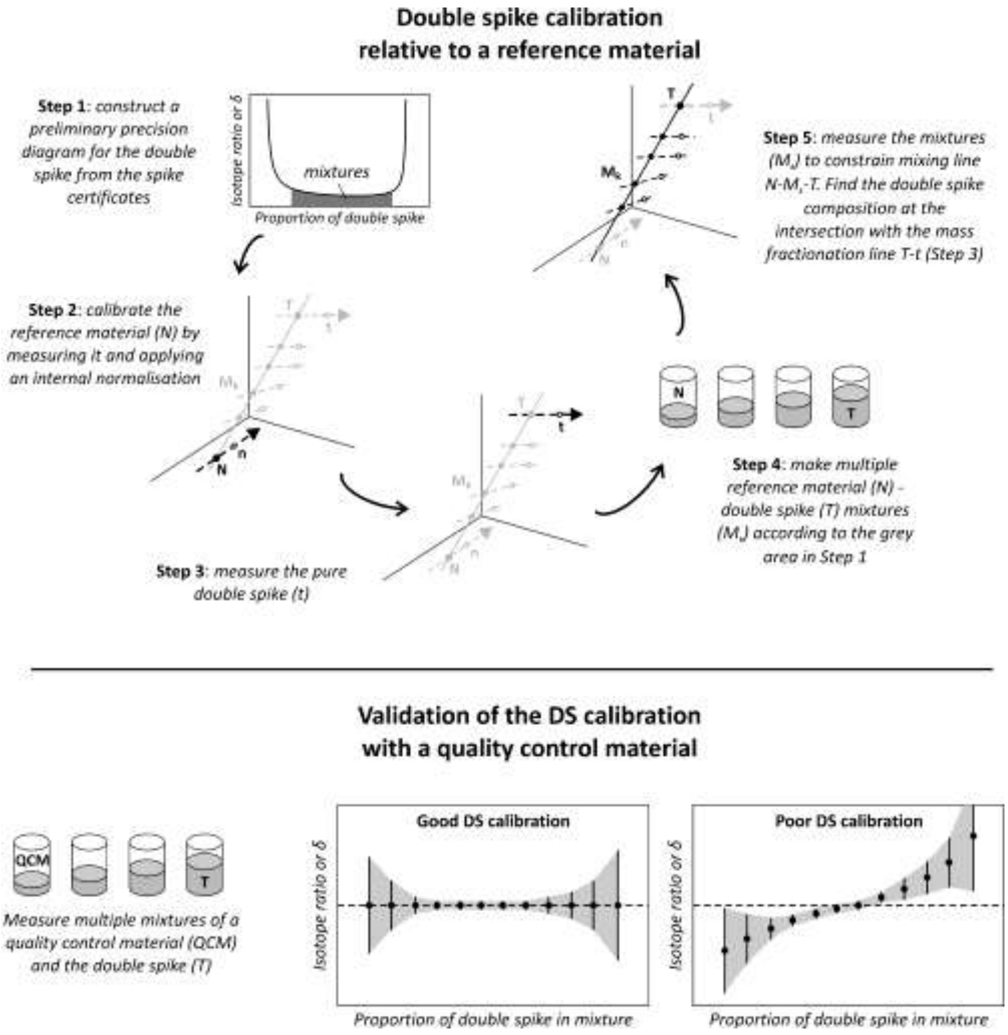

Figure 6. Flowchart diagram for the calibration procedure of a double spike (*T*) against a reference material (*N*) and its validation using a quality control material (QCM).

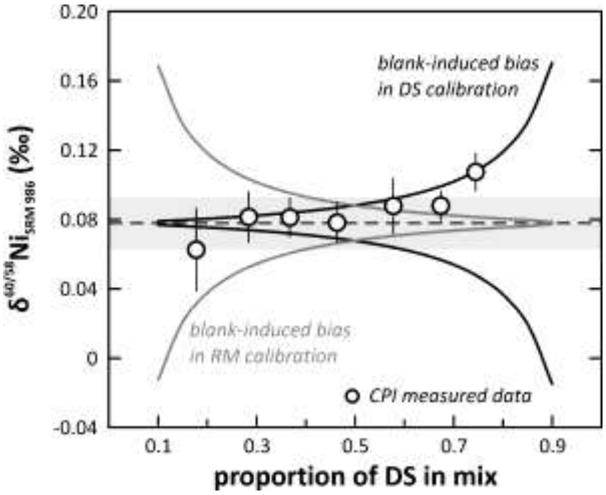

Figure 7. Effects of errors in blank corrections on the accuracy of double spike data. Modelled curves illustrate the effect of under- and over-correcting for blank contribution on the pure reference material (RM; grey curves) and double spike (DS; black curves) compositions. The bias introduced by a DS blank correction error increases at higher double spike proportions; contamination of the pure RM measurement with double spike introduces a bias at low double spike proportions; see main text for more discussion. The in-house CPI Ni solution was measured at different sample-spike proportions and yield results within uncertainty of the intermediate measurement precision (light grey bar) for $0.15 < p < 0.75$; the measurement at p ~0.8 is marginally higher and might indicate a small bias in the double spike calibration.

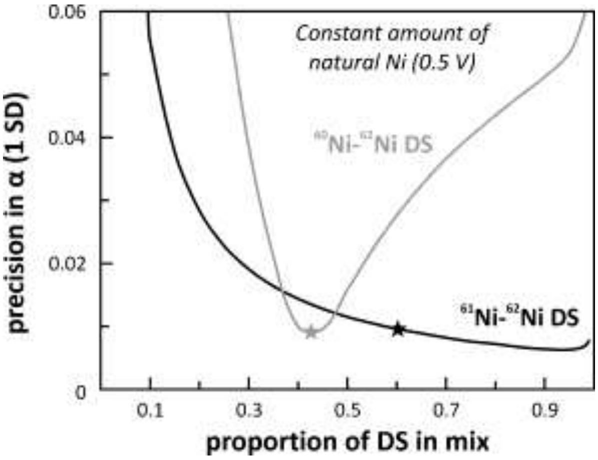

Figure 8. The precision in α as a function of sample-spike ratio and total beam intensity for the two Ni double spikes shown in Figures 3 and 4. Here, the amount of sample is fixed at 0.5 V natural Ni while the amount of double spike added to this sample is varied to obtain different sample-spike proportions. The optimal double spike composition at a total beam intensity of 1 V is indicated by the stars. In the case of a ^{61}Ni-^{62}Ni spike, increasing the amount of spike in the mixture past the optimal proportion at 1 V leads to a marginal improvement in precision, but potentially at the cost of a bias introduced by inaccuracies in the double spike calibration (compare to Figure 6). A ^{60}Ni-^{62}Ni spike does not offer any advantage for over-spiking.