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Use of Ga for mass bias correction for the accurate determination of copper isotope ratio in NIST SRM 3114 Cu standard and geological samples by MC-ICPMS

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Abstract: First absolute determination of Cu isotope ratio in NIST SRM 3114 is performed based on a regression mass bias correction model and use of NIST SRM 944 Ga as the calibrant. A value of 0.4471±0.0013 (2SD, n=37) for ^{65}Cu/^{63}Cu ratio was obtained with a value of +0.18±0.04 ‰ (2SD, n=5) for δ^{65}Cu relative to NIST 976. The availability of the NIST SRM 3114 material, now with the absolute value of ^{65}Cu/^{63}Cu ratio and a δ^{65}Cu value relative to NIST 976 make it suitable as a new candidate reference material for Cu isotope studies. In addition, a protocol is described for the accurate and precise determination of δ^{65}Cu values in geological reference materials. Purification of Cu from sample matrix was performed using AG MP-1M Bio-Rad resin. Column recovery for geological samples was found to be 100 ± 2% (2SD, n=15). A modified method of standard-sample bracketing with internal normalization for mass bias correction was employed by adding natural Ga to both the sample and the solution of NIST SRM 3114 used as the bracketing standard. Absolute value of 0.4470±0.0013 (2SD, n=37) for ^{65}Cu/^{63}Cu quantified in this study was used to calibrate the ^{69}Ga/^{71}Ga ratio in the two adjacent bracketing standards of SRM 3114, their average value of ^{69}Ga/^{71}Ga was then used to correct ^{65}Cu/^{63}Cu ratio in the sample. Measured δ^{65}Cu values of 0.18±0.04‰ (2SD, n=20), 0.13±0.04‰ (2SD, n=9), 0.08±0.03‰ (2SD, n=6), 0.01±0.06(2SD, n=4) and 0.26±0.04‰ (2SD, n=7) were obtained in five geological reference materials of BCR-2, BHVO-2, AGV-2, BIR-1a, and GSP-2, respectively, in agreement with values obtained in previous studies.

Introduction

Copper has two stable isotopes, ^{63}Cu and ^{65}Cu, with relative abundances of 69.17% and 30.83%, respectively.[1, 2] As an important ore-forming element, copper exists widely in different geological systems and is active in ore-forming and rock-forming processes.[3] Therefore, copper isotopes can be a useful geochemical tracer and play an important role in the study of sources of Cu in the ore-forming process and mechanism.[4-6] Copper isotopes have also been used as a new tracer in the study of the evolution of the Earth's environment, geosphere and biosphere interactions, and other aspects of the formation mechanism of the deposit.[7, 8] It is of great significance to obtain high precision and accuracy copper isotope ratio data. Significant variations of copper isotope composition have been reported in nature. Walker *et al.*[1] and Shields *et al.*[2] used thermal ionization mass spectrometry (TIMS) to investigate the distribution of Cu isotope ratio in natural samples. Modern advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) have allowed high precision isotope ratio measurements, and the relative precision of Cu isotope ratio measurements can be as low as 40-50 ppm on a variety of ores, rocks, and biological materials.[9-10] Moreover, MC-ICPMS benefits from simple and robust sample introduction, high sample throughput, and high mass resolution. The advantages above have generated a renewed research interest in copper isotopes.[11-12]

MC-ICPMS suffers from large mass bias which needs to be properly corrected for the accurate isotope ratio measurements. For Cu isotope ratio measurements, various mass bias correction models can be employed, such as the direct standard-sample bracketing (SSB) model,[13] the combined SSB with internal mass bias correction model and regression mass bias correction model[9]. The SSB approach is capable of correcting instrumental mass bias providing analyte and sample matrix are matched between the standard and the sample. However, it does not account for short-term fluctuations in mass bias between bracketing standards. Recent studies[14-19] have reported use of a combined SSB with internal mass bias correction model whereby a standard with known analyte ratio is used to calibrate the ratio of the internal standard; this calibrated ratio of the internal standard is then used to calibrate the analyte ratio in the sample. The advantage of this correction model is that the short-term fluctuations in mass bias between bracketing standards are corrected. As demonstrated in these studies,[14-19] precision of analyte ratio has improved at least twofold by using the combined SSB with internal standard when compared to the direct SSB.

