High-precision Cu and Zn isotope analysis by plasma source mass spectrometry
Part 2.† Correcting for mass discrimination effects

Thomas F. D. Mason,[*a] **Dominik J. Weiss,**[a,b] **Matthew Horstwood,**[c]
Randall R. Parrish,[c,d] **Sara S. Russell,**[b] **Eta Mullane**[b] **and Barry J. Coles**[a]

[a]*Department of Earth Science and Engineering, Imperial College London, UK SW7 2BP. E-mail: thomas.mason@ic.ac.uk; Fax: 0207 594 7444; Tel: 0207 594 6395*
[b]*Department of Mineralogy, The Natural History Museum, London, UK SW7 5BD*
[c]*NERC Isotope Geosciences Laboratory, Keyworth, Nottinghamshire, UK NG12 5GG*
[d]*Department of Geology, University of Leicester, Leicester, UK LE1 7RH*

Two approaches to correct for mass discrimination effects associated with Cu and Zn isotopic measurements on two different MC-ICP-MS instruments (a Micromass IsoProbe and a VG Axiom) have been compared and assessed in detail: (1) sample-standard bracketing (SSB), and (2) the 'empirical external normalisation' (EEN) whereby a second element is used to simultaneously correct for mass discrimination. This has provided new insights into the mass discrimination behaviours of Cu and Zn under varying instrumental set-ups, and has allowed improvements to be made to the existing correction procedures. With the SSB approach, mass bias stability is a prerequisite, and matrix components must be removed from the analyte to avoid matrix-related mass discrimination effects. By comparison, the EEN approach requires a degree of mass bias instability, and automatically corrects for matrix-related mass discrimination effects. The EEN correction may therefore appear more robust. However, while the EEN correction yields high-precision $^{65}Cu/^{63}Cu$ and $^{66}Zn/^{64}Zn$ data, an as yet unidentified source of systematic drift in the ^{67}Zn and ^{68}Zn signals through time hinders analyses of ratios incorporating these isotopes. Using the EEN correction where analyte and spike ratios were measured sequentially within a peak-switching protocol led to a three-fold deterioration in precision relative to static measurements. This is consistent with mass bias drift on the scale of a single five-second-measurement integration. For relative $^{65}Cu/^{63}Cu$ and $^{66}Zn/^{64}Zn$ ratio measurements, the SSB and EEN corrections give long-term reproducibilities of less then $\pm 0.07‰$ (2SD) for pure Cu and Zn reagents. This is sufficient for resolving mass-dependent isotopic variability in natural and anthropogenic materials.

Introduction

Raw isotope ratios measured by plasma-source mass spectrometry typically deviate from their true values by up to 10% per unified atomic mass unit (amu^{-1}).[1,2] The causes of this phenomenon, known as mass discrimination, remain a subject of much debate, although both supersonic expansion of ions though the sample cone,[3] and space–charge effects in the wake of the skimmer cone[4] are likely involved. Both of these processes favour transmission of the heavier isotope into the mass spectrometer, and with MC-ICP-MS instruments it has been argued that each constitute roughly 50% of the total mass discrimination effect.[5]

Mass discrimination incorporates two components: (1) instrumental mass discrimination effects (known as mass bias) and (2) matrix-dependent non-spectral mass discrimination effects induced by changes in sample composition.[6] Random fluctuations in mass bias through time present a significant hindrance to isotope measurements. Consequently, to enable high-precision isotope analyses using MC-ICP-MS, a measurement protocol that overcomes both mass bias and non-spectral mass discrimination is required. Furthermore, when assessing isotopic variability within stable isotope systems such as Cu and Zn, this correction should preserve mass-dependent isotopic information.

Two types of mass discrimination correction are commonly adopted when studying mass-dependent isotopic anomalies by MC-ICP-MS: (1) sample-standard bracketing (SSB), whereby unknown samples are 'bracketed' by standards that are used to interpolate and correct for mass bias drift during data collection and (2) 'inter-element' normalisation, whereby a second element, close in mass to that of the analyte, is used to monitor and correct for mass discrimination within the analytical run. The SSB approach enables relative shifts between standards and samples to be determined directly without requiring any prior knowledge of the relationship between mass discrimination and mass. Although it has been successfully used to study a variety of stable isotope systems (*e.g.* Mg,[7] Fe,[8,9] Cu[10]), it does not account for short-term fluctuations in mass bias between bracketing standards, nor non-spectral matrix induced mass discrimination effects. By contrast, the 'inter-element' approach corrects for non-spectral effects and short-term instrumental mass bias drift by providing a continuous monitor of mass discrimination, and thus may be considered more robust. However, doubts have been raised as to whether different elements always share a predictable matrix-independent mass discrimination relationship that is a prerequisite of the inter-element approach,[11] and whilst modified forms of the inter-element correction have been developed to account for differences in the mass discrimination behaviours of analyte and spike elements,[12–15] important issues remain to be addressed with respect to how instrumental design and sample introduction techniques influence such corrections.

In light of the these continuing uncertainties, a systematic investigation has been undertaken to evaluate the SSB and

† Part 1: Preceding paper (ref. 16).

'inter-element' mass discrimination corrections for high-precision Cu and Zn isotope measurements on two MC-ICP-MS instruments: a Micromass IsoProbe and a VG Axiom. This involved comparing direct solution nebulisation and solution desolvation sample introduction techniques. Through this work, fundamental differences in the mass bias behaviours of Cu and Zn on the Axiom and IsoProbe under varying running conditions have been quantitatively described. Furthermore, modifications to the SSB and 'inter-element' corrections are presented that offer improvements in both accuracy and robustness for relative Cu and Zn isotope ratio measurements. Work is currently ongoing to assess these modified mass discrimination corrections for high-precision Cu and Zn measurements in natural materials, as will be the focus of subsequent publications.

Experimental

Full experimental details of the reagents and standards, instrumental set-up, and measurement protocols used during the study are given in the Experimental section of the companion paper.[16] Consequently only a brief overview is given here.

A series of ultra-pure Cu and Zn standards (NIST Cu, IMP Cu, JMC Cu, IMP Zn, JMC Zn, Romil Zn and Spec-pure Zn)[16] and a single element Claritas 1000 µg ml^{-1} Ga ICP-MS standard (SPEX CertiPrep, Metuchen, NJ) were used for the experiments. Unless otherwise specified, solutions were prepared in 0.2% (v/v) ultra-pure HNO$_3$ following clean laboratory protocols, and for each set of experiments, solutions were concentration matched to ensure >4 V signals on ^{63}Cu, ^{64}Zn (and ^{69}Ga).

The instrumental set-ups used on the VG Axiom and Micromass IsoProbe were identical to those previously described,[16] and measurements were made using both direct solution nebulisation (referred to as wet plasma conditions) and an Aridus desolvation system (referred to as dry plasma conditions). With the exception of the peak-switching protocol used to measure Cu, Zn and Ga together, measurements were made using a static collection protocol. All data were collected at a mass resolution of 400–500 $M/\Delta M$ and typical analyses comprised 25–200, 5 s integrations.

