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

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7

8 **ABSTRACT**

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

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

23

24 **1. Introduction**

25 Isotope geochemistry, the study of variation in the isotopic composition of elements, is a key aspect of the
26 Earth Sciences. It has proven to be a crucial tool in establishing major concepts such as absolute dating of
27 geological materials, the formation of the Earth in our solar system and the recycling of the Earth's crust into
28 the mantle through plate tectonics. Traditionally, isotope geochemistry focused on isotopic anomalies arising
29 from the decay of long-lived nuclides, such as the radiogenic ^{87}Rb - ^{87}Sr and ^{238}U - ^{206}Pb systems, and the mass-
30 dependent isotopic fractionation of light elements (H, C, N, O, S) in the low-temperature geochemical realm.
31 The latter, often but inappropriately called stable isotope fractionation, comprises fractionation of isotopes of
32 an element through physicochemical processes as a function of the masses following a limited class of well-
33 known functions (e.g., linear, power and exponential fractionation laws; Bigeleisen and Mayer 1947, Schauble
34 2004, Young *et al.* 2015). Elements heavier than S were traditionally regarded not to show isotopic

35 fractionation in nature due to the small relative mass differences between their isotopes, but at present mass-
36 dependent isotope fractionation has been detected for elements as heavy as Tl (Prytulak *et al.* 2013) and U
37 (Andersen *et al.* 2015). The use of these “non-traditional stable isotopes” has taken flight to address a wide
38 range of research questions across the Earth sciences. In particular, the advent of ICP-MS instruments heralded
39 a new era of increasingly precise isotopic measurements that could, in principle, be applied to every non-
40 monoisotopic, non-gaseous element in the periodic table. Improving the precision (repeatability) of isotopic
41 measurements is relatively straightforward and relies for a large part on optimising counting statistics by longer
42 measurements of higher-intensity ion beams (e.g., Albarede *et al.* 2004). The current levels of measurement
43 precision, however, require a concomitant small bias, meaning the minimisation of (systematic) measurement
44 errors both within and between laboratories, which has proven to be more of a challenge. A strict control on
45 the accuracy of high-precision isotope ratio data is clearly required.

46 The double spike technique, where a tracer consisting of two artificially enriched isotopes is mixed with the
47 sample, provides the most reliable method to obtain accurate isotopic compositions for elements with at least
48 four isotopes (Albarède and Beard 2004, Rudge *et al.* 2009). Its fundamentals were proposed by Dodson
49 (1963), but at first the double spike technique saw little use apart from the application to Pb (e.g., Compston
50 and Oversby 1969, Cumming 1973, Hamelin *et al.* 1985, Galer and Abouchami 1998) and Ca isotope
51 measurements (Russell *et al.* 1978). It took over three decades and a significant increase in measurement
52 precision with new MC-ICP-MS instruments before the geochemical community became aware of the full
53 potential of the double spike technique and the first doubly-spiked studies of mass-dependent fractionation of
54 non-traditional isotopes appeared (e.g., Johnson and Beard 1999), thus vindicating Dodson’s (1963) statement
55 that, with the double spike technique, “*it would be possible in principle to measure precisely the natural*
56 *isotopic fractionation of a large number of polyisotopic elements, for example Mg, Ca, Ti, Cr, Ni, Fe, Mo, Sn*”.

57 Despite the clear advantages, Rudge *et al.* (2009) noted a general hesitation in the implementation of double
58 spike measurement protocols, possibly related to the perceived difficulty of their practical use. Even though
59 ready-to-use data reduction software and spreadsheets are available (e.g., Rudge *et al.* 2009, Creech and Paul
60 2015), designing, making and calibrating a double spike might present a significant inertia barrier. This article
61 aims to lower this barrier by providing a practical guide to double spiking. The solutions to the double spike
62 equations have been presented in various forms in the literature (e.g., Dodson 1963, Russell 1971, Hamelin *et al.*
63 *et al.* 1985, Galer 1999, Johnson and Beard 1999, Siebert *et al.* 2001, Albarede and Beard 2004). The most recent
64 version by Rudge *et al.* (2009) is generally accepted by the geochemical community and we will follow their
65 nomenclature and definitions throughout. As Rudge *et al.* (2009) have published the definitive approach for
66 solving the double spike equation and its uncertainty propagation, and most researchers use publicly available
67 data reduction programs such as the Double Spike Toolbox Matlab code (Rudge *et al.* 2009), we will not delve
68 into a detailed discussion of the mathematics behind double spiking. Rather, we will focus on practical
69 considerations when working with double spikes, aimed at researchers new to the subject. We aim to address
70 questions arising when setting up a mass spectrometry protocol for a new element, including the advantages of
71 double spiking over other corrections methods, how to choose a suitable double spike, ways to calibrate and

72 validate a double spike, etc. To aid the discussion, we will often refer to the new Ni double spike that we
73 recently implemented at the University of Bristol as an example.

74

75 **2. Principles of the double spike technique**

76 **2.1. Instrumental mass fractionation**

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

$$85 \text{ Eq. (1) } N_i = n_i e^{-\alpha P_i}$$

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

97 For radiogenic isotope systems, such as Sr and Nd, internal normalisation eliminates all mass-dependent
98 fractionation, both natural and IMF. In this case the sample is assumed to be fractionated (by a natural process)
99 relative to some reference ratio for a non-radiogenic isotope pair to (e.g., $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$; Nier 1938). During
100 measurement, IMF further fractionates this ratio and the combined effect is rolled into a single value of α , the
101 solution of equation (1), with N set equal to the reference ratio. Thus, the radiogenic isotope ratio (e.g.,
102 $^{87}\text{Sr}/^{86}\text{Sr}$), devoid of all mass-dependent effects and leaving only the radiogenic excess or deficit, is readily
103 determined from the measured ratio and the previously solved-for value of α .