Previously published Cu isotope data are reported relative to the reference material of NIST SRM 976, which is certified for Cu isotope amount ratio.[20-23] Unfortunately, the NIST SRM 976 is no longer available, thus alternative reference materials with known isotopic composition are in urgent need for the Cu isotope ratio studies in various scientific fields. Ideally, the new reference material is calculated against NIST SRM 976 in order to have comparative data from different research labs. For example, the reference materials ERM-AE633 and ERM-AE647 from IRMM (Institute for Reference Materials and Measurements, Belgium) were calibrated against the NIST SRM 976 for δ^{65}Cu.[22] Liu et al. [24] also used the GSB from the National Standard Substances of China as a new Cu standard, where the average $\delta^{65}\mathrm{Cu}_{\mathrm{GSB}}$ for Cu solutions is +0.44±0.04 (2SD; n=32) relative to NIST

976. However, absolute isotope amount ratio of Cu in these standards was not measured.

The homogeneous quantities and proper storage of reference materials from international reference producers, such as the National Institute of Standards and Technology (NIST), the Institute for Reference Materials and Measurements (IRMM), the International Atomic Energy Agency (IAEA), or the Federal Institute for Materials Research and Testing (BAM), are guaranteed. In this study, NIST 3114 copper standard solution was selected as a candidate Cu reference material and its absolute Cu isotope amount ratio was determined by MC-ICPMS using the regression mass bias correction model[25] which is based on temporal drifts between the measured Cu and Ga isotope ratios in their log space. Note that other calibrant such as Zn isotopic standard can also be used. However, Ga isotopes have no isobaric interferences and less polyatomic interferences compared to Zn isotopes. Moreover, the isotopic reference material NIST SRM 994 Ga is certified for Ga isotopic composition with high precision and accuracy, and it is commercially avaiable. Thus, it was used as the calibrant for the absolute determination of Cu isotope ratio. Cu isotope ratio of several common geological reference materials were determined relative to the new characterized reference material (NIST SRM3114) using the combined SSB and internal normalization method with the internal standard of Ga. These geological reference materials were subjected to ion exchange column separation of Cu from geological and Fe-rich matrices prior to MC-ICPMS measurements.

Experimental Section

Instrumentation

All Cu isotope ratio measurements were carried out on a MC-ICPMS (Neptune Plus, Thermo Finnigan Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, Wuhan, China. This instrument is equipped with nine Faraday cups, a spray chamber containing a Scott-type spray chamber on the top and a cyclonic spray chamber on the bottom with a MCN50 PFA self-aspirating nebulizer (Elemental Scientific, Omaha, NE, USA) operating at 50 µl min^{-1} was used for Cu isotope ratio measurements at the low-resolution mode. Optimization of the Neptune was performed daily, and typical operating conditions are summarized in Table 1. The gain calibration for Faraday cups was performed daily to ensure correction for its efficiency. A quadrupole ICPMS from Agilent Technologies (Yokogawa, Japan) was used for semi-quantitative analysis of matrix elements concentrations in rinse and eluate fractions collected from column separation.

Reagents and Materials

Nitric and hydrofluoric acids were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a DST-1000 acid purification system (Savillex, Eden Prairie, USA), and hydrochloric acid used to load sample was prepared by dilution of Suprapur® grade hydrochloric acid (Merck KGaA., Darmstadt, Germany) with DI water. High purity deionized water (DIW) 18 M Ω was obtained from a Milli-Q water system (Millipore Corp., Billerica, MA, USA). All lab wares, including Savillex® containers and disposable plastics, were cleaned in concentrated reagent-grade acids and deionized H_2O prior to use.

The candidate reference material NIST SRM 3114 Cu and the internal standard of NIST SRM 994 Ga were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Gallium metal isotopic reference material, NIST SRM 994, is certified for $^{69}Ga/^{71}Ga=1.50676\pm0.00039$ (U, at 95% condidence interval), determined by thermal-ionization mass spectrometry.[26] A 2000 μg g^{-1} stock solution of NIST SRM 994 was prepared by quantitative dissolution of Ga in concentrated HNO_3 and HCl with heating and then diluted with DIW. In addtion, for comparsion of SRM 3114 Cu to other Cu standards, a 100 μg g^{-1} standard solution of copper was prepared by dilution of a high-purity Cu solution of 1000 mg l^{-1} Cu (copper ICP standard, Merck KGaK, Darmstadt, Germany batch Cu011017) in 2% nitric acid. A 200 ng g^{-1} Cu (Alfa Cu A) solution was prepared by dilution of the 10,040 μg g^{-1} Cu stock (Alfa Aesar, Karlsruhe, Germany; batch 23·16498C) in 2 % HNO_3 solution. Another Alfa Aesar Cu stock solution (Alfa Cu B) of 1000 μg g^{-1} was prepared by quantitative dissolution of Puratronic® Cu wire (batch 04·1792K) in HNO_3 and diluted with DIW. GSB Cu standard was obtained from the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing, China.