An on-peak acid blank subtraction baseline correction was employed throughout, and those data collected on the Axiom under wet plasma conditions were also corrected for Zn hydride interferences as previously described.[16] No statistical outlier rejection scheme has been used during data reduction.

Results and discussion

Sample-standard bracketing: direct approach

The SSB approach assumes that temporal drift in mass bias between bracketing standards is predictable and approximates to a simple mathematical expression (typically a linear interpolation). This requires mass bias to change slowly over the measurement session, and for there to be no significant jumps in mass bias between adjacent analyses. To test whether these criteria are met, two synthetic Cu standard solutions (NIST Cu and JMC Cu) were analysed on the Axiom following a SSB protocol under both wet and dry plasma conditions (see Fig. 1).

For wet plasma conditions, the measured ^{65}Cu/^{63}Cu ratio changes erratically throughout the measurement session (Fig. 1(a)). This behaviour typifies wet plasma measurements on both the Axiom and IsoProbe, and reflects temporal fluctuations in mass bias over the time scale of a few minutes. In contrast, under dry plasma conditions the ^{65}Cu/^{63}Cu ratio is relatively stable (Fig. 1(b)), and shows only a gradual downward drift during the measurement session. A similar increase
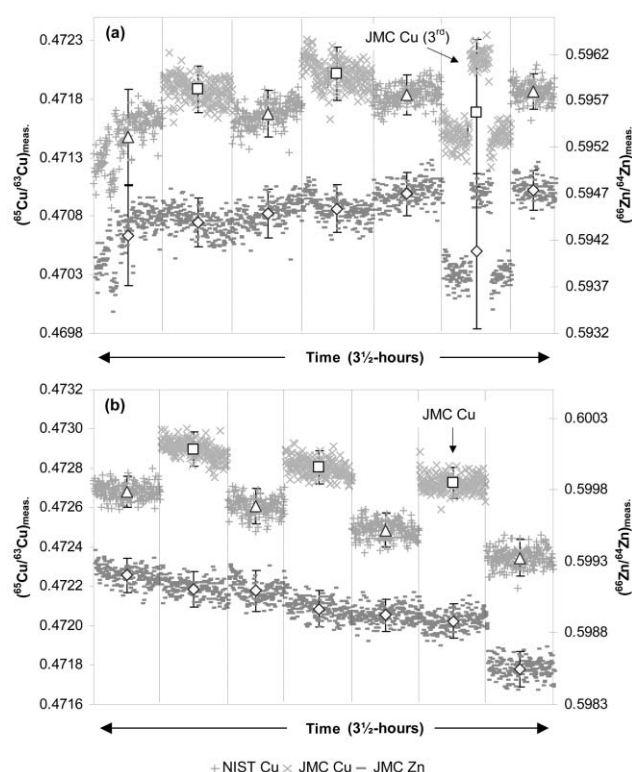

Fig. 1 Sample-standard bracketing (SSB) measurements of the isotopic difference between two Cu standards, 0.4 µg ml^{-1} NIST Cu ($\triangle$) and 0.4 µg ml^{-1} JMC Cu ($\square$). (a) Data collected under wet plasma conditions and (b) data collected under dry plasma conditions. Both Cu solutions were spiked with 1 µg ml^{-1} JMC Zn ($\diamond$) to act as an internal mass discrimination monitor. Measurements were made on the Axiom and have been on-peak baseline corrected. Data collected under 'wet' plasma conditions have been corrected for Zn hydride. $\pm$2SD error bars are given for each analysis of 200 measurement integrations. Vertical dashed lines indicate sample changeovers.

in mass bias stability is observed with the IsoProbe under dry plasma conditions (data not shown). This behaviour is consistent with a reduction in plasma loading and/or a narrowing in the size distribution of particulates entering the plasma associated with the desolvation process.[17,18]

Assuming mass bias varies linearly between bracketing standards, a $\delta^{65/63}$Cu value for each JMC Cu analysis relative to its bracketing NIST Cu standards has been calculated using:

$$\delta^{65/63}\text{Cu} = \left(\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{JMC}} - (^{65}\text{Cu}/^{63}\text{Cu})_{\text{Av.NIST}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{Av.NIST}}} \right) \times 1000 \quad (1)$$

where the subscripts JMC and Av. NIST refer to JMC Cu and average of the two bracketing NIST Cu standards, respectively (see Table 1). With the exception of the third analysis of JMC Cu made under wet plasma conditions, all $\delta^{65/63}$Cu data fall within error of the $\delta^{65/63}$Cu value of 0.60 $\pm$ 0.04‰ (2SD) for JMC Cu relative to NIST Cu as reported by Maréchal et al.[12] Nevertheless, $\delta^{65/63}$Cu data collected using dry plasma conditions give a relatively wide range (0.53–0.65‰) that is significantly greater than the internal precisions for individual measurements (ca. $\pm$0.02‰). This is suggestive of an additional source of error that is unaccounted for by the SSB correction.

Sample-standard bracketing: modified approach

The additional source of error noted in the previous section may reflect temporal shifts in mass discrimination that are not fully accounted by the linear approximation used within the SSB correction. To investigate this, JMC Zn was added to both

Table 1 $\delta^{65/63}$Cu values for the isotopic difference between JMC Cu and NIST Cu as calculated using the SSB approach

	$\delta^{65/63}$Cu (‰)[a]	$\pm 2\sigma$	$\delta^{66/64}$Zn (‰)[b]	$\pm 2\sigma$	$\delta^{65/63}$Cu − $\delta^{66/64}$Zn (‰)[c]	$\pm 2\sigma$
'Wet' plasma measurements						
JMC Cu: 1st analysis	0.656	0.054	0.035	0.057	0.621	0.079
JMC Cu: 2nd analysis	0.561	0.043	−0.096	0.042	0.657	0.061
JMC Cu: 3rd analysis	−0.360	0.097	−1.072	0.102	0.712	0.141
'Dry' plasma measurements						
JMC Cu: 1st analysis	0.533	0.018	−0.072	0.021	0.605	0.028
JMC Cu: 2nd analysis	0.546	0.018	−0.070	0.021	0.616	0.028
JMC Cu: 3rd analysis	0.654	0.018	0.241	0.020	0.414	0.027

[a] $\delta^{65/63}$Cu values calculated using the 'direct' SSB correction. [b] $\delta^{66/64}$Zn values calculated using the 'direct' SSB correction for a JMC Zn spike added to both the JMC Cu and NIST Cu standards. [c] $\delta^{65/63}$Cu − $\delta^{66/64}$Zn values give the 'modified' SSB corrected $\delta^{65/63}$Cu values.

JMC Cu and NIST Cu standards for use as an internal standard to monitor mass discrimination. For both wet and dry plasma measurements, the ^{66}Zn/^{64}Zn ratio normally maintains a relatively constant value when switching between the two Cu standards (see Fig. 1), indicating mass discrimination is unchanged. However, a sudden shift in ^{66}Zn/^{64}Zn occurs prior to the final analysis in Fig. 1(b), which is consistent with a jump in mass discrimination at this point. This is not apparent from the Cu isotope data alone, and highlights, from a purely qualitative prospective, the value of using an independent elemental mass discrimination monitor.