104 When a non-radiogenic isotope pair is not available, notably for Pb, or the magnitude of natural mass-
105 dependent fractionation is investigated, an external method is required to correct for IMF. The most commonly
106 used method is sample-standard bracketing. Here, a reference material (standard) with a known composition is

107 measured alongside the unknown samples and used to monitor IMF. A clear advantage of this approach is that
108 the absolute composition of the reference material need not be known as long as results are expressed as the
109 relative difference of an isotopic ratio (δ notation; Coplen 2011). By alternately measuring the reference
110 material and unknown samples (“bracketing”) and using the mean isotope ratios of the adjacent reference
111 materials to correct the unknown, drift in IMF during the measurement session can be corrected for (Albarede
112 *et al.* 2004). A critical prerequisite for sample-standard bracketing is that samples and reference materials
113 fractionate to the same extent during measurement, which is very difficult to validate as we will discuss below.

114 A third correction method involves doping samples with an element that has at least two interference-free
115 isotopes and a mass close to that of the element of interest to monitor IMF, such as Tl in case of Pb (e.g.,
116 Longerich *et al.* 1987). The isotope composition of the dopant element is presumed to be known and, when
117 one assumes that the magnitude of IMF is the same for elements of similar mass, can be used to correct the
118 IMF of the element of interest. Whether IMF is indeed sufficiently similar for different elements is contentious
119 and doping with another element can produce precise data that are nevertheless inaccurate (e.g., Thirlwall
120 2002, Waight *et al.* 2002, Taylor *et al.* 2015).

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

125 **2.2. The double spike equation**

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

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

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

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

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

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

158 2.3. Double spiking applied to natural mass-dependent fractionation

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

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

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

177 **2.4. Two special cases**

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

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

196

197 **3. The advantages of double spiking**

198 **3.1. Matrix effects and variable mass fractionation**

199 The main advantage of double spiking is that it provides accurate correction for IMF as long as the double spike
200 is properly calibrated. It does not rely on an *a priori* assumption of identical IMF behaviour of samples and
201 reference material – in clear contrast to sample-standard bracketing (SSB). To illustrate this point, we present a
202 comparison between double spike and SSB-corrected $\delta^{60/58}\text{Ni}$ data, obtained by MC-ICP-MS (see Appendix A),
203 for the same measurements of a pure Ni solution in Figure 2. Because the double spike inversion yields a value
204 for β (the magnitude of the IMF) for every measurement, double spike corrected data can be re-corrected
205 assuming constant IMF between samples and the reference material as in SSB. Repeated double spike
206 measurements of a pure Ni solution (our in-house CPI Ni solution) yield results with a high intermediate
207 measurement precision. Correcting the same data through SSB leads to more scatter of the data points and
208 introduces a bias compared to the double spike results. This is particularly evident in the case of CPI standards
209 processed through the chemical separation procedure: whereas double spike-corrected results are
210 indistinguishable from unprocessed CPI solutions, SSB-corrected data can yield over 1 ‰ lower $\delta^{60/58}\text{Ni}$ values.
211 This is a significant effect considering that natural variations in Ni isotopes are often <0.1 ‰. Clearly, the
212 requirement of identical IMF of the reference material and processed CPI standards is not met. In this case, the

213 likely cause is residual organic material (from the dimethylglyoxime used to elute Ni) in the processed Ni
214 solutions. The presence of a small amount of matrix (any element or compound other than the one of interest)
215 in samples can affect plasma conditions to such an extent that the IMF behaviour becomes significantly
216 different compared to the matrix-free reference material. Such matrix effects are very common and very hard
217 to systematically suppress (e.g., Barling and Weis 2008, Tipper *et al.* 2008, Shiel *et al.* 2009, van den Boorn *et*
218 *al.* 2009, Nan *et al.* 2015, Peters *et al.* 2015), making it extremely difficult to obtain bias-free isotope data
219 through sample-standard bracketing. Strikingly, the repeatability measurement precision (the 2 SE of the mean
220 of 6-8 independent measurement results) is only a factor ~3 worse than for the DS-corrected data, indicating
221 that SSB can induce a significant measurement bias yet yield relatively precise results, with the high precision
222 potentially giving a false sense of security. The double spike method, on the other hand, has no trouble dealing
223 with these matrix effects and produces accurate results.

224 **3.2. Correcting for fractionation during chemical purification**

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

244

245 **4. Designing a double spike**

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

249 Obviously, one would prefer a double spike that produces the best possible precision, either in a ratio of
250 interest (e.g., $^{207}\text{Pb}/^{204}\text{Pb}$) or in α when natural mass-dependent fractionation is investigated. Rudge *et al.*
251 (2009) included a model in their Double Spike Toolbox that can be used to calculate the theoretical precision in
252 α or an isotope ratio for a wide range of variable parameters. Briefly, their precision model is based on linear
253 propagation of the variance associated with the measurement of ion beam intensities: i) thermal noise of the
254 resistors fitted in the amplifier feedback loop of the Faraday detectors (Johnson-Nyquist noise) and ii) counting
255 statistics of the ion beam intensities (Poisson or shot noise; see e.g., Albaredo *et al.* 2004). If the double spike is
256 calibrated perfectly, the double spike inversion does not introduce a bias and only leads to magnification of the
257 measurement precision. As such, the precision model provides a theoretical limit on the highest precision that
258 can be achieved for a given total ion beam intensity and integration time.

