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The influence of the double spike proportion effect on stable isotope (Zn, Mo, Cd, and Sn) measurements by multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS)†

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This study investigates the double spike (DS) proportion effect on measurements of stable Zn, Mo, Cd, and Sn isotopes by multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). The effect of DS proportion values between 0.1 and 0.9 (*i.e.*, 10–90% DS) on the compositions of measured reference materials was determined. The $\delta^{66/64}\text{Zn}$, $\delta^{114/110}\text{Cd}$, and $\delta^{120/118}\text{Sn}$ values positively correlate with the proportion of the DS within a mixture, whereas $\delta^{98/95}\text{Mo}$ values negatively correlate with the proportion of DS. Stable Mo, Cd, and Sn isotopes have a range of DS values around the optimum where the resulting delta values are insensitive to DS proportion values and reflect the values of the reference materials with the optimum DS proportion values. However, Zn isotopes do not have a stable DS proportion range, indicating that $\delta^{66/64}\text{Zn}$ values are much more sensitive to DS proportion values than those of the other three elements. The measured $\delta^{98/95}\text{Mo}$ values of a mixture of the IAPSO seawater reference with variable amounts of DS solution also show a negative correlation with DS proportions. This indicates that although it is difficult to explain why DS proportion values have a significant influence on isotopic analyses, we suspect that the iterative calculations involved in the three algebraic equations used to resolve DS data generate correlations between delta and DS proportion values. This study highlights the importance of assessing DS proportion effects when establishing analytical protocols for stable isotope measurements using the DS technique. Any correlation between the resulting measured isotopic compositions and the associated DS proportion values means that DS solutions must be precisely added to unknown samples to ensure that appropriate proportions of DS are used.

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Introduction

Many studies over the past two decades have investigated non-traditional stable isotope geochemistry, with this approach being regularly used in archaeological, earth science, and medical science research.^{1–3} All of these elements (barring those that can be introduced as gases, such as Br) are analysed using either multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) or thermal ionisation mass spectrometry (TIMS). The instrumental mass fractionation during analysis is corrected using standard sample bracketing (SSB), elemental spike (ES), or double spike (DS) methods. The SSB method assumes that mass bias drift over the time interval of one set of standard–sample–standard measurements is linear. However, these sets of measurements take several minutes to perform, meaning that mass bias drift may not be linear. In addition,

instrumental mass bias is affected by the presence of matrix impurities. The ES method uses an approach where an element is artificially incorporated to correct for instrumental mass bias (*e.g.*, Cu for Zn isotope measurements). This approach is limited if the behaviour of the added element is different from that of the measured element during standard (*i.e.*, matrix-free) and sample analyses. The precision of the ES method also relies on the identification of the correlation that controls the mass biases of both measured and added elements by the use of doped standards that bracket the analysis of individual unknown samples. Finally, the DS technique is thought to be the most precise method of correcting for instrumental mass fractionation for elements with at least four isotopes during mass spectrometry. The DS technique consists of adding a DS to a natural sample and measuring the isotopic ratios of the mixture by MC-ICP-MS, providing a precise measurement not only of the concentrations of the elements of interest but also of their isotopic ratios. The DS technique has two main advantages: (a) it allows for the correction of mass fractionation during instrumental measurement as well as fractionation induced during chemical purification, meaning that the full recovery of

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elements during chemical purification is not a critical necessity; and (b) it provides both isotopic compositions and concentration data for the elements of interest in a single analytical run. This technique forms the basis for numerous analytical protocols for non-traditional stable isotopes, including Ca,⁴⁻⁶ Cr,^{7,8} Fe,^{9,10} Ni,¹¹ Zn,¹²⁻¹⁵ Sr,^{16,17} Mo,^{18,19} Cd,²⁰⁻²² Sn,^{23,24} Ba,²⁵ and Hg.²⁶ Determining the weight ratio of an element between a DS and a sample in a mixture is critical for DS analysis. Many previous studies have ensured reasonable calibrations by keeping the proportion of DS within samples and references in small and similar ranges.^{9,11,24,27-29} Rudge *et al.*²⁸ theoretically calculated the influence of DS composition and the proportion of DS in a mixture on analytical precision. They found that exceeding a reasonable range of proportion values for a DS and a sample would yield large uncertainties that propagate through to the final results. Here, we mix different Zn, Mo, Sn, and Cd reference materials with various proportions of the corresponding DS before determining the Zn, Mo, Sn, and Cd isotopic compositions of these reference materials using the DS technique. The results enable an evaluation of the influence of the proportion of DS used on stable isotope measurements.