Five geological reference materials of BCR-2, BHVO-2 and BIR-1a (basalts), AGV-2 (andesite) and GSP-2 (granite) purchased from United States Geological Survey (Reston, VA, USA) were used as test samples for Cu isotope ratio measurements.

Sample preparation and analysis of NIST SRM 3114 Cu standard for absolute Cu isotope ratio

The absolute isotope ratio of Cu standard (NIST 3114) was measured following an early method described by Yang et al.[25], using a regression mass bias correction model with Ga as calibrant. Replicate solutions of 200 ng g^{-1} Cu were prepared by diluting the Cu stock solution in 2% HNO_3 followed by spiking with the gallium standard solution, yielding a mass fraction of 200 ng g^{-1} for Ga. Samples were introduced into MC-ICP-MS at a flow rate of 50 µl min^{-1}. Intensities of Cu and Ga isotopes obtained from a 2% HNO_3 blank solution were subtracted from those of all samples. A static run was employed to collect ^{63}Cu, ^{65}Cu, and ^{69}Ga and ^{71}Ga isotopes simultaneously using the Faraday cup configuration shown in Table 1. A total of 15 measurements were made on each sample solution and the duration of each session of measurements was about 5-6 h. Data acquisition parameters are summarized in Table 1.

Geological sample preparation and analysis

Sample preparation was carried out in a metal-free clean room fitted with an HEPA-filtered air supply and laminar low benches. 50 mg sub-samples were dissolved in 3 ml HF/HNO_3 (1:1) at 190°C for 48h in Teflon beakers. The contents were evaporated to dryness on a hot plate at 105°C. 1 ml of HNO_3 was added to each sample and then evaporated to dryness to completely remove HF. 1 ml of 8.5 N HCl + 0.03% H_2O_2 solution was then added to each beaker. All beakers were placed in an oven and heated at 120°C for 10h. Contents were then evaporated to dryness on a hot plate at 105°C. 0.25 ml 8.5N HCl+0.03% H_2O_2 solution was added to each beaker and the contents were evaporated to dryness. This process was repeated three times to ensure that all cations were converted to chloride species. The final residues were redissolved in 8 ml 8.5 N HCl+0.03% H_2O_2 for the purification of Cu using anion exchange resin.

Copper was separated from the matrix using new type of anion exchange AG MP-1M Bio-Rad resin (100–200 mesh) and followed a protocol by Maréchal et al.[11] (1999) with some modifications. Instead of 7 N HCl used by Maréchal et al. 8.5 N HCl was used in this study to achieve more efficient separation of Cu from matrix elements, especially Co. The resin was first cleaned by sequential leaching twice with 10 ml of 2N HNO_3 and twice with 10 ml 2N HCl, respectively.[27, 28] Columns containing 1 ml of AG MP-1M resin were cleaned and preconditioned using acidic solutions as detailed in Table 2. Most matrix elements (e.g. Na, Mg, Al, K, Ca, Ti, Cr, Ni and Mn) were eluted in the first 4 ml of 8.5 N HCl, and Cu was eluted in the following 8 ml 8.5 N HCl, leaving Co, Fe and Zn retained on the resin. These eluents containing Cu were evaporated to dryness on a hot plate at 105^{o}C and redissolved in 0.1 ml concentrated HNO_3 and diluted to 4 ml with DIW.

0.5 ml of purified Cu fractions were taken and diluted to 4 ml in 2% HNO_3 (v/v), and were measured by ICP-MS (POEMS III ICP-MS) for total Cu concentration to check the recovery of column separation for each sample. The remaining purified Cu fractions in 2% HNO_3 were spiked with Ga standard solution, yielding a concentration of 200 ng g^{-1}. Solutions of SRM 3114 in 2% HNO_3 containing similar concentrations of Cu as in the purified BCR-2, BHVO-2, BIR-1a, AGV-2and GSP-2 solutions, respectively, were prepared and spiked with Ga to yield a concentration of 200 ng g^{-1}. Samples and standards were introduced into the MC-ICPMS in the following sequence: SRM 3114 – sample – SRM 3114. Four replicate measurements or more of each sample solution were performed.