259 A double spike that leads to minimal magnification of the measurement precision is considered optimal and a
260 “cocktail list” of double spikes that yield the highest theoretical precision is provided by Rudge *et al.* (2009). We
261 strongly prefer their approach of linear propagation of variances to assess the performance of a double spike
262 over geometrical methods proposed by e.g., Galer (1999) and Johnson and Beard (1999). The latter predict that
263 the precision of a double spike solution is dependent on the choice of denominator isotope in the ratios used in
264 the double spike inversion. Because mixing and mass fractionation processes are coordinate-independent,
265 there is no physical basis for the choice of denominator isotope to have any effect, as discussed by Rudge *et al.*
266 (2009).

267 There are several factors that can influence the choice of the isotopes used in a double spike and, in the case of
268 elements with five or more isotopes, the four isotopes used in the double spike inversion. Selecting the four
269 inversion isotopes should be the first step in choosing an appropriate double spike: the same double spike can
270 perform better or worse depending on the choice of inversion isotopes. The presence of isobaric interferences
271 can make some isotopes less suitable as an inversion isotope. In the case of Ni, five stable isotopes are
272 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.*
273 1989). We decided to avoid the use of ^{64}Ni as it suffers from isobaric interference by a major isotope of Zn (^{64}Zn
274 has an abundance of 48.6 %; Rosman 1972), even though double spikes with ^{64}Ni yield the best possible
275 precision. It is difficult to quantitatively remove Zn from samples as it is a common contaminant in labware and
276 the environment. Correction for Zn interference is possible but undesirable as monitoring ^{66}Zn would require a
277 magnet jump in the method and thus consume time and analyte. Hence, we have opted to exclude ^{64}Ni and use
278 ^{58}Ni , ^{60}Ni , ^{61}Ni and ^{62}Ni as inversion isotopes. Isobaric interferences have also affected the choice of, for
279 instance, Mo (Siebert *et al.* 2001) Cd (Ripperger and Rehkämper 2007) and Pt (Creech *et al.* 2013) inversion
280 isotopes. In addition to isobaric interferences, the presence of nucleosynthetic anomalies in extra-terrestrial
281 materials can also be taken into account when choosing the four inversion isotopes (e.g., Millet and Dauphas
282 2014).

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

286 Rudge *et al.* (2009) to generate contour diagrams of the precision in α as a function of double spike
287 composition and the proportion of spike in the sample-spike mixture for two different double spikes (Figure 3).
288 Excluding ^{64}Ni , a ^{60}Ni - ^{62}Ni double spike yields the best possible precision, albeit only marginally better than a
289 ^{61}Ni - ^{62}Ni spike. The performance of the ^{60}Ni - ^{62}Ni spike, however, is much more dependent on getting the
290 sample-spike proportion exactly right: a small deviation from the optimal sample-spike proportion leads to a
291 significant decrease in precision. If the double spike deviates from the optimal composition, this becomes even
292 more pertinent. On the other hand, the ^{61}Ni - ^{62}Ni spike has a broad precision minimum with very little
293 deterioration in precision over a wide range in the sample-spike ratio. Versatility of a double spike in terms of
294 sample-spike proportion is desirable, in particular when the concentration of the element in the double spike
295 or, more likely, the sample is poorly known. As such, we preferred the use of a ^{61}Ni - ^{62}Ni double spike.

296 The default precision model of the Double Spike Toolbox employs a total beam intensity for the four inversion
297 isotopes of 100 pA (10 V), integration time of 8 s and a $10^{11} \Omega$ amplifier feedback resistor. These measurement
298 conditions are typical for MC-ICP-MS and TIMS measurements, but if the double spike method will be applied
299 to much larger or smaller sample sizes it is worth investigating the effect of total beam intensity on the
300 expected precision. Figure 4 shows the precision in α as a function of sample-spike proportion for two Ni
301 double spikes at a total beam intensity that varies by three orders of magnitude. The broad precision minimum
302 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
303 contrast, the deterioration in the precision when moving away from the optimal sample-spike proportion is
304 more acute for the ^{60}Ni - ^{62}Ni double spike although the best possible precision is always higher than for the ^{61}Ni -
305 ^{62}Ni double spike. Thus, use of a ^{60}Ni - ^{62}Ni double spike would require more stringent control on mixing of
306 sample and double spike in the optimal proportion, in particular for small sample sizes. If only a small amount
307 of sample is available, one might not want to sacrifice an aliquot for concentration measurement prior to
308 spiking and hence one would have to rely on published or estimated concentration data for the element of
309 interest. In such a case, a versatile double spike with a wide precision minimum is preferable as it allows for
310 significant deviation from the optimal sample-spike proportion without suffering a large decrease in precision.
311 Another argument for choosing the ^{61}Ni - ^{62}Ni spike is that it boosts the intensity of the minor ^{61}Ni isotope (1.14
312 % abundance). Although the precision model of Rudge *et al.* (2009) incorporates the Johnson-Nyquist noise
313 that is the dominant source of predictable variance at low beam intensities, it does not take into account
314 unpredictable, non-proportional effects, such as the variable effects of background and blank corrections on
315 minor isotopes, which diminish at higher beam intensities.

316 A final consideration is the required purity of the single spikes and their cost. Optimal double spikes commonly
317 include at least one minor (<5 % abundance) isotope of the element (Rudge *et al.* 2009) and the cost of single
318 spikes is typically higher for isotopes with a low abundance in nature and increases with the enrichment factor
319 of an isotope. Although the double spike technique does not critically rely on high purity single spikes as do
320 isotope dilution methods (e.g., Stracke *et al.* 2014), the enrichment factor of the single spikes does have some
321 influence on the versatility of a double spike and the precision that can be obtained. If reliable IMF correction is
322 required but not the highest possible precision, it might be cost-efficient to opt for less-enriched single spikes

323 of isotopes with a reasonably high natural abundance. Moreover, a double spike with a low proportion of spike
324 in the optimal sample-spike mixture allows more measurements for a given quantity of double spike. The
325 Double Spike Toolbox precision model allows the spike compositions to be varied so that the effects of single
326 spike purity on the performance of double spikes can be investigated for a specific application.