Experimental

Instrumentation

The Zn, Mo, Cd, and Sn isotopic analyses were performed using a Thermo Fisher Scientific Neptune Plus MC-ICP-MS instrument at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS), Guangzhou, China. The Neptune Plus instrument is a double-focus mass spectrometer that has low, medium, and high mass resolution modes. It has a collector array that consists of nine Faraday cups and eight ion counters, and is able to measure isotopic ratios with a relative mass range of 17%. The instrument incorporates a newly designed large dry interface pump (100 m³ h⁻¹ pumping speed) and an X skimmer cone, both of which significantly improve instrumental sensitivity. Sample solutions were introduced into the plasma using a self-aspiration PFA nebulizer (~50 μL min⁻¹, ESI†) and a dual cyclonic-Scott spray chamber from Thermo Fisher Scientific. All isotope measurements were performed in static mode at a low mass resolution (~400). Prior to analysis, samples were diluted to about 200 ppb concentration for the target elements (Zn, Mo, Cd, and Sn). Each measurement consisted of 60 cycles with an integration time of ~4.2 s per cycle. The collector arrays used for the Zn, Mo, Cd, and Sn isotopic measurements during this study are outlined in Table 1. The inlet of the instrument was washed

Table 1 Summary of the collector arrays used for Zn, Mo, Cd, and Sn isotopic analyses by MC-ICP-MS

	L4	L3	L2	L1	C	H1	H2	H3	H4
Zn			64		66	67	68		70
Mo		92	94	95	96	97	98	100	
Cd		110	111	112	113	114		116	
Sn	116	117	118	119	120		122	124	

between each of the measurements with 2% HNO₃ and 2% HNO₃ + 0.01% HF in turn, with ⁶⁴Zn, ⁹⁸Mo, ¹¹⁰Cd, and ¹²⁰Sn signals decreasing by <0.5 mV after ~5 minutes of wash out. The typical instrumental settings used during this study are given in Table 2.

Double spike experimental design for Zn, Mo, Cd, and Sn isotopic analysis

Two criteria were used to determine which isotopes were employed as the DS during Zn, Mo, Cd, and Sn isotopic analyses: (a) the isotopes selected should have low abundances relative to the other isotopes of an element present in the DS to deduce the measurement uncertainty;[†] and (b) the selected isotopes should be free of isobaric or polyatomic interference. Based on the criteria, our double spikes made up of ⁶⁸Zn–⁷⁰Zn, ⁹⁷Mo–¹⁰⁰Mo, ¹¹¹Cd–¹¹³Cd and ¹¹⁷Sn–¹¹⁹Sn were used to calibrate the instrumental mass bias for Zn, Mo, Cd and Sn isotope measurements, respectively. All of these spikes were purchased from the Oak Ridge National Laboratory, USA, and each DS was mixed to an optimal isotopic composition that was determined using the simulation method of Rudge *et al.*²⁸ The isotopic compositions of the four DSs used during this study are given in ESI Table S1.†

Preparation of solutions with different DS proportions

The IRMM-3702 and NIST SRM 3134, 3108, and 3161a standards were used as reference materials for Zn, Mo, Cd, and Sn isotopic analysis, respectively. Different amounts of DS were mixed with these reference materials to obtain solutions with a large range of DS proportion values (~0.1–0.9, *i.e.*, 10–90% DS; Table 2). The volumes of the added DS were calculated according to different DS proportions determined by the analysed concentrations of the mixed DS and reference material. The isotopic composition of the DS and the reference materials also allowed theoretical relationships between the proportion of the DS present and the isotopic ratio of the mixture to be determined. An example of this is shown in Fig. 1, which illustrates the relationship between DS proportion and ¹⁰⁰Mo/⁹⁸Mo values in a mixture. Accurate DS proportion values within the mixtures analysed during this study were derived

Table 2 Typical instrumental setup used during MC-ICP-MS analysis in this study

Instrument	Neptune Plus
RF power	1180 W (optimised daily)
Auxiliary gas (Ar) flow rate	0.98 L min ⁻¹ (optimised daily)
Sample gas (Ar) flow rate	0.975 L min ⁻¹ (optimised daily)
Cooling gas (Ar) flow rate	16.00 L min ⁻¹
Measurement mode	Static
Interface cones	H sample cone + X skimmer cone (nickel)
Acceleration voltage	10 kV
Detection system	Faraday cups
Amplifier	10 ¹¹ Ω
Integration time	4.19 s
Mass resolution	~400 (low)
Nebuliser	MicoFlow PFA-50; speed: ~50 μL min ⁻¹
Spray chamber	Dual cyclonic-Scott (quartz)