As with Cu, $\delta^{66/64}$Zn values can be calculated for each unknown (JMC Cu) relative to its bracketing standards (NIST Cu) using an analogous form of eqn. (1) (see Table 1). This provides an 'index' of how mass discrimination differs between samples and bracketing standards. $\delta^{66/64}$Zn values can also be subtracted from their corresponding $\delta^{65/63}$Cu values to correct for changes in mass discrimination that are not accounted for in the SSB correction (see Table 1). This approach, here coined the 'modified' SSB correction, makes the assumption that the magnitude of mass discrimination experienced during ^{66}Zn/^{64}Zn and ^{65}Cu/^{63}Cu ratio measurements are equivalent; a case which is not always satisfied (see below). However, this modification accounts for only a small fraction (*ca.* 0.4% at maximum) of the total mass discrimination experienced during the measurement, with the majority of mass discrimination being corrected out in the sample-standard bracketing step. Hence, inaccuracies associated with this assumption will be much smaller than if Zn is used directly to correct for mass discrimination using only an inter-element correction. With the exception of the third dry plasma analysis of JMC Cu (which can be discounted as these data have been influenced by the nebuliser blocking during data acquisition), the $\delta^{65/63}$Cu − $\delta^{66/64}$Zn values for both wet and dry plasma measurements show better agreement with the reported $\delta^{65/63}$Cu value of 0.60‰ than the raw $\delta^{65/63}$Cu data (see Table 1), providing empirical evidence that the modification is justified.

This 'modified' SSB correction has been assessed on the IsoProbe whereby repeat measurements of the isotopic difference between two Cu standards (IMP Cu and NIST Cu) were made over a two-week period using IMP Zn as an internal mass discrimination monitor. The raw $\delta^{65/63}$Cu data yields a relatively high measurement reproducibility of ± 0.38‰ (2SD). By comparison, the reproducibility using the modified SSB approach is ± 0.049‰ (2SD). This is similar to the combined internal precisions calculated for individual analyses (*ca.* 0.05‰ 2SE), indicating the dominant source of error is not associated with the mass discrimination correction. This suggests that even a basic simultaneous mass discrimination correction can significantly improve data quality.

'Inter-element' approach: theory

A second element can be used directly to quantitatively correct for mass discrimination effects without the need for bracketing standard runs. This 'inter-element' correction was pioneered by Longerich et al.[19] who used Tl to simultaneously correct for mass discrimination effects during Quadrupole-ICP-MS Pb isotopic measurements. When using this type of correction, it is necessary to assume a mathematical form that relates mass discrimination to mass. Two mathematical equations are commonly used to correct for mass discrimination during MC-ICP-MS measurements: (1) the power law and (2) the exponential law.[20–22] These are specific cases of the 'generalised power law' (GPL):[12]

$$r = Rg(M_2^n - M_1^n) \qquad (2)$$

where r represents the measured isotope ratio, R represents the true isotope ratio, g is the mass fractionation coefficient that describes the mass discrimination behaviour of the element per atomic mass unit, M_2 and M_1 are the absolute atomic masses of the isotopes in question, and n defines the mathematical relationship between mass discrimination and mass (for $n = 1$ the expression takes the form of the power law, for $n = 0$ the expression takes the form of the exponential law[12]).

Rewriting the GPL for (i) analyte r' and (ii) spike r'', taking natural logarithms and dividing (i) by (ii), the following equation is derived:

$$\ln(r') = \left[\frac{\ln\left(g'\left(M_{2'}^n - M_{1'}^n\right)\right)}{\ln\left(g\left(M_{2''}^n - M_{1''}^n\right)\right)}\right](\ln(r'') - \ln(R'')) + \ln(R') \qquad (3)$$

For simultaneous measurements of r' and r'', eqn. (3) can be solved for R' if the true isotopic ratio (R'') of the spike, the specific form of the general power law (n), and the ratio of the mass fractionation coefficients of the analyte and spike are all known. Using this approach, several studies have corrected for mass discrimination assuming that the mass fractionation coefficients of the analyte and spike are equivalent and that n is fixed.[19,23–27] However, the equivalence of the mass fractionation coefficients of the spike and analyte has been questioned by Hirata,[15] who proposed that discrepancies between Pb isotope data for NIST standard reference materials determined by MC-ICP-MS and TIMS reflect differences between the fractionation coefficients of Pb and Tl (*i.e.* $g_{Tl} \neq g_{Pb}$). This was confirmed by White et al.,[13] and additional studies have proposed differences in the mass discrimination behaviours of analyte and spike element pairs for a variety of isotope systems including Cu–Zn,[12] Mo–Ru and Mo–Zr,[14] Se–Sr,[28] Fe–Cu[29,30] and Fe–Ni.[30]

As proposed by Maréchal et al.,[12] eqn. (3) can be used to correct for mass discrimination effect even if the fractionation coefficients of the analyte and spike element are known to differ. With this approach eqn. (3) is rewritten as

$$\ln(r') = m \ln(r'') + c \qquad (4)$$

where:

$$m = \frac{\ln\left(g'\left(M_{2'}^n - M_{1'}^n\right)\right)}{\ln\left(g''\left(M_{2''}^n - M_{1''}^n\right)\right)} \qquad (5)$$

$$c = \ln(R') - m\ln(R'') \qquad (6)$$

Assuming n and $\ln(g')/\ln(g'')$ are invariant during an analytical session, m and c become constants and eqn. (4) takes the form of a straight line. The gradient m of this line is independent of the isotopic composition of the analyte and spike analysed, and its intercept c is a function of the true isotopic compositions of the analyte and spike. Therefore, two samples (A and B) with differing analyte and/or spike isotopic compositions analysed during the same measurement session will theoretically plot as parallel linear arrays in ln–ln ratio space, where the difference in intercept values (Δc) for the arrays is given by:

$$\Delta c = c_A - c_B = \ln\left(\frac{R'_A}{R'_B}\right) - m\ln\left(\frac{R''_B}{R''_A}\right) \qquad (7)$$

For two isotopically distinct samples, doped with the same elemental spike solution (R''), the second term in eqn. (7) cancels, and the true isotopic difference between the two solutions is simply a function of the difference between the intercepts (Δc). Substituting Cu as the analyte, this can be expressed in δ-notation as:

$$\delta^{65/63}\mathrm{Cu} = \left(e^{(\Delta c)} - 1\right) \times 1000 \; (\text{‰}) \qquad (8)$$

Because eqn. (3) has been derived directly from the GPL, it is not necessary to invoke anything about the specific form of the generalised power law (i.e. power, exponential). The correction is therefore applicable in all cases where mass discrimination of the analyte and spike approximate to the GPL, and both n and $\ln(g')/\ln(g'')$ remain constant during data collection. We here call this approach the 'empirical external normalisation' (EEN) following Clayton et al.[31]