327

328 **5. Calibrating a double spike**

329 **5.1. Calibration relative to a reference material**

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

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

350 The next step is calibrating the composition of the double spike itself, which can be addressed in multiple ways
351 but generally requires a measurement of the pure double spike. One can apply an external IMF correction to
352 the pure double spike measurement by doping with another element (e.g., Pd for Mo or Cu for Ni; Siebert *et al.*
353 2001, Gall *et al.* 2012). The same caveat as for samples (section 2.1) applies here: an external estimate of IMF
354 critically relies on the assumption of identical IMF behaviour between double spike and reference materials. In
355 the absence of a geological matrix in these materials this could be justifiable and a small difference in IMF will
356 not directly have a disastrous effect on the accuracy of double spike data, as discussed below. The second and
357 our preferred approach entails the construction of the mixing line N - T between the double spike and a
358 reference material through the measurement of one or more mixtures of the two (M_k ; Figure 5). In theory, only

359 a single mixture M_k is required (in addition to the measurement of the pure double spike) to solve Equation 5
360 for the composition of the double spike: simply substitute the composition of the reference material for the
361 double spike (i.e., use the reference material as a “quadruple spike”) and treat the pure double spike
362 measurement as the unknown sample. A more accurate result can be obtained by measuring multiple mixtures
363 with different proportions of sample to double spike. These mixtures serve to define the N - T mixing line in
364 four-isotope space; the composition of the double spike lies at the intersection of this mixing line and the mass
365 fractionation line defined by the measurement of the pure double spike (Figure 5). Two mixtures are required
366 to constrain the direction of the N - T mixing line; the measurement of more mixtures leaves the system
367 overdetermined and a least-squares approach can be used improve the precision with which the direction of
368 the mixing line is determined (Rudge *et al.* 2009). Note that, in isotope systems where the total range of
369 geological variation in mass-dependent isotope fractionation is small, the accuracy of the double spike
370 inversion is largely dependent on how well the direction of the N - T mixing line is known, rather than the
371 location of the double spike composition on this line (Rudge *et al.* 2009).

372 **5.2. Validation of the calibration and possible biases**

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

385 Systematic errors in the measurement of the pure double spike are the most likely source of inaccuracies in the
386 double spike calibration. Due to its extremely non-natural isotopic composition and generally low abundance of
387 all but the spike isotopes, correction for the contribution of instrumental background has a pronounced effect
388 on the measured isotopic composition of the double spike. Making blank corrections without introducing a bias
389 can be problematic for isotopic measurement by MC-ICP-MS. Blanks corrections are usually made by
390 subtracting the on-peak intensity measured in the pure solvent, the same as that used for dissolution and
391 dilution of the analyte. The intensities so measured will include: i) trace levels of the analyte and other
392 elements present in the solvent, ii) plasma-generated molecular species and iii) instrument “memory” of
393 previously analysed solutions. In particular, memory effects (iii) are of special concern in the case of double
394 spike measurements because of the variable isotopic composition of the double-spike sample mixtures in
395 combination with a mass-fractionation of the instrumental memory, which is often distinct from the IMF of the

396 analyte. We have modelled, therefore, the effect of over- and under-correcting a) the double-spike
397 composition with an IMF-affected reference material composition and b) the reference material isotopic
398 composition with an IMF-affected double-spike composition. Figure 7 shows that an increasingly inaccurate
399 double-spike inversion results as the proportion of double-spike in the mixture increases and decreases for
400 cases (a) and (b) respectively. The sign and magnitude of the bias are a function of the composition of this
401 blank and the error in correcting for it, but the overall form of the bias, as shown in Figure 7, is independent of
402 these parameters. The magnitude of the bias at a given sample-spike proportion is constant and does not scale
403 with α , meaning that samples spiked in exactly the same proportion will yield results that are correct relative to
404 one another, but will be wrong in an absolute sense; any difference in sample-spike proportion will lead to bias
405 between samples.

406 For a double-spike calibrated by direct measurement of the pure double-spike and corrected for IMF by
407 sample-standard bracketing, or by internal normalisation by addition of another element, such as Cu in the
408 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
409 will not be accurate. From the mixing equation (4) it is easily shown that the effect of this inaccuracy on the
410 calibration is to offset the apparent sample fractionation α by the same magnitude but with the opposite sign.
411 This effect is independent of the proportion of double-spike in the mixture: all samples and all mixtures are
412 offset the same. Therefore, an external correction may be applied, based on measurements of double-spiked
413 reference materials, or, equivalently, the double-spike calibration can be adjusted.