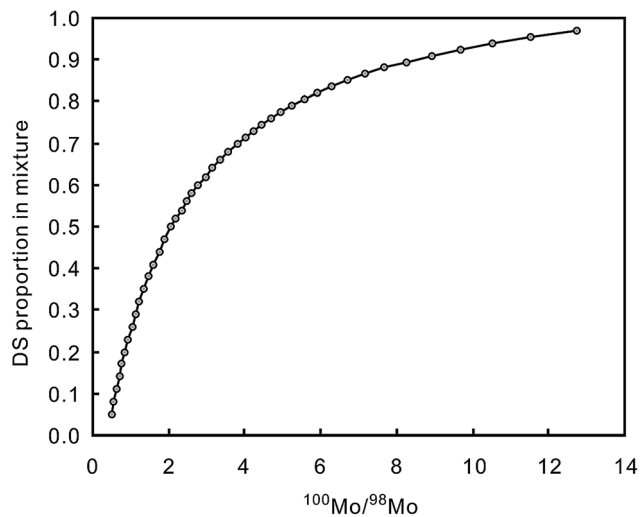


Fig. 1 Calculated relationship between DS proportion and $^{100}\text{Mo}/^{98}\text{Mo}$ values. This calculation uses ^{100}Mo and ^{98}Mo contents within the reference material of 0.0958 and 0.2407, respectively, and contents within the DS of 0.4637 and 0.0292, respectively.

from measured isotope ratios based on the relationship shown in Fig. 1. The optimum DS proportions for Zn, Mo, Cd, and Sn isotopic analyses were determined using the DS software toolbox developed by Rudge *et al.*²⁸ (Fig. 2).

Traditionally, stable isotope ratios are normalised to a reference material and are expressed using the δ notation in parts per mil:

$$\delta_{\text{sam}} = \left[\frac{\text{IsoRatio}_{\text{sam}}}{\text{IsoRatio}_{\text{ref}}} - 1 \right] \times 1000 \quad (1)$$

where $\text{IsoRatio}_{\text{sam}}$ and $\text{IsoRatio}_{\text{ref}}$ are the selected isotope ratios (e.g., $^{66}\text{Zn}/^{64}\text{Zn}$, $^{98}\text{Mo}/^{95}\text{Mo}$, $^{114}\text{Cd}/^{110}\text{Cd}$, and $^{120}\text{Sn}/^{118}\text{Sn}$) of the measured sample and the reference material, respectively. Here, we use calibrated isotope ratios determined by measuring reference materials mixed with the optimum proportion of DS to yield $\text{IsoRatio}_{\text{ref}}$ values. Each isotope analysis involved measurements of the mixture of the reference material with the optimum proportion of DS every 4–6 analyses of reference materials mixed with other proportions of DS solution. The measured raw data were then subjected to a DS calculation procedure that used an in-house Microsoft Virtual Basic program based on a mathematical algorithm presented in a previous study.³⁰

Chromatographic separation of Mo

The influence of DS proportion values on isotope measurements was further examined by measuring the Mo isotope composition of the IAPSO Atlantic seawater reference material. The protocol for chemical purification of Mo has been described in detail in previous studies^{18,31} and is summarised here. Ten duplicate samples of ~ 10 g seawater (containing ~ 100 ng Mo) were weighed accurately before being mixed with different proportions of a ^{97}Mo – ^{100}Mo DS in 15 mL PFA beakers to ensure that the resulting 10 mixtures cover a wide range of DS proportion values (from 0.19 to 0.84; Table 3). The spiked solutions were acidified before column separation by adding 1 mL of concentrated HCl in beakers. Molybdenum was separated from matrix elements using an in-house manufactured BPHA extraction chromatographic resin¹⁸ that was packed in an 8×40 mm Bio-Rad Poly-Prep column. The concentrated and spiked seawaters were loaded onto the columns before being washed with 8 mL of 0.1 mol L^{-1} HF/ 1 mol L^{-1} HCl. The Mo was