Quantifying measurement precision with the EEN correction

A statistical approach for automating the EEN correction and estimating combined internal measurement precisions was developed during the study (Fig. 2). Here all integration data for the reference standard collected during a measurement session are regressed using a least mean square bisector (LMS-B)
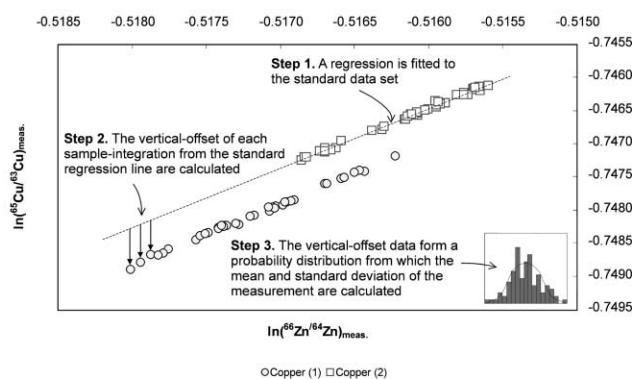
regression to define a 'calibration line' to which unknown samples are compared. Theoretically, this 'calibration line' shares the same gradient as regression lines passing through each unknown sample, and the vertical offset of each sample integration from this line is a function of the true isotopic difference between that sample and the reference standard (following eqn. (8)). The vertical offsets for all sample integrations thus define a population from which the mean and standard deviation are calculated.

The LMS-B regression procedure was adopted as it accounts for random errors in both ratios.[32] Because the LMS-B regression is calculated using the mean of the data set, data points that fall far from the mean disproportionately influence the regression estimate and may bias the EEN correction. MC-ICP-MS data acquisition software commonly use a 10% filter for eliminating outlying data points. However, such procedures also reject data points that legitimately fall on the regression line, deteriorating the regression estimate. Therefore, the preferred solution is to combine all standard data for the measurement session (which typically number over 1000 integrations) to define the 'calibration' line. This minimises the influence of random statistical outliers, while maintaining data integrity.

Using the EEN approach to measure isotopic variability in synthetic solutions

The EEN correction has been used to calculate the isotopic difference between two Cu standards (NIST Cu and JMC Cu) using JMC Zn as an internal mass discrimination monitor. These measurements were made under wet and dry plasma conditions on the Axiom (see Fig. 3), and represent the data presented in Fig. 1. Under wet plasma conditions, the two Cu samples define clearly separable parallel linear arrays in ln–ln space (see Fig. 3(a)). The average for the three JMC Cu
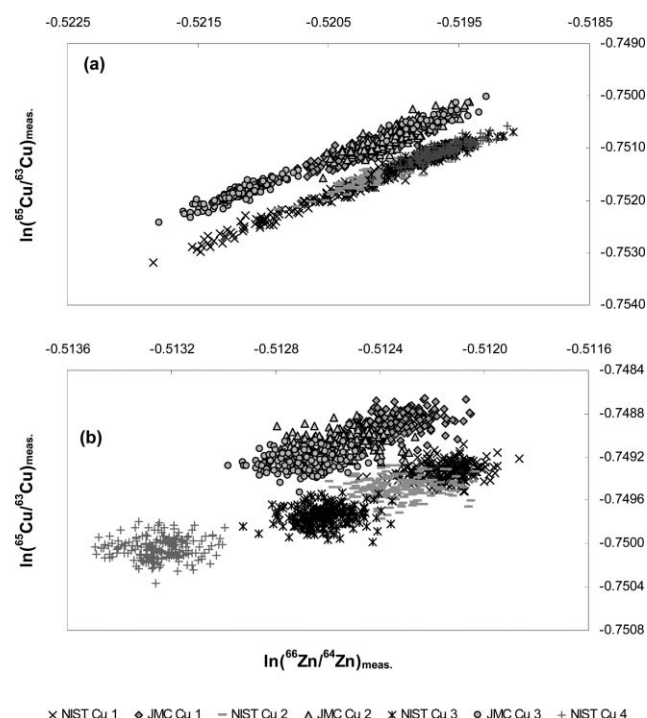

Fig. 3 $\ln(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})$ vs. $\ln(^{66}\mathrm{Zn}/^{64}\mathrm{Zn})$ plots constructed from integration data collected on two Cu standards (JMC Cu and NIST Cu) spiked with the JMC Zn standard. (a) Data collected under wet plasma conditions and (b) data collected under dry plasma conditions. All measurements were made on the Axiom and each plot represents a single measurement session. Data have been baseline corrected using an on-peak acid blank subtraction procedure and data collected under wet plasma conditions have been corrected for Zn hydride. JMC Cu and NIST Cu data sets define separate arrays, indicating that these standards are isotopically distinct.

Fig. 2 Schematic diagram of the 'empirical external normalisation' mass discrimination correction. The quantification of this approach involves three steps: (1) a regression line is fitted to the raw integration standard data set, (2) the vertical off-set of each individual sample integration from this standard 'calibration line' are calculated and (3) the mean and standard deviation of these residuals are determined and converted into δ-notation following eqn. (8) (see text for details).

analyses yields a $\delta^{65/63}$Cu value of 0.655 $\pm$ 0.072‰ (2SD) relative to NIST Cu. This is in agreement with the SSB data (see Table 1). Under dry plasma conditions, the sample data form clusters in ln–ln space (see Fig. 3(b)). This clustering directly reflects the reduction in mass bias drift associated with the dry plasma. Nevertheless, the sample and standard data continue to define diffuse co-parallel linear arrays as predicted by the EEN correction, and the average for the three JMC Cu analyses gives δ^{65}Cu/^{63}Cu = 0.586 $\pm$ 0.040‰ (2SD) relative to NIST Cu. These data provide empirical evidence that the fundamental assumptions underlying the EEN correction are satisfied under both wet and dry plasma conditions.

Because the EEN correction relies upon defining a standard regression line to which unknown samples are compared, as instrumental mass bias drift falls and standard data cluster, the confidence on the fitted regression line deteriorates, and uncertainty on the correction increases. This is illustrated in Fig. 4, which presents data collected on two Cu standards (IMP Cu and NIST Cu spiked with IMP Zn) measured on the IsoProbe under (a) wet and (b) dry plasma conditions, respectively. Even under wet plasma conditions, individual analyses form clusters, whilst under dry plasma conditions no observable linear trend exists between ln(^{65}Cu/^{63}Cu) and ln(^{66}Zn/^{64}Zn), leading to a breakdown in the EEN correction. Rehkämper and Mezger,[33] and later Woodhead,[34] observed similar problems when attempting to use variants of the EEN approach to correct Pb isotopes using Tl under dry plasma conditions. Thus, unlike the SSB correction, where mass bias stability is favoured, a degree of mass bias instability a required to successfully apply the EEN correction.
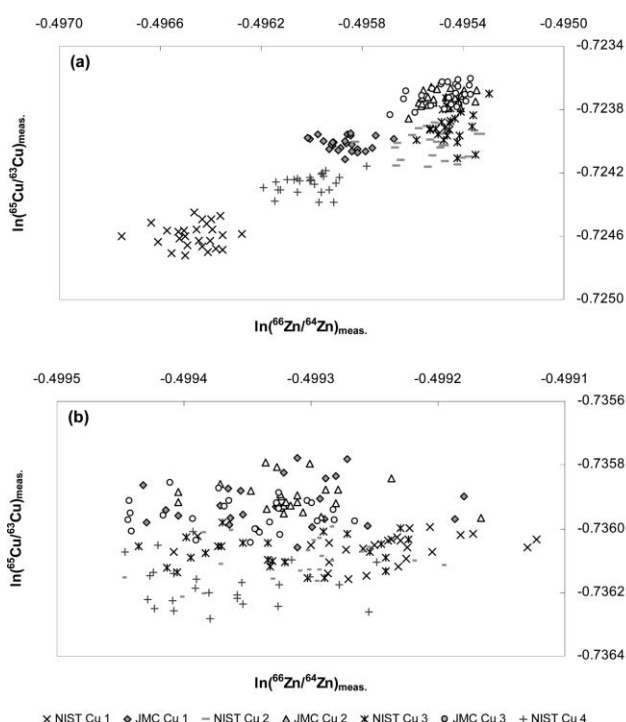
Selecting an isotope ratio for the EEN correction