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

420 **5.3. Improving a double spike calibration?**

421 From the discussion above it is evident that the measurement of the pure double spike is likely the weak spot
422 of the calibration. Blank correction has a significant effect on the measured composition and it is questionable
423 to what degree a blank or background correction can be bias-free. In particular for ICP-MS instruments,
424 memory effects can be pronounced and such a background can have a distinctly non-natural composition due
425 to complex mass fractionation effects (e.g., Albarede *et al.* 2004). Bias introduced by the blank correction on
426 the sample-spike mixtures are less of an issue because it induces a translation largely along the sample-spike
427 mixing line, thus hardly influencing the obtained direction of the mixing line. A way to circumvent the need to
428 measure the pure double spike involves a second mixing line between the double spike and a secondary
429 standard with a very different isotopic composition to the primary reference material (Rudge *et al.* 2009). This
430 is illustrated in Figure 5. Multiple mixtures EM_k between the secondary, exotic standard E and the double spike
431 will allow the construction of the secondary mixing line; the double spike composition lies at the intersection
432 between the mixing lines $N-T$ and $E-T$. This approach requires the use of a secondary standard with a

433 sufficiently exotic composition, potentially by doping with an isotopic spike that is not used in the double spike.
434 Its composition need not be known as long as at least four mixtures (including an unspiked exotic standard) are
435 measured. In theory, this method might yield a more precise double spike calibration as it does not rely on
436 accurately blank-correcting a pure double spike measurement. Practical impedances include the availability of
437 a suitable exotic secondary standard, introducing such a material in the mass spectrometer in the light of
438 possible memory effects and the complicated mathematics required to solve for the intersection of the two
439 mixing lines.

440

441 **6. Double spike measurement strategies**

442 **6.1. General considerations**

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

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

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

475 **6.2. Data reduction**

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

486 A mass spectrometric measurement is typically divided into multiple cycles with a discrete integration time
487 (e.g., 50 cycles of 4.2 s integration time yielding a total measurement duration of 210 s). This means that there
488 are two ways to approach data reduction: the double spike inversion can be carried out on a cycle-by-cycle
489 basis after which an average can be calculated for the results of the individual cycles, or the average of the
490 measured cycles can be used in the inversion. In other words, the difference lies in taking an average before or
491 after performing the double spike inversion. If the input data are identical (i.e., no cycles are rejected at any
492 stage), the results of the two approaches should be almost identical and thus we assert no preference for
493 either one. Treating the data on a cycle-by-cycle basis has the advantage that it provides an easy way to assess
494 the uncertainty of a single measurement by taking the standard error of the results for all cycles (Creech and
495 Paul 2015) rather than having to rely on complex linear uncertainty propagation (formulated by Rudge *et al.*
496 2009) or Monte Carlo approaches.

497 In the case of our Ni method, we perform all data reduction in an automated offline spreadsheet. Data are
498 corrected for isobaric interference of ^{58}Fe on a cycle-by-cycle basis after which the corrected ratios are
499 screened for outliers (>4 interquartile ranges from the median), which typically originate from memory effects of
500 the introduction system (see Appendix A). We then use the average ratios for the double spike inversion and
501 apply no uncertainty propagation or estimate for individual measurements. Rather, we analyse every sample 6-
502 10 times, bracketed by the spiked SRM 986 reference material, in at least two different measurement sessions
503 and report the average and standard error for these repeat measurements.

504 6.3. Mass-independent anomalies and double spiking

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

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

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

538 Extra-terrestrial materials often display mass-independent anomalies as a result of cosmogenic and/or
539 nucleosynthetic effects. Meteorites display systematic mass-independent variations resulting from the
540 heterogeneous distribution of the products of stellar nucleosynthesis in the Solar System, roughly as a function

541 of heliocentric distance (e.g., Dauphas 2017, Kruijer *et al.* 2017). In addition, materials exposed in space
542 undergo neutron-capture reactions induced by interactions with cosmic rays, thus producing cosmogenic
543 anomalies. Again, the simplest way to deal with these mass-independent anomalies is to perform a spiked and
544 an unspiked measurement for a sample, but this might not be possible when the amount of sample is limited,
545 such as in the case of precious meteoritic samples, or when contamination of the unspiked sample with double
546 spike during sample preparation or measurement is an issue. In this case, it is still possible to perform some
547 corrections to account for the mass-independent anomalies if additional data are available. For instance,
548 measurements of another element have been successfully used as neutron dosimeter to correct cosmogenic
549 anomalies in the element of interest (e.g., Kruijer *et al.* 2013). When internally-normalised mass-independent
550 data are reported in the literature, ideally for the same meteorite/sample or at least the same meteorite class,
551 these data can be used to correct for nucleosynthetic anomalies given that these are expressed relative to
552 the same reference material. The most direct approach is to impose the nucleosynthetic anomaly of the sample
553 on the composition of the reference material; this is equivalent to making an unspiked measurement and, in
554 other words, synthesising an unspiked measurement from the reference ratios and mass-independent
555 anomalies. The obtained alternative reference material is related to the sample only by mass-dependent
556 fractionation and can then be used as an input parameter in the double spike inversion to solve for the natural
557 mass-dependent fractionation. Alternatively, one can apply an *a posteriori* correction to double spike data
558 given that the magnitude of the mass-independent anomalies is known (Burkhardt *et al.* 2014, Hu and Dauphas
559 2017). The latter is likely easier to implement and we found no significant difference between the two methods
560 correcting our mass-dependent Ni data.