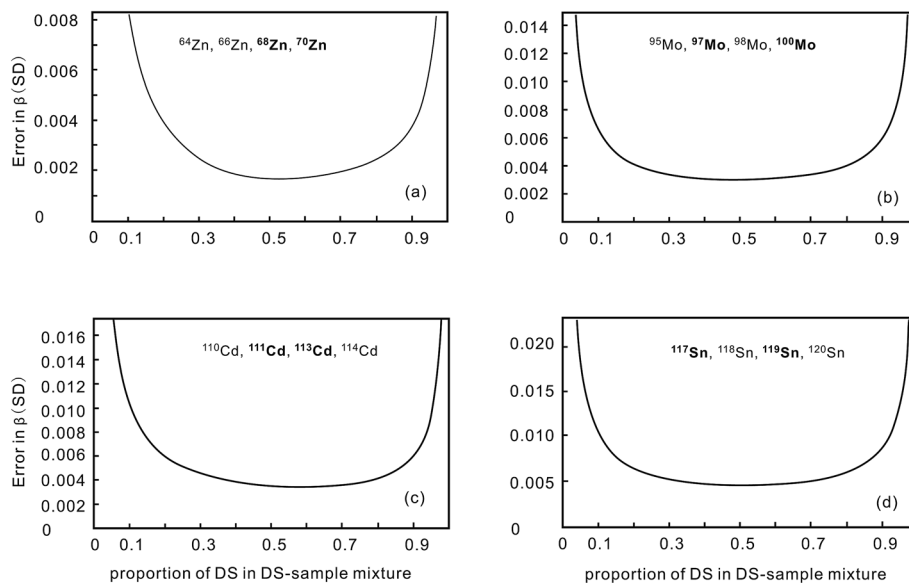


Fig. 2 Theoretical mass fractionation factor (β) error curves shown as a function of DS proportion values for Zn (a), Mo (b), Cd (c), and Sn (d) isotopic analyses. These curves were calculated using the approach of Rudge *et al.*²⁸ The lowest point of each curve represents the optimum DS proportion value. These values were also derived using the approach of Rudge *et al.*²⁸ and are used in the calculations of the present study. Bold indicates the isotopes present in artificially enriched spikes.

Table 3 Measured isotopic compositions of mixtures of reference materials with different proportions of DS

Zn	DS proportion	$\delta^{66/64}\text{Zn}$	2SE	Mo	DS proportion	$\delta^{98/95}\text{Mo}$	2SE
IRMM3702 + DS-Mix-1	0.57	0.07	0.03	NIST3134 + DS-Mix-1	0.33	0.04	0.02
	0.57	0.07	0.03		NIST3134 + DS-Mix-2	0.22	0.14
IRMM3702 + DS-Mix-2	0.70	0.43	0.03	NIST3134 + DS-Mix-3	0.16	0.17	0.03
	0.70	0.43	0.04		NIST3134 + DS-Mix-4	0.10	0.24
IRMM3702 + DS-Mix-3	0.72	0.51	0.03	NIST3134 + DS-Mix-5	0.42	-0.02	0.02
	0.72	0.47	0.03		0.42	0.01	0.02
IRMM3702 + DS-Mix-4	0.43	-0.14	0.03	NIST3134 + DS-Mix-6	0.64	0.04	0.04
	0.43	-0.16	0.02		0.64	0.01	0.05
IRMM3702 + DS-Mix-5	0.49	-0.10	0.03	NIST3134 + DS-Mix-8	0.13	0.34	0.03
	0.49	-0.09	0.04		0.13	0.32	0.03
IRMM3702 + DS-Mix-6	0.39	-0.17	0.03	NIST3134 + DS-Mix-9	0.74	-0.07	0.05
	0.39	-0.16	0.03		0.74	-0.07	0.04
IRMM3702 + DS-Mix-7	0.30	-0.29	0.04	NIST3134 + DS-Mix-10	0.78	-0.09	0.04
	0.30	-0.30	0.04		0.78	-0.08	0.04
IRMM3702 + DS-Mix-8	0.28	-0.33	0.03	NIST3134 + DS-Mix-11	0.60	0.03	0.03
	0.28	-0.38	0.03		0.60	-0.03	0.04
IRMM3702 + DS-Mix-9	0.22	-0.38	0.02	NIST3134 + DS-Mix-12	0.83	-0.13	0.03
	0.22	-0.35	0.02		0.83	-0.15	0.04
IRMM3702 + DS-Mix-10	0.66	0.24	0.03	NIST3134 + DS-ref	0.53	0.03	0.02
	0.66	0.27	0.02		0.53	0.00	0.03
IRMM 3702 + DS-ref	0.52	0.01	0.03	0.53	-0.05	0.03	
	0.52	-0.04	0.03	0.53	-0.02	0.02	
	0.52	0.04	0.02	0.53	-0.01	0.03	
	0.52	-0.01	0.03	0.53	0.02	0.03	
	0.52	-0.01	0.03	0.53	0.02	0.03	
	0.52	0.03	0.03	0.53	0.02	0.03	
	0.52	-0.03	0.03	0.53	-0.04	0.03	
	0.52	0.00	0.03	0.53	-0.04	0.03	
Mean		0.00			0.00		
2SD		0.05			0.06		
Cd	DS proportion	$\delta^{114/110}\text{Cd}$	2SE	Sn	DS proportion	$\delta^{120/118}\text{Sn}$	2SE
NIST3108 + DS-Mix-1	0.39	-0.01	0.04	NIST3161a + DS-Mix-1	0.62	0.03	0.04
	0.39	-0.04	0.03		0.62	0.01	0.05
NIST3108 + DS-Mix-2	0.29	-0.02	0.03	NIST3161a + DS-Mix-2	0.68	0.01	0.04
	0.29	-0.04	0.03		0.68	0.03	0.04
NIST3108 + DS-Mix-3	0.22	-0.21	0.04	NIST3161a + DS-Mix-3	0.80	0.04	0.04
	0.22	-0.16	0.04		0.80	0.06	0.04
NIST3108 + DS-Mix-5	0.19	-0.29	0.03	NIST3161a + DS-Mix-4	0.44	0.05	0.04
NIST3108 + DS-Mix-6	0.58	0.01	0.04	NIST3161a + DS-Mix-5	0.44	0.01	0.04
	0.58	-0.03	0.04		0.32	-0.01	0.04
NIST3108 + DS-Mix-7	0.71	0.05	0.05	NIST3161a + DS-Mix-6	0.32	0.02	0.04
	0.71	0.01	0.05		0.25	-0.04	0.03
NIST3108 + DS-Mix-8	0.66	0.02	0.04	NIST3161a + DS-Mix-7	0.25	-0.02	0.04
	0.66	0.00	0.03		0.17	-0.11	0.03
NIST3108 + DS-Mix-9	0.76	0.10	0.05	NIST3161a + DS-Mix-7	0.17	-0.09	0.04
	0.76	0.07	0.04				
NIST3108 + DS-Mix-10	0.87	0.13	0.06				
	0.87	0.08	0.04				
NIST3108 + DS-Mix-11	0.80	0.07	0.04				
	0.80	0.08	0.05				
NIST3108 + DS-Mix-12	0.20	-0.32	0.03				
NIST3108 + DS-ref	0.49	0.02	0.04	NIST3161a + DS-ref	0.51	0.03	0.04
	0.49	-0.02	0.03		0.51	-0.03	0.04
	0.49	0.00	0.04		0.51	-0.01	0.04
	0.49	-0.02	0.03		0.51	0.01	0.04
	0.49	0.04	0.04		0.51	0.01	0.04
	0.49	-0.04	0.03		0.51	-0.01	0.04
	0.49	0.03	0.03		0.51	-0.01	0.04
	0.49	0.03	0.03		0.51	-0.01	0.04
Mean		0.00		Mean	0.00		
2SD		0.05		2SD	0.05		