Results and Discussion

Absolute Cu isotope ratio measurements in NIST SRM 3114. For the absolute determination of Cu isotope ratio in NIST SRM 3114, the log-linear regression mass bias correction model was used to measure isotope ratio of Cu in this study, in a manner similar to that used in previous studies of Cu[11], Fe[29, 30], Hg[31, 32], Ge[25], Ag[15] and In[15] isotopes. This model is based on monitoring the temporal drift in the simultaneous isotopic ratio measurements where the intercept and slope of the constructed log-linear regressions between the observed (uncorrected) isotope ratio of the measurand $r^{\mathrm{Cu}}_{65/63}$and the calibrant $r^{\mathrm{Ga}}_{69/71}$ forms the basis for calibration of Cu isotope ratio. The major advantage of the regression model over the traditional exponential correction model is that the regression approach is free of the requirement for identical fractionation behavior between the element pairs[25, 33]. In recent years, the assumption of identical mass bias for the analyte and internal standard used in the traditional exponential correction model has proven to be wrong within MC-ICPMS ($f^{\mathrm{Pb}} \neq f^{\mathrm{Tl}}$, $f^{\mathrm{Hg}} \neq f^{\mathrm{Tl}}$ or $f^{\mathrm{Sr}} \neq f^{\mathrm{Zr}}$, etc.)[9, 14-19] and thus it should not be used for the absolute ratio measurements. From our preliminary experiments, Cu isotope ratio measured in a 15 ng g^{-1} Cu standard solution of SRM 3114 was found to be significantly different from that measured in a 700 ng g^{-1} Cu standard solution of SRM 3114 using the traditional exponential mass bias correction model with Ga as an internal standard (Eq. 4), confirming mass bias for Ga and Cu is not identical. Additionally, the regression model is not hampered by the untestable assumption regarding the very nature of the fractionation (linear, exponential, etc.) since it is based on measured raw data, but measurement time required for the regression model is longer. Equation 1 forms the basis for the Cu isotope ratio calibration with Ga as the calibrant:[18, 25]

$$\ln r^{\mathrm{Cu}}_{65/63} = \underbrace{\ln R^{\mathrm{Cu}}_{65/63} - \frac{\ln K^{\mathrm{Cu}}_{65/63}}{\ln K^{\mathrm{Ga}}_{69/71}} \ln R^{\mathrm{Ga}}_{69/71}}_{\text{intercept, } a} + \underbrace{\frac{\ln K^{\mathrm{Cu}}_{65/63}}{\ln K^{\mathrm{Ga}}_{69/71}}}_{\text{slope, } b} \cdot \ln r^{\mathrm{Ga}}_{69/71} \qquad (1)$$

Note that Equation 1 is a logarithnic rearrangment of the expressions of $R^{\mathrm{Cu}}_{65/63} = K^{\mathrm{Cu}}_{65/63} \cdot r^{\mathrm{Cu}}_{65/63}$ and $R^{\mathrm{Ga}}_{69/71} = K^{\mathrm{Ga}}_{69/71} \cdot r^{\mathrm{Ga}}_{69/71}$, where K is the isotope ratio correction factor that links the measured isotope ratio (*r*) with the mass bias corrected isotope ratio (*R*). As evident from Figure 1, the measured drift of the $r^{\mathrm{Cu}}_{65/63}$ and $r^{\mathrm{Ga}}_{69/71}$ isotope ratios shows a well-defined log-linear relationship over a measurement session of 5-6 h in accordance with the Equation 1. The corresponding intercept (*a*) and slope (*b*) of the log-linear regression are calculated using the least squares regression and these values are then used to obtain the mass-bias corrected Cu isotope ratio, by algebraic rearrangement of Equation 1:

$$R^{\mathrm{Cu}}_{65/63} = \left(R^{\mathrm{Ga}}_{69/71}\right)^{b} \cdot \mathrm{e}^{a} \qquad (2)$$