561 **6.4. Optimising measurements when sample is limited**

562 In our arguments for choosing an appropriate double spike above, we assumed that an unlimited amount of
563 sample material is available, i.e. one can always hold the total beam intensity constant regardless of the double
564 spike contribution. This is rarely the case and the amount of analyte available for measurement can be
565 relatively small, thus restricting the presumed flexibility in choosing sample-spike proportions. John (2012)
566 suggested that increasing the amount of double spike in excess of the optimum proportion can improve the
567 precision, which might be beneficial when sample-limited. There is some merit to this argument: a higher total
568 beam intensity leads to an improvement in counting statistics, which might exceed the decrease in precision
569 caused by a suboptimal sample-spike proportion. That this is, however, not always the case is illustrated in
570 Figure 8. We modelled the theoretical precision in α as a function of sample-double spike proportion with the
571 Double Spike Toolbox, but instead of adopting a constant total beam intensity we fixed the amount of natural
572 Ni to 0.5 V and varied the amount of double spike added. For our ^{61}Ni - ^{62}Ni double spike, precision indeed
573 improves marginally when double spike was added in excess of the optimal proportion (denoted by a star in
574 Figure 8), as found by John (2012), but this is not the case for a hypothetical ^{60}Ni - ^{62}Ni spike (the optimal
575 composition based on Oak Ridge single spikes). This makes sense when comparing the behaviour of these
576 spikes at a constant total beam intensity (Figure 4): the ^{60}Ni - ^{62}Ni double spike is characterised by a steeper
577 decrease in precision away from the optimum that is not balanced by the improvement in counting statistics

578 obtained through over-spiking. Note that, for a ^{60}Ni - ^{62}Ni double spike, over-spiking holds no benefit even when
579 prepared from isotopically pure single spikes. Another important constraint is the trade-off with a potential
580 decrease in accuracy at higher sample-spike proportions as a result of a bias in the double spike calibration
581 (Figure 7). We argue that the marginal gain in precision at high sample-spike proportions is not sufficient to
582 potentially jeopardize the robustness of the data. Hence, we are wary of over-spiking to improve precision
583 unless the accuracy of the double spike data at high sample-spike proportions is explicitly demonstrated.

584

585 **7. Summary and outlook**

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

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

612

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621

622 **Appendix A – Analytical details**

623

624 All Ni isotope data shown in the figures were collected using a Thermo-Finnigan Neptune multi-collector ICP-
625 MS and a CETAC Aridus introduction system at the University of Bristol. When applicable, samples were spiked
626 prior to ion-exchange purification. All measurements were carried out in medium resolution ($m/\Delta m > 6000$, 5-
627 95% peak edge definition) to resolve isobaric interferences, notably $^{40}\text{Ar}^{18}\text{O}^+$ on $^{58}\text{Ni}^+$ and trace argide and oxide
628 interference on the other masses. Isobaric interference of ^{58}Fe on ^{58}Ni could not be resolved but was corrected
629 by monitoring $^{56}\text{Fe}^+$ and $^{57}\text{Fe}^+$ and subtracting IMF-corrected $^{58}\text{Fe}^+$ from $^{58}\text{Ni}^+$; this correction was found to be
630 robust to at least $^{56}\text{Fe}/^{60}\text{Ni} \geq 0.6$ while samples had $^{56}\text{Fe}/^{60}\text{Ni} < 0.15$. Samples were measured at a concentration
631 of total Ni (sample plus double spike) of $\sim 1 \mu\text{g ml}^{-1}$ in $0.3 \text{ mol L}^{-1} \text{ HNO}_3$, yielding a total Ni ion beam intensity of
632 50-85 V on $10^{11} \Omega$ amplifiers compared to a background of $< 20 \text{ mV}$. Each sample was measured 6-8 times (50
633 cycles of 4.2 s integration time) in at least two measurement sessions, always bracketed by measurements of
634 double spiked SRM 986 reference material. Results are expressed as $\delta^{60/58}\text{Ni}$ relative to this reference material
635 (Equation 5) with a quoted precision that is 2 standard error of the mean of the replicate measurements.

636

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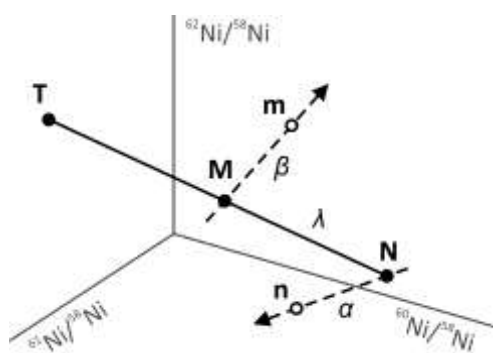
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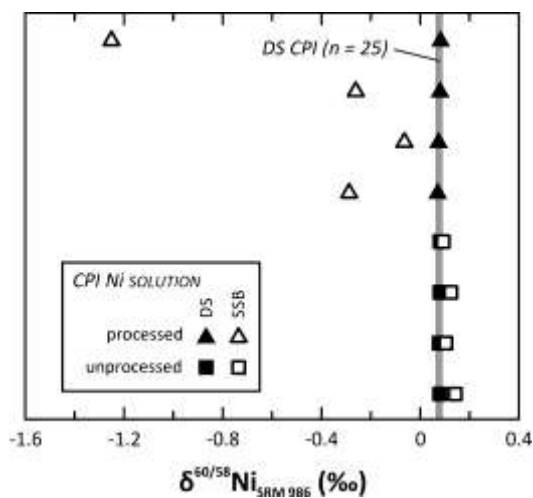
768 **FIGURE CAPTIONS**