eluted with 8 mL of 6 mol L⁻¹ HF/1 mol L⁻¹ HCl and the eluted Mo was evaporated to dryness. Any organic residue was decomposed by the addition of three drops of concentrated HNO₃ and H₂O₂. Finally, 1 mL of 2% HNO₃ was added to the Mo residue, making the solution ready for Mo isotopic analysis by MC-ICP-MS.

Results and discussion

The results of the analyses are listed in Table 3 and shown in Fig. 3. These data indicate that variations in the proportion of DS within the mixtures had a significant influence on delta values, with $\delta^{66/64}\text{Zn}$, $\delta^{114/110}\text{Cd}$, and $\delta^{120/118}\text{Sn}$ values being positively correlated with DS proportion values, whereas $\delta^{98/95}\text{Mo}$ values are negatively correlated. The delta values generated during Mo, Cd, and Sn isotopic analyses are insensitive to DS proportion values for values close to the optimum. Assuming that the measured values that fall within the grey bands in Fig. 3 are acceptable, Mo and Cd have optimum DS proportion values of 0.3 to 0.7. In comparison, Sn isotopic compositions are more resistant to the influence of variations in DS proportion values, yielding measured $^{120/118}\text{Sn}$ values that are within two standard deviations (2SD) of the certified value for the reference material for a range of DS proportions between 0.2 and 0.8. If the proportion of DS mixed with the reference material exceeds this range, then the delta value of the measured reference material will deviate by zero \pm 2SD of the delta values calculated using the IsoRatio_{ref} value. Finally, Zn is unlike Mo, Cd, and Sn in that although the theoretical modelling indicates that Zn isotope measurements are accurate over a relatively wide range of DS proportions (similar to Mo, Cd, and Sn; Fig. 2), the results of our experiments indicate that this is not the case. Instead, $\delta^{66/64}\text{Zn}$ values are much more sensitive to changes in DS proportion values than are the other three elements (Fig. 3), with a 10%

change in the proportion of DS incorporated into the mixture inducing a 0.1 delta unit offset in terms of $^{66}\text{Zn}/^{64}\text{Zn}$ values.