In this work, the NIST certified value[26] of 1.50676(39)$_{95\%}$ was used for $R^{\mathrm{Ga}}_{69/71}$ to obtain the mass bias corrected $R^{\mathrm{Cu}}_{65/63}$. Although Equation 2 resembles the traditional exponential mass-bias correction in its appearance, but the underlying logic is not the same.[14, 25] This "regression" approach is capable of generating accurate isotope ratio results as demonstrated in previous studies,[15,25,31,34] however, it suffers from poorer precision due to the need for linear regression fitting to generate the slope and intercept, which are subsequently used to calculate a mass bias corrected analyte ratio. To reduce the uncertainty associated with this process, the number of measurement sessions should be increased.[14] During a six-month period between December 2013 and June 2014, many sets of isotope ratio log-linear regressions were acquired for $^{65}Cu/^{63}Cu$ vs $^{69}Ga/^{71}Ga$, each yielding the respective intercept and slope. Of these, 37 high-quality sets exhibiting a coefficient of determination larger than 0.999 ($R^2 \geq 0.999$) were selected for calculation of the final results. The mass bias corrected Cu isotope ratio of 0.4470±0.0013 (2SD, n=37) was obtained.

Comparison of SRM 3114 to other Cu standards. As mentioned above, previously published Cu isotope data are reported relative to the reference material of NIST SRM 976, which is certified for Cu isotope amount ratio.[24, 35-39] Unfortunately, this reference material is no longer available. In order to compare results of Cu isotope ratio generated from different research labs, it is essential to compare Cu isotope ratio value in SRM3114 to other Cu standards or internationally accepted common standard material. Delta notation (δ) for the Cu isotope ratio is thus employed relative to the SRM3114 in accordance with:

$$\delta^{65}\mathrm{Cu}=\left(\frac{R_{sample}}{R_{standard}}-1\right)\times 1000 \tag{3}$$

To correct mass bias, a combined standard sample bracketing and internal normalization method (C-SSBIN) is undertaken in this study. Ga is used as the internal standard and added to both sample and standard solutions, a variation of the methodology as typically used for other isotope systems.[14-19] However, this mass bias correction model still requires the matching of analyte concentration in the sample and standard solutions[24]. Thus in this study, concentrations of analyte and internal standard in the sample and standard were matched within 10% to ensure accurate measurement results. To the best of our knowledge, this is the first report of implementing this C-SSBIN mass bias correction model with use of Ga as the internal standard for the determination of Cu isotope ratio. The obtained absolute value of 0.4470±0.0013 (2SD, n=37) for ^{65}Cu/^{63}Cu in SRM 3114 was used to calculate mass bias corrected ratios of ^{69}Ga/^{71}Ga in two adjacent bracketing standard solutions of SRM 3114 in accordance with Equation 4 of Russell's law:[40, 41]

$$R^{69/71}_{\mathrm{SRM3114}} = r^{69/71}_{\mathrm{SRM3114}} \cdot \left(\frac{m_{71}}{m_{69}}\right)^{f^{\mathrm{Cu}}} \quad \text{and} \quad f^{\mathrm{Cu}} = \frac{\ln\left(\dfrac{R^{65/63}_{\mathrm{SRM3114}}}{r^{65/63}_{\mathrm{SRM3114}}}\right)}{\ln\left(\dfrac{m_{63}}{m_{65}}\right)} \qquad (4)$$

$$R^{65/63}_{\mathrm{sample}} = r^{65/63}_{\mathrm{sample}} \cdot \left(\frac{m_{63}}{m_{65}}\right)^{f\mathrm{Ga}} \quad \text{and} \quad f^{\mathrm{Ga}} = \frac{\ln\left(\dfrac{\overline{R^{69/71}_{\mathrm{SRM3114}}}}{r^{69/71}_{\mathrm{sample}}}\right)}{\ln\left(\dfrac{m_{71}}{m_{69}}\right)} \qquad (5)$$

where *r* and *R* are the measured and true isotope ratios, respectively, *m* is nuclide mass of the isotope of interest which can be found elsewhere,[42] and *f* is the mass bias factor. Their average value of ^{69}Ga/^{71}Ga was then used to calculate mass bias corrected Cu isotope ratio in the sample using Equation 5. Note that the Ga internal standard in the sample serves as the mass-bias correction proxy to correct time-dependent variation of the mass bias. Therefore the absolute value of the Ga isotope ratio is not needed. Even though the value obtained for the Ga isotope ratio may be biased due to the limitations of the employed mass-bias correction model (e.g., assumption of $f^{\mathrm{Cu}} = f^{\mathrm{Ga}}$), this bias is largely negated in the second step of the calibration (Ga→Cu). However, this mass bias correction model is only fully valid if matrix and concentration matching is fully attained.