The EEN correction has thus far been illustrated using the ^{66}Zn/^{64}Zn ratio to correct for mass discrimination during ^{65}Cu/^{63}Cu measurements. It is also desirable to use the correction with other Zn isotopic ratios that incorporate ^{67}Zn and ^{68}Zn to screen potential interferences on ^{64}Zn, ^{66}Zn, ^{67}Zn and ^{68}Zn by ensuring mass-dependent behaviour. ln–ln plots of ^{65}Cu/^{63}Cu vs. ^{66}Zn/^{64}Zn, ^{67}Zn/^{64}Zn and ^{68}Zn/^{64}Zn have been constructed for twelve analyses of a NIST Cu + IMP Zn standard run over a 16 h period (see Fig. 5). These data were collected on the Axiom under wet plasma conditions.

For ln(^{66}Zn/^{64}Zn) vs. ln(^{65}Cu/^{63}Cu), the data define a single regression line throughout the measurement session (Fig. 5(a)) with a gradient of 1.0487 $\pm$ 0.0056 (2σ), intercept of 0.2682 $\pm$ 0.0037 (2σ) and R^2 value of 0.995. By comparison, for ln(^{67}Zn/^{64}Zn) vs. ln(^{65}Cu/^{63}Cu) and ln(^{68}Zn/^{64}Zn) vs. ln(^{65}Cu/^{63}Cu) plots, the linear trend is less well defined, and successive runs drift towards more negative ln(^{67}Zn/^{64}Zn) and ln(^{68}Zn/^{64}Zn) values through time (Fig. 5(b) and (c)). This behaviour is observed on a daily basis on the Axiom, under

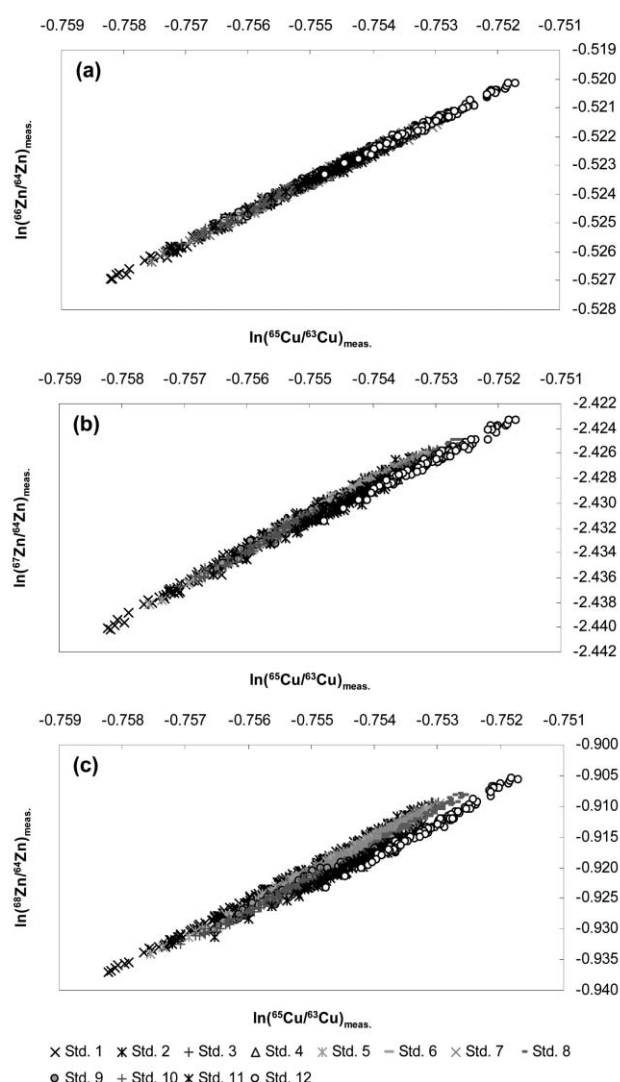**Fig. 4** ln(^{65}Cu/^{63}Cu) vs. ln(^{66}Zn/^{64}Zn) plots constructed from integration data collected on two Cu standards (1 µg ml^{-1} IMP Cu and 1 µg ml^{-1} NIST Cu) spiked with 1 µg ml^{-1} IMP Zn. (a) Data collected under wet plasma conditions and (b) data collected under dry plasma conditions. All measurements were made on the IsoProbe and each plot represents a single measurement session. Data have been baseline corrected using an on-peak acid blank subtraction procedure. No Zn hydride correction was applied. For both wet and dry plasma measurements, the IMP Cu and NIST Cu data define separable arrays, indicating that these standards are isotopically distinct. However, the data have a tendency to cluster due to the relatively stable instrumental mass bias characteristics of the IsoProbe. This clustering hinders the EEN correction, which requires instrumental mass bias drift to define the mass discrimination relationship between Cu and Zn.