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

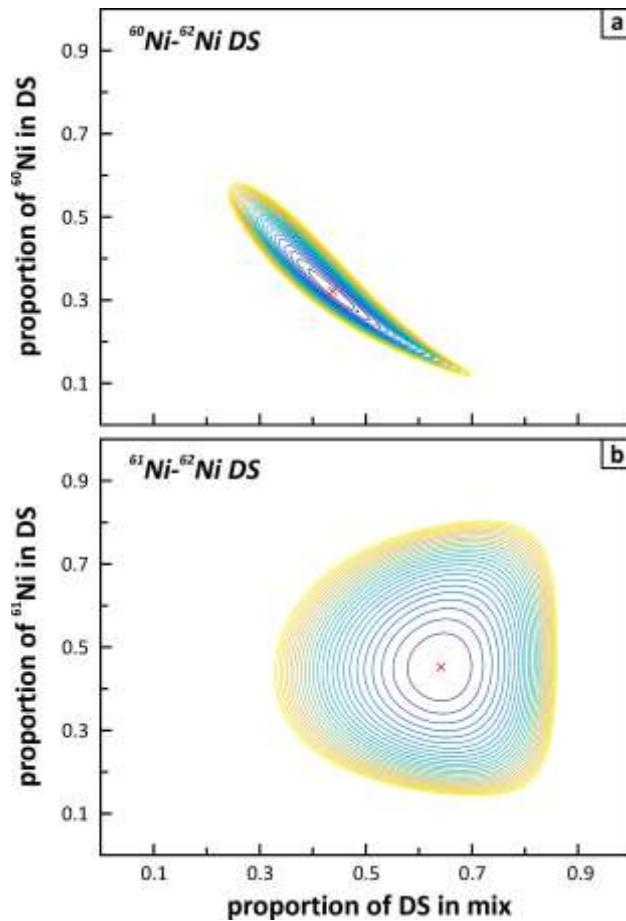
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780 **Figure 2.** Comparison of double spike (DS) versus sample-standard bracketing (SSB) corrected data for our in-
 781 house CPI Ni solution. Data points are the average of 6-8 repeats of the same solution measured in at least two
 782 measurement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

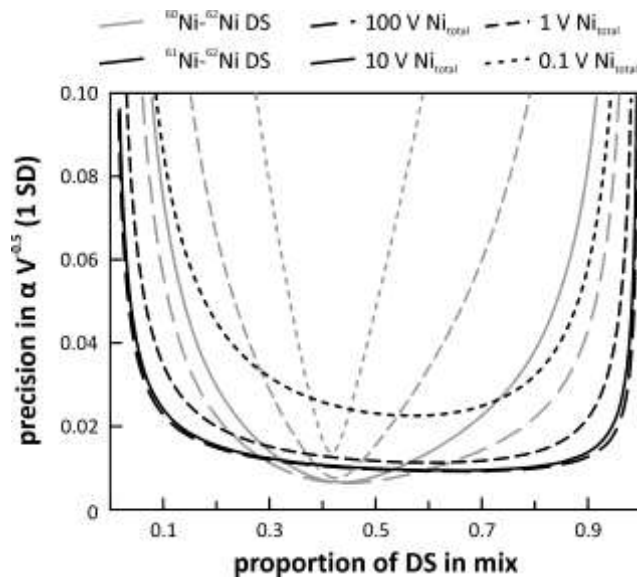
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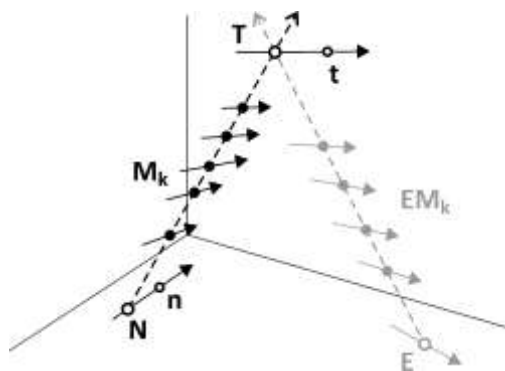
793 **Figure 3.** Contour diagram of the theoretical precision in α (see Figure 1) as a function of double spike
 794 composition and sample-spike ratio for two different Ni double spikes, generated using the default settings of
 795 the precision model in the Double Spike Toolbox (Rudge et al. 2009)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

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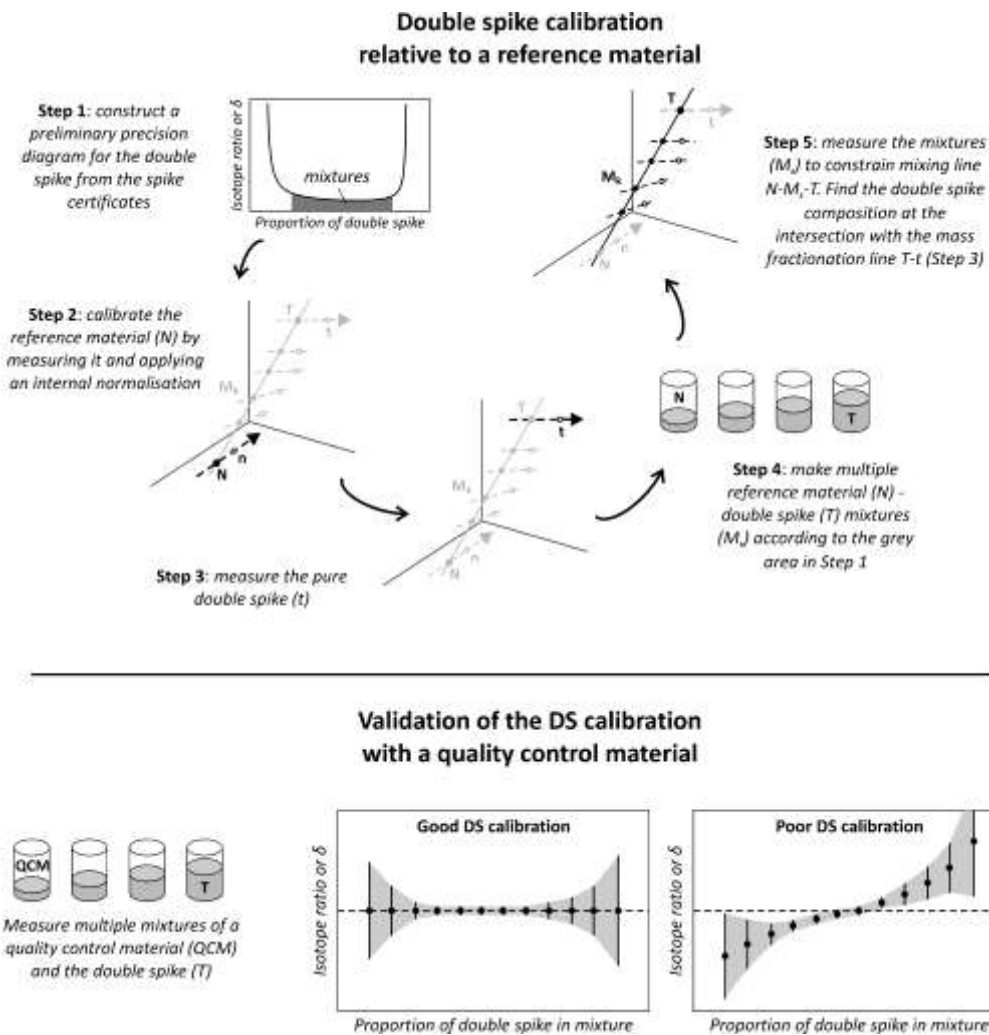
Figure 4. The theoretical precision in α as a function of sample-spike ratio and total beam intensity (in V for $10^{11} \Omega$ amplifier feedback resistors) for the two Ni double spikes (the optimal double spike composition shown in Figure 3), generated using the precision model in the Double Spike 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 $10^{11} \Omega$ 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.