NIST SRM 3134 with the optimum DS proportion was measured with the IAPSO standard to calculate the delta value. The results are listed in Table 4 and shown in Fig. 4. These data indicate that the measured $\delta^{98/95}\text{Mo}$ values of the IAPSO standard also negatively correlate with DS proportion values, although the measured $\delta^{98/95}\text{Mo}$ values of the IAPSO standard are relatively uniform and agree with the preferred value^{18,31–33} at DS proportion values between 0.30 and 0.75. However, lower DS proportion values cause a rapid increase in measured $\delta^{98/95}\text{Mo}$ values, whereas DS proportion values above 0.75 cause a slight decrease in measured $\delta^{98/95}\text{Mo}$ values. This result is consistent with those of the analysis of the NIST 3134 Mo standard mixed with different proportions of DS (Fig. 3).

It is difficult to explain why changes in the proportion of DS in a mixture have a significant effect on isotopic compositions. It is likely that the mathematical computational approaches used in the DS technique exert an important control on these variations in isotopic composition. The DS technique resolves

Table 4 Measured $\delta^{98/95}\text{Mo}$ values for mixtures of the IAPSO seawater standard with different proportions of DS

	Ds proportion	$\delta^{98/95}\text{Mo}$	2SE
Seawater-sp-1	0.19	2.28	0.03
Seawater-sp-2	0.20	2.25	0.06
Seawater-sp-3	0.34	2.07	0.04
Seawater-sp-4	0.54	2.05	0.04
Seawater-sp-5	0.64	2.11	0.06
Seawater-sp-6	0.64	2.06	0.05
Seawater-sp-7	0.70	2.06	0.06
Seawater-sp-8	0.71	2.07	0.06
Seawater-sp-9	0.76	2.01	0.05
Seawater-sp-10	0.84	1.96	0.05

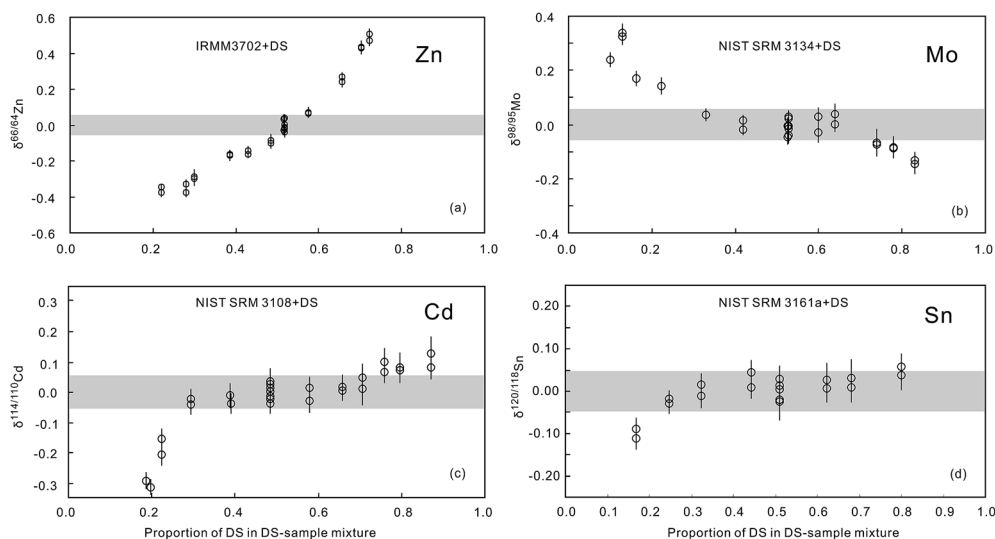


Fig. 3 Variations in measured (a) $\delta^{66/64}\text{Zn}$, (b) $\delta^{98/95}\text{Mo}$, (c) $\delta^{114/110}\text{Cd}$, and (d) $\delta^{120/118}\text{Sn}$ values for different reference materials mixed with various proportions of DS. These diagrams show that the proportion of DS present in a mixture has a significant impact on the resulting isotopic composition values.