Fig. 5 ln(^{65}Cu/^{63}Cu) vs. (a) ln(^{66}Zn/^{64}Zn), (b) ln(^{67}Zn/^{64}Zn) and (c) ln(^{68}Zn/^{64}Zn) for integration data collected on a 1 µg ml^{-1} IMP Zn + 0.4 µg ml^{-1} NIST Cu solution run repeatedly on the Axiom over a 16 h period. Measurements were made using wet plasma conditions. Data have been on-peak baseline corrected and Zn data have been corrected for Zn hydride. In plot (a) data define a single array, supporting the use of the EEN correction. However, for plots (b) and (c) data define a diffuse array, indicative of 'drift' in the ^{67}Zn and ^{68}Zn signals. This effect presents a major analytical challenge to high-precision Zn measurements for ratios incorporating ^{67}Zn and ^{68}Zn.
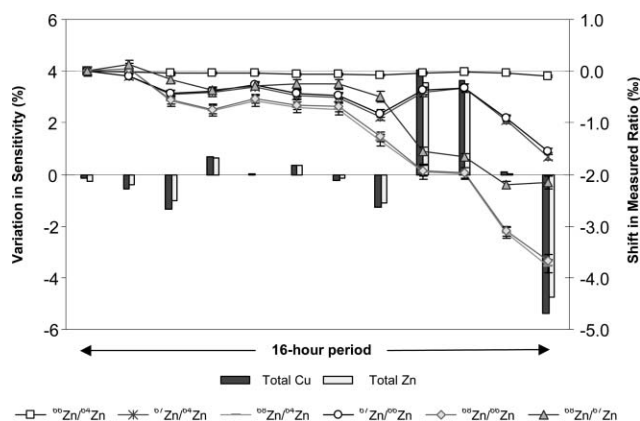
Fig. 6 Quantification of the 'drift' in ratios incorporating ^{67}Zn and ^{68}Zn in ln(Cu) *vs.* ln(Zn) ratio space for repeat analyses of a 1 μg ml^{-1} IMP Zn + 0.4 μg ml^{-1} NIST Cu standard on the Axiom. The deviation of each standard relative to the first standard analysis of the measurement session has been calculated assuming the shift only occurs in the Zn ratio data. These data represent the same dataset presented in Fig. 5. Error bars give the 95% confidence interval for each determination. For ^{66}Zn/^{64}Zn, no significant drift is observed relative to the first standard analysis. However, for ratios incorporating ^{67}Zn the data are observed to decrease by *ca.* 1.6‰ through the session. For ratios incorporating ^{68}Zn this decrease is more pronounced reaching *ca.* 3.8‰ by the last run of the session. Instrumental sensitivity data are presented as the percentage deviation from the mean sensitivity for the standard through the entire measurement session. No clear relationship exists between instrumental sensitivity and the drift of ^{67}Zn or ^{68}Zn.

both wet and dry plasma conditions. Furthermore, similar effects have been observed on the IsoProbe under wet plasma conditions (data not shown), suggesting this phenomenon is not exclusive to the Axiom. These findings may also explain the relatively poor measurement reproducibilities reported by Maréchal *et al.*[12] for $\delta^{67/64}$Zn and $\delta^{68/64}$Zn compared to $\delta^{66/64}$Zn data determined using the graphical EEN correction on the VG P54 MC-ICP-MS.

The drift observed in Fig. 5(b) and (c) has been quantified by comparing each successive analysis to the first standard run of the measurement session, effectively using this first standard to define the 'calibration line' to which all runs are compared (see Fig. 6). With this approach, it is apparent that the drift in ln(^{65}Cu/^{63}Cu) *vs.* ln(^{67}Zn/^{64}Zn) and ln(^{68}Zn/^{64}Zn) plots through time are perfectly matched when substituting ^{67}Zn/^{64}Zn and ^{68}Zn/^{64}Zn for ^{67}Zn/^{66}Zn and ^{68}Zn/^{66}Zn, respectively. This suggests the variations are not related to the mass difference between the isotopes included in the ratio (and are thus not related to mass discrimination), but are

specific to ^{67}Zn and ^{68}Zn measurements. Thus, this behaviour is not consistent with a breakdown in the GPL associated with the analyte and spike ratios becoming further apart in mass as has been proposed to explain inaccuracies in Nd isotope ratio measurements by MC-ICP-MS.[35]

These shifts might represent interference contributions to ^{67}amu and ^{68}amu that progressively decrease during the measurement session. However, this has been discounted as the on-peak baseline procedure should account for systematic drift in instrumental backgrounds, and high-resolution mass scans observed no significant interferences from the standards used at ^{67}amu or ^{68}amu. Drift in the amplifier gains during the session might also explain the shifts. Again, however, this is not favoured as it is unlikely that only the collectors detecting ^{67}Zn and ^{68}Zn would drift, and that this occurs systematically between these two collectors on a daily basis, and on different instruments.

Although the exact cause of this drift remains elusive, it is possible to compensate for it using a modified version of the EEN correction whereby the first standard run of the measurement session is used to define the 'calibration line' from which δ-values are calculated for both samples and subsequent standard runs. Adjacent standard runs are then used to correct for drift in ^{67}Zn and ^{68}Zn for bracketed samples, assuming this drift is linear between standard analyses. This modification is a sample-standard bracketing correction, and suffers from the same inaccuracies associated with the inability to correct for non-linear drift between standard runs as occurs with the SSB correction.

Both the 'unmodified' and 'modified' EEN corrections have been used to calculate the isotopic differences between a series of synthetic solutions (JMC Cu *vs.* NIST Cu, IMP Cu *vs.* NIST Cu, IMP Zn *vs.* JMC Zn and Romil Zn *vs.* JMC Zn) from data collected within a single analytical session on the Axiom (see Table 2). For the unmodified EEN correction, $\delta^{66/64}$Zn, $\delta^{67/64}$Zn and $\delta^{68/64}$Zn data show poor agreement per atomic mass unit (amu^{-1}), as expected given the temporal drift in the ^{67}Zn and ^{68}Zn signals. By contrast, the 'modified' EEN correction yields $\delta^{66/64}$Zn and $\delta^{67/64}$Zn data that show mass-dependency, providing empirical evidence that the modified approach works. For $\delta^{68/64}$Zn, the agreement with $\delta^{66/64}$Zn data is poor. This likely reflects inadequacies in the linear drift approximation.

Simultaneous *vs.* sequential data collection

Gallium, with two stable isotopes (^{69}Ga and ^{71}Ga), has been successfully used to correct for mass discrimination during Zn isotope measurements by Quadrupole ICP-MS.[23] Given its

Table 2 Comparison between data collected^{a} using the 'unmodified' and 'modified' EEN corrections

| Sample *vs.* standard | 'Unmodified' EEN Corr. ($\delta^{65/63}Cu$) | | | 'Modified' EEN Corr. ($\delta^{65/63}Cu$) | | |
	vs. ^{66}Zn/^{64}Zn	*vs.* ^{67}Zn/^{64}Zn	*vs.* ^{68}Zn/^{64}Zn	*vs.* ^{66}Zn/^{64}Zn	*vs.* ^{67}Zn/^{64}Zn	*vs.* ^{68}Zn/^{64}Zn
JMC Cu *vs.* NIST Cu	0.61	0.78	0.86	0.61	0.65	0.66
IMP Cu *vs.* NIST Cu	0.12	−0.06	−0.17	0.13	0.17	0.14
JMC Cu *vs.* NIST Cu	0.63	0.65	0.67	0.62	0.61	0.62

| Sample *vs.* standard | 'Unmodified' EEN Corr. (*vs.* $^{65}Cu/^{63}Cu$) | | | 'Modified' EEN Corr. (*vs.* $^{65}Cu/^{63}Cu$) | | |
	$\delta^{66/64}$Zn	$\delta^{67/64}$Zn	$\delta^{68/64}$Zn	$\delta^{66/64}$Zn	$\delta^{67/64}$Zn	$\delta^{68/64}$Zn
IMP Zn *vs.* JMC Zn (amu^{-1})	0.09	0.30	0.66	0.08	0.07	0.24
IMP Zn *vs.* JMC Zn (amu^{-1})	0.08	0.29	0.64	0.08	0.06	0.22
Romil Zn *vs.* JMC Zn (amu^{-1})	−4.48	−4.29	−3.94	−4.48	−4.47	−4.30