Results from measurements of an Alfa Cu (A) standard solution relative to NIST SRM

3114 using direct SSB (Fig. 2a) and C-SSBIN (Fig. 2b) mass bias correction models, respectively, are presented in Figure 2. The results were acquired over a period of four days. Values of 0.22±0.05‰ (2SD, n=10) and 0.20±0.01‰ (2SD, n=10) for δ^{65}Cu in Alfa Cu (A) relative to NIST 3114 standard were obtained with use of direct SSB and C-SSBIN for mass bias correction, respectively. Clearly both mass bias models could generate accurate results for δ^{65}Cu, but an approximately five-fold improvement in precision of determination of δ^{65}Cu was obtained with the use of the proposed C-SSBIN mass bias correction approach compared to that obtained solely using the SSB approach. Based on this observation, the C-SSBIN mass bias correction approach was thus selected for all subsequent measurements. A value of 0.06 ±0.03‰ (2SD, n=6) for δ^{65}Cu in Alfa Cu (B) relative to NIST 3114 standard was obtained. The long-term reproducibility of Alfa Cu (A) was 0.01‰ (2 SD, n = 32). Hence, both standards of Alfa Cu (A) and Alfa Cu (B) may be used as in-house standards for quality control.

GSB Cu (>99.99%) standard was measured against the SRM 3114 using the C-SSBIN for mass bias correction, and a value of +0.27±0.02‰ (2SD, n=6) for δ^{65}Cu was obtained, in agreement with the value of +0.26±0.04‰ (2SD, n=5) measured by the Isotope Geochemistry Laboratory of the China University of Geosciences, Beijing, China. Liu et al.[24] reported a value of +0.44±0.04‰ (2SD, n=32) for $\delta^{65}\mathrm{Cu}_{\mathrm{GSB}}$ in GSB Cu relative to NIST SRM 976. Based on these results, δ^{65}Cu value of +0.18±0.02‰ (2SD, n=6) relative to NIST SRM 976 for NIST 3114 is thus calculated.

Since the NIST SRM3114 is commercially available and now with the absolute Cu isotope ratio determined, we recommend use of this material over the SRM 976 for future Cu isotopic studies. Based on the study by Moeller et al.[22] wherein $\delta^{65/63}$Cu isotope ratio of NIST SRM 976 was determined against ERM-AE633 and ERM-AE647 Cu reference standards and values of -0.01 ± 0.05‰(2SD,n=40) and value of -0.21 ± 0.05‰ (2SD,n=60) were obtained, respectively. Alternatively, two Cu standards, ERM-AE633 and ERM-AE647, can also be used as new certified reference materials for future Cu isotopic studies. Regardless of which Cu standard is selected, we strongly recommend report final Cu isotope ratio data relative to NIST SRM976 by using available $\delta^{65/63}$Cu values between these four Cu standards of NIST SRM976, SRM3114, IRMM ERM-AE633 and ERM-AE647 for calculations, in order to obtain comparable results from different research labs.

Matrix separation. As noted earlier, the CSSBIN mass bias correction model and other correction models, requires matrix matching between the sample and the standard solutions to ensure accuracy. Since it is practically impossible to match all matrix elements between a sample (e.g. geological samples) and a standard solution, separation of matrix elements is the method of choice. It is widely recognized that non-quantitative recovery of analyte during such a process may result in isotope fractionation,[43-44] and quantitative recovery (above 95 %) of analyte is thus required to ensure accurate results. Recovery was thus checked for every geological sample by ICP-MS and a value of 100 ± 2% (2 SD, n=15) was obtained for these samples.

The collected Cu fractions in 2% HNO_3 solution were examined by semi-quantitative analysis to check the efficiency of matrix separation. Concentrations of concomitants were significantly reduced and only a few matrix elements (i.e., Na, Fe, Co and Ti) remained at levels greater than 0.01 (expressed as ratio of individual matrix element concentration to the Cu concentration in the