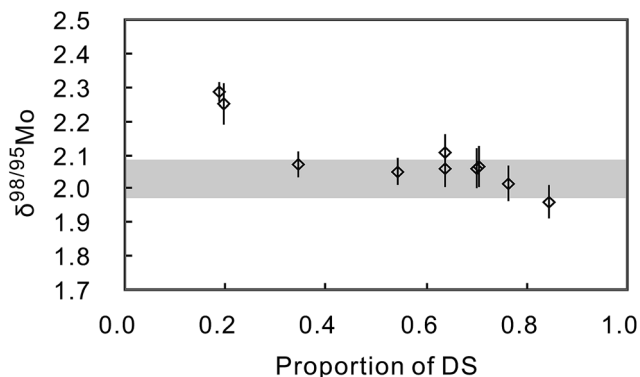


Fig. 4 Measured $\delta^{98/95}\text{Mo}$ values for the IAPSO seawater standard mixed with different proportions of DS, showing a clear negative correlation between $\delta^{98/95}\text{Mo}$ and DS proportion values. The grey band at $2.03\text{‰} \pm 0.06\text{‰}$ represents the preferred value for the standard.³¹

three algebraic equations with three variables during data reduction, as follows:

$$\lambda_j^{\text{sp}} R_{ij}^{\text{sp}} + (1 - \lambda_j^{\text{sp}}) R_{ij}^{\text{ref}} \left(\frac{M_i}{M_j}\right)^{\beta^{\text{ref}}} = r_{ij}^{\text{mix}} \left(\frac{M_i}{M_j}\right)^{\beta^{\text{mix}}} \quad (2)$$

where λ_j^{sp} is the atomic proportion of isotope i in a mixture containing the spike; R_{ij}^{sp} and R_{ij}^{ref} are the isotopic ratios of isotopes i and j with masses M_i and M_j within the DS and the reference material, respectively; r_{ij}^{mix} is the isotopic ratio of the mixture of the DS and reference determined by mass spectrometry; β^{ref} is the mass fractionation factor of a sample derived from the reference material; and β^{mix} is the mass fractionation factor of the mixture during instrumental analysis, assuming an exponential mass fractionation law. This assumption is based on the fact that an exponential mass fractionation law can describe the behaviour of numerous isotopic systems during MC-ICP-MS analysis.^{19,21,34}

Here, we use Mo as an example to illustrate the three algebraic equations outlined above. These equations correspond to the $^{97}\text{Mo}/^{95}\text{Mo}$, $^{98}\text{Mo}/^{95}\text{Mo}$, and $^{100}\text{Mo}/^{95}\text{Mo}$ isotopic ratios as follows:

For $^{97}\text{Mo}/^{95}\text{Mo}$, we have

$$\lambda_{95}^{\text{sp}} \left(\frac{^{97}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{sp}} + (1 - \lambda_{95}^{\text{sp}}) \left(\frac{^{97}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{ref}} \left(\frac{97}{95}\right)^{\beta^{\text{ref}}} = \left(\frac{^{97}\text{Mo}}{^{95}\text{Mo}}\right)_{\text{measured}}^{\text{mix}} \left(\frac{97}{95}\right)^{\beta^{\text{mix}}}$$

for $^{98}\text{Mo}/^{95}\text{Mo}$,

$$\lambda_{95}^{\text{sp}} \left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{sp}} + (1 - \lambda_{95}^{\text{sp}}) \left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{ref}} \left(\frac{98}{95}\right)^{\beta^{\text{ref}}} = \left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}}\right)_{\text{measured}}^{\text{mix}} \left(\frac{98}{95}\right)^{\beta^{\text{mix}}}$$

and for $^{100}\text{Mo}/^{95}\text{Mo}$,

$$\lambda_{95}^{\text{sp}} \left(\frac{^{100}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{sp}} + (1 - \lambda_{95}^{\text{sp}}) \left(\frac{^{100}\text{Mo}}{^{95}\text{Mo}}\right)^{\text{ref}} \left(\frac{100}{95}\right)^{\beta^{\text{ref}}} = \left(\frac{^{100}\text{Mo}}{^{95}\text{Mo}}\right)_{\text{measured}}^{\text{mix}} \left(\frac{100}{95}\right)^{\beta^{\text{mix}}}$$

These equations and their three associated variables represent three curved planes in X - Y - Z three-dimensional space. Fig. 5 shows these planes for the isotopic analysis of mixtures of the NIST SRM 3134 Mo standard with different proportions of DS. The fact that the DS is artificially enriched in ^{97}Mo and ^{100}Mo means that the $^{97}\text{Mo}/^{95}\text{Mo}$ and $^{100}\text{Mo}/^{95}\text{Mo}$ planes have much smaller intersection angles with the X - Y plane than the $^{98}\text{Mo}/^{95}\text{Mo}$ plane. Resolving the three equations outlined above