^{a} The data presented were collected on the Axiom using wet plasma conditions and reflect the isotopic differences in δ-notation between a series of Cu and Zn metal standards. While the unmodified EEN data show poor agreement between $\delta^{66/64}$Zn, $\delta^{67/64}$Zn and $\delta^{68/64}$Zn estimates, the 'modified' EEN corrected data yield consistent $\delta^{66/64}$Zn and $\delta^{67/64}$Zn data per atomic mass unit (amu^{-1}). However, this is not true for $\delta^{68/64}$Zn, which deviates from $\delta^{66/64}$Zn estimates. Thus, although the 'modified' EEN correction can adequately account for drift in ^{67}Zn, it is insufficient to fully correct for drift effects during ^{68}Zn measurements.

similar mass to Cu and Zn, a series of experiments have been undertaken to assess its potential for correcting mass discrimination effects during simultaneous Cu and Zn isotope measurements. Because of restrictions imposed by the collector arrays on the Axiom and IsoProbe, it is not possible to include all of the isotopes of interest from [63]amu to [71]amu within the same static collector array. Consequently, a procedure was adopted whereby Cu and Zn were measured in one magnet position followed by Ga in a second magnet position, switching the magnet after each cycle. This magnet switching protocol increases analysis times by roughly a factor of 2.5 for the same number of measurement integrations. Because the quality of data collected using the SSB approach is in part controlled by how often standards are analysed, this slower data acquisition compromises data quality and this approach is therefore not favoured. By contrast, the time elapsed between standard runs is not as critical with the EEN correction, and Ga doping potentially offers increased sample throughput by reducing the number of sample changeovers required.

Fig. 3(a) has been re-plotted substituting ^{66}Zn/^{64}Zn for ^{71}Ga/^{69}Ga using data collected on a Claritas Ga standard added to the JMC Cu and NIST Cu standards (see Fig. 7(a)). When compared to using Zn as an internal mass bias monitor (see Fig. 3(a)), the ln(^{71}Ga/^{69}Ga) vs. ln(^{65}Cu/^{63}Cu) plot shows a significant increase in data scatter, with the combined internal precision of the three $\delta^{65/63}$Cu measurements deteriorating from ca. ± 0.02‰ to ca. ± 0.06‰ (2SE). The average $\delta^{65/63}$Cu value using Ga for the three repeat analyses of JMC Cu vs. NIST Cu is 0.56 ± 0.12‰ (2SD). This falls within error of the value reported by Maréchal et al.[12] Thus, while the Ga-corrected data is less precise, it does not appear to have significantly deteriorated measurement accuracy. Comparable results have been obtained for the IsoProbe using a

peak-switching routine (data not shown), suggesting this effect is not specific to the experimental set up used on the Axiom.

As Ga is measured sequentially with respect to Cu and Zn, the deterioration in measurement precision may represent temporal shifts in mass bias over the time scale of the peak switching procedure. To assess this, the data in Fig. 3(a) has been filtered such that ^{65}Cu/^{63}Cu and ^{66}Zn/^{64}Zn are effectively measured sequentially by discarding alternate ^{65}Cu/^{63}Cu and ^{66}Zn/^{64}Zn measurements (see Fig. 7(b)). The modified data set shows increased scatter when compared to the original data set, and closely resembles the behaviour of Ga within the peak switching procedure. This provides strong evidence that instrumental mass bias on the Axiom fluctuates on a time scale comparable to the 5 s integration time used during data acquisition, supporting the above hypothesis. However, this result does not in itself rule out the possibility that the mass discrimination behaviour of Ga was significantly different to that of Cu during the data collection, and further work is warranted. Rapid fluctuations in instrumental mass bias may also explain the relatively poor precisions reported for Fe-isotope measurements when adopting Cu as an internal mass discrimination monitor in association with a peak switching protocol.[9,29]

Long-term reproducibility for the EEN correction

The combined analytical uncertainty associated with the EEN has been estimated by calculating the reproducibility of repeat analyses of the isotopic differences between two Cu standards (NIST Cu and JMC Cu) measured on seventeen separate occasions over a nine-month period. The mean of the combined data set gives a $\delta^{65/63}$Cu value of 0.619 ± 0.058‰ (2SD). Similar results have been obtained for repeat measurements of the difference between two Zn standards (IMP Zn and JMC Zn), where $\delta^{66/64}$Zn $= -0.087 \pm 0.070$‰ (2SD) from data collected on ten separate measurement sessions over a two week period. If these measurements are compared to those for JMC Cu vs. NIST Cu made during the same analytical sessions, the data show a statistically significant correlation ($R^2 = 0.63$, $n = 10$), with $\delta^{66/64}$Zn tending towards more negative values as $\delta^{65/63}$Cu moves towards more positive values. This suggests a systematic error is associated with the isotope measurements.

Inadequacies in the on-peak baseline correction might explain these systematic variations in δ-values. However, this has been discounted because no statistically significant correlations were observed between $\delta^{65/63}$Cu values for JMC Cu vs. NIST Cu and the average ^{65}Cu/^{63}Cu and ^{66}Zn/^{64}Zn acid blank ratios used for baseline correction. Similarly, inaccuracies in the Zn hydride correction cannot readily explain this error as no significant correlation exists between $\delta^{65/63}$Cu values and the ^{64}ZnH$^+$/^{64}Zn$^+$ ratio used in their determination.

It is possible that systematic bias is introduced by the EEN correction itself. If the fundamental assumptions underlying the EEN correction are met, the gradient of individual runs in ln(^{65}Cu/^{63}Cu) vs. ln(^{66}Zn/^{64}Zn) space will be constant throughout an analytical session, and no correlation is expected between the gradient values used in the EEN correction and the corresponding δ-estimate between measurement sessions. Using this test, no statistically significant correlations were found between $\delta^{65/63}$Cu and (1) the gradient values for the combined NIST Cu standard data set used to calculate each respective δ-value, (2) the gradient of each individual JMC Cu sample run, or (3) the difference in the gradient of each NIST Cu standard data set and the associated JMC Cu sample run. These results thus suggest the systematic error does not originate from the EEN correction, and provide further justification for using this approach.

One parameter that does correlate with $\delta^{65/63}$Cu and $\delta^{66/64}$Zn is instrumental sensitivity ($R^2 = 0.53$ and 0.84 ($n = 10$),
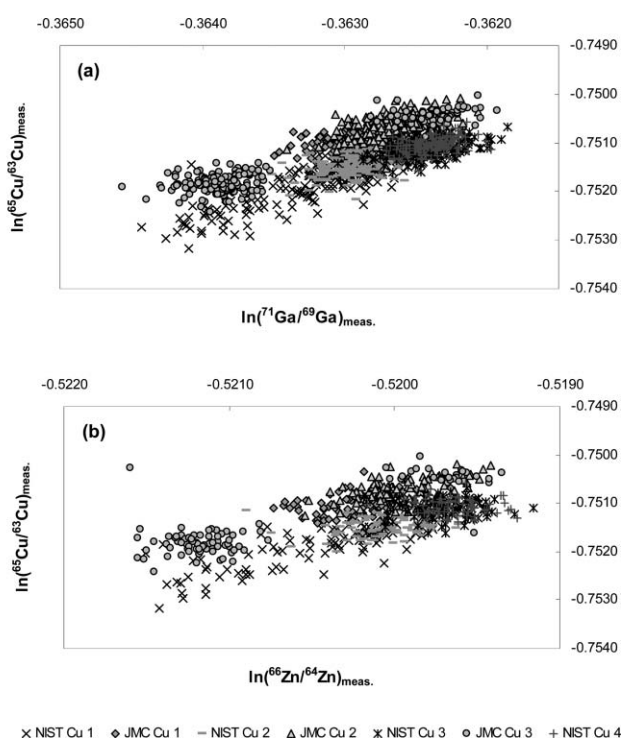

Fig. 7 Raw integration data for two Cu standards (0.4 μg ml^{-1} JMC Cu and 0.4 μg ml^{-1} NIST Cu) spiked with 0.4 μg ml^{-1} Claritas Ga and 1 μg ml^{-1} JMC Zn run on the Axiom under wet plasma conditions. (a) ln(^{65}Cu/^{63}Cu) data vs. ln(^{71}Ga/^{69}Ga) data collected using a peak switching measurement protocol. (b) ln(^{65}Cu/^{65}Cu) data vs. ln(^{66}Zn/^{64}Zn) where alternate Cu and Zn ratios have been discarded from the data set, such that the Cu and Zn measurements are sequential. The increased scatter exhibited by these plots relative to Fig. 3(a) reflects temporal drift in instrumental mass bias over the period of a single 5 s integration.

Table 3 Copper and Zn isotopic variability between a series of commercially available metal standards as measured on the Axiom and IsoProbe

Cu δ-values relative to NIST-SRM 976 Cu

Sample	Instrument	$\delta^{65/63}$Cu (‰)	±2SD	No. analyses
JMC Cu	Axiom[a]	0.619	0.058	21
	IsoProbe[a]	0.641	0.019	3
IMP Cu	IsoProbe[b]	0.20	0.10	22
	IsoProbe[c]	0.207	0.049	35

Zn δ -values relative to IMP Zn

Sample	Instrument	$\delta^{66/64}$Zn (‰)	±2SD	No. Analyses
Romil Zn	Axiom[a]	−9.00	0.041	8
	IsoProbe[b]	−9.09	0.081	6
JMC Zn	Axiom[a]	−0.087	0.070	10
Spec-pure Zn	Axiom[a]	−6.84	—	1
	IsoProbe[a]	−7.15	—	1

[a] Measurements made using the EEN approach under wet plasma conditions. [b] Measurement made using a SSB approach under dry plasma conditions where an independent mass discrimination monitor has been used to reject analyses where the shift in mass discrimination between samples and bracketing standards exceeds ±0.025‰ per atomic mass unit (amu^{-1}). [c] Measurements made using the 'modified' SSB approach under dry plasma conditions.

respectively, calculated relative to the total Zn signal). Several processes may be invoked to explain this relationship, and further investigation is required to identify the exact cause of the systematic error.

Isotopic variability of Cu and Zn metal standards

The relative isotopic compositions of the Cu and Zn metal standards used during the investigation are presented in Table 3. The isotope data collected on the Axiom and IsoProbe using the SSB and EEN corrections are in good agreement for all of the standards analysed, suggesting the two mass discrimination corrections are justified. An interesting feature of this data set is the relatively restricted range in isotopic composition of Cu (at 0.00 to $+0.32‰$ amu^{-1}) relative to Zn (at -4.50 to $0.00‰$ amu^{-1}). This contrasts with published data on the isotopic variability of Cu and Zn in terrestrial samples, where Cu exhibits a greater range in isotopic composition at -4.1 to $+4.6‰$ amu^{-1} relative to Zn at -0.20 to $+1.34‰$ amu^{-1}.[10,12,36–42] Tanimizu and co-workers[43] reported relatively large isotopic differences between commercially available Zn standards of up to $1.2‰$ amu^{-1}, which they proposed reflect isotopic fractionation effects associated with distillation of Zn metal during anthropogenic purification. Whilst the isotopic compositions of the Zn ores used in the production of the standards analysed in this study remain unconstrained, the highly fractionated values observed support the hypothesis of distillation-induced fractionation of Zn during anthropogenic processing. This potentially provides an isotopic marker for distinguishing anthropogenic smelter emissions from natural Zn contaminants.

Summary

Mass discrimination effects have been successfully corrected during Cu and Zn isotope measurements on a VG Axiom and Micromass IsoProbe using (1) a SSB correction and (2) an EEN correction. The internal precision offered by each method is strongly influenced by the magnitude of instrumental mass bias drift experienced during analysis; the former favouring mass bias stability (which can be achieved using dry plasma conditions), and the latter improving with increased mass bias drift (which can be achieved using wet plasma conditions).

The direct SSB approach does not account for non-linear drift in mass discrimination between bracketing standards, which can significantly deteriorate measurement reproducibility on both the Axiom and IsoProbe. Using a modification to the SSB correction, whereby a second element (Zn in the case of Cu measurement) is used to simultaneously correct for these deviations, high-precision Cu and Zn data have been obtained. This approach yields measurement reproducibilities for $\delta^{65/63}$Cu analyses that are comparable to the combined internal precisions associated with individual analyses, indicating that inaccuracies within this modified SSB correction are not the main source of error during isotope measurements.

Temporal drift associated with measuring ratios incorporating ^{67}Zn and ^{68}Zn effectively prevent high-precision measurements of these isotopes on the Axiom and IsoProbe with the EEN correction. These effects have been successfully corrected for during high-precision ^{67}Zn measurements using a modified version of the EEN approach. However, this approach did not enable high-precision ^{68}Zn measurements, possibly reflecting inaccuracies in the linear approximation used.

Instrumental mass bias on the Axiom and IsoProbe fluctuates on a time scale comparable to the 5 s integration time used during data acquisition. This drift effectively prevents the use of sequential data acquisition protocols for high-precision isotope measurements with the EEN approach.

Both the EEN correction and the modified sample standard bracketing approach yield levels of measurement reproducibility (of less than $±0.07‰$ for $\delta^{65/63}$Cu and $\delta^{66/64}$Zn measurements) that are sufficient for identifying natural and anthropogenic variability of copper and zinc in terrestrial samples. This has identified significant mass-dependent isotopic variations in both Cu and Zn in a series of commercially available metal standards. For Zn, these anomalies are proposed to relate to distillation processes during metal purification, potentially providing an isotopic marker for distinguishing between anthropogenic and natural zinc contaminants within the environment.

Acknowledgements

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