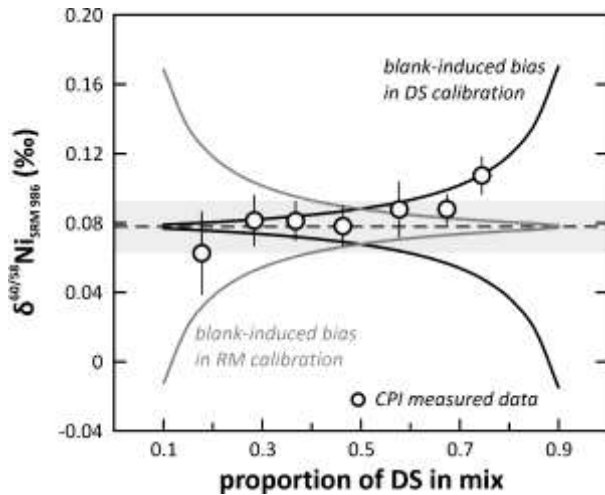
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Figure 5. Schematic four-isotope diagram illustrating the calibration of a double spike. Solid arrows indicate mass fractionation lines; dashed arrows mixing lines. The measured composition of a reference material (n) and double spike (t) is offset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

820 line $N-T$; the calibrated double spike composition is the intersection between the mixing line and the mass
 821 fractionation line $t-T$. Alternatively, a reference material with an exotic composition (E) and mixtures EM_k ($k = 1,$
 822 $2, \dots$) can be used to construct a secondary mixing line $E-T$ such that the calibrated double spike composition
 823 lies at the intersection of mixing lines $N-T$ and $E-T$, thus obviating the need of a pure double spike
 824 measurement.
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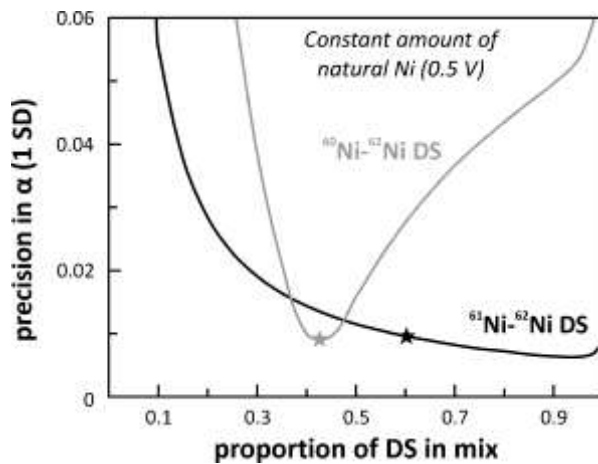
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 827 **Figure 6.** Flowchart diagram for the calibration procedure of a double spike (T) against a reference material (N)
 828 and its validation using a quality control material (QCM).
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831 **Figure 7.** Effects of errors in blank corrections on the accuracy of double spike data. Modelled curves illustrate
 832 the effect of under- and over-correcting for blank contribution on the pure reference material (RM; grey
 833 curves) and double spike (DS; black curves) compositions. The bias introduced by a DS blank correction error
 834 increases at higher double spike proportions; contamination of the pure RM measurement with double spike
 835 introduces a bias at low double spike proportions; see main text for more discussion. The in-house CPI Ni
 836 solution was measured at different sample-spike proportions and yield results within uncertainty of the
 837 intermediate measurement precision (light grey bar) for $0.15 < p < 0.75$; the measurement at $p \sim 0.8$ is
 838 marginally higher and might indicate a small bias in the double spike calibration.

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841 **Figure 8.** The precision in α as a function of sample-spike ratio and total beam intensity for the two Ni double
 842 spikes shown in Figures 3 and 4. Here, the amount of sample is fixed at 0.5 V natural Ni while the amount of
 843 double spike added to this sample is varied to obtain different sample-spike proportions. The optimal double
 844 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,
 845 increasing the amount of spike in the mixture past the optimal proportion at 1 V leads to a marginal
 846 improvement in precision, but potentially at the cost of a bias introduced by inaccuracies in the double spike
 847 calibration (compare to Figure 6). A ^{60}Ni - ^{62}Ni spike does not offer any advantage for over-spiking.