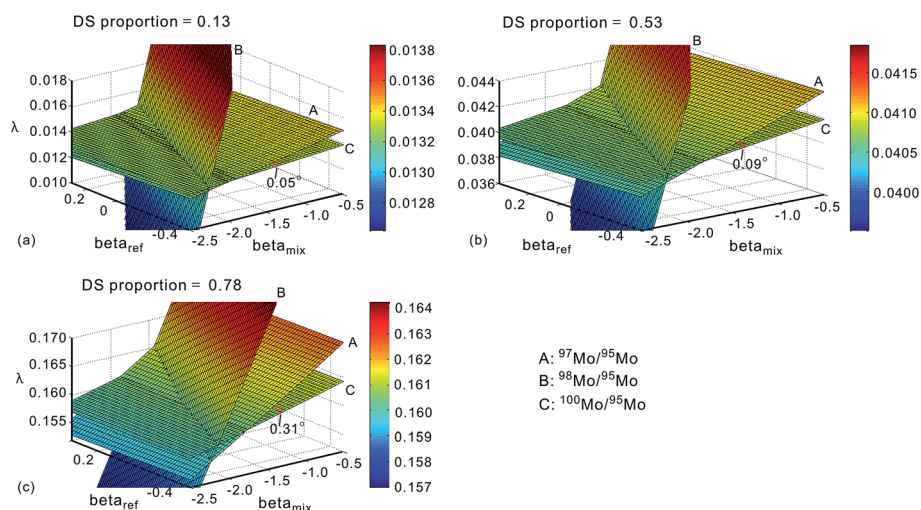


Fig. 5 Three planes representing the three equations used in Mo isotope data reduction with DS proportion values of 0.13, 0.53, and 0.78 in (a), (b), and (c), respectively. The A, B, and C planes represent the equations for $^{97}\text{Mo}/^{95}\text{Mo}$, $^{98}\text{Mo}/^{95}\text{Mo}$ and $^{100}\text{Mo}/^{95}\text{Mo}$ isotopic ratios, respectively. The numbers given in degrees in each diagram represent the angle of the intersection corners between the planes of $^{97}\text{Mo}/^{95}\text{Mo}$ and $^{100}\text{Mo}/^{95}\text{Mo}$. The MATLAB code used to construct this figure is provided in the ESI.†

requires determining the point at which all three planes intersect. Increases in the DS proportion value cause a coincident increase in the angle of intersection between the $^{97}\text{Mo}/^{95}\text{Mo}$ and $^{100}\text{Mo}/^{95}\text{Mo}$ planes, meaning that small amounts of DS would cause these planes to become parallel. In addition, a decrease in intersection angle between these two planes yields an increase in the uncertainty of the intersection point between them. This suggests that the intersection angle of these two planes controls the iterative calculation of the three algebraic equations outlined above, leading to a coincident correlation between the delta value and the DS proportion values, as shown in Fig. 3 and 4.

Significance and conclusions

The correlation between the isotope ratio and the DS proportion values in Fig. 3 and 4 clearly indicates that determining the proportion of DS within measured samples is critical for the accurate analysis of stable isotopes using the DS technique. A stable range of DS proportion values is present within the Mo, Cd, and Sn systems, with DS proportion values in this range yielding measured isotopic compositions that are not affected by changes in the amount of DS present. However, DS proportion values outside of this stable range will yield measured isotopic compositions that correlate with these values, and DS proportion values below this ideal range have a stronger effect than values above this range. Consequently, accurate Mo, Cd, and Sn isotopic analyses require at least a rough determination of the concentrations of these elements to allow the determination of the DS proportion values (and to ensure that these values are within the optimum range) during analysis. In addition, Zn isotopic analysis contrasts with the results of theoretical modelling (Fig. 2) in that $\delta^{66/64}\text{Zn}$ values clearly correlate with DS proportion values, meaning that there is no single range of DS proportion values that would yield relatively stable and accurate $\delta^{66/64}\text{Zn}$ values. Therefore, the samples used for Zn isotopic analysis need to be mixed with the DS in the same proportion as that for the standard used for calibration (e.g., IRMM3702). This means that precise Zn concentrations must be determined prior to mixing to ensure that a precisely weighed amount of DS can be added to the sample. Samples without precise Zn concentrations may be mixed with the DS according to experience, but reference materials with the same DS proportion values (as determined using raw Zn isotopic ratios such as $^{68}\text{Zn}/^{64}\text{Zn}$) must be prepared and measured along with these samples.

Although this study only measured Zn, Mo, Cd, and Sn isotopic compositions, the DS proportion effect may also be present during the isotopic analysis of other elements using the DS technique.^{2,28} This means that it is necessary to determine the effect of variations in DS proportion values while establishing analytical protocols for measurements of stable isotopic compositions using the DS technique. Any correlation between measured isotopic compositions and DS proportion values means that the DS must be precisely added to samples to ensure that appropriate amounts of DS are used.

Conflicts of interest

There are no conflicts to declare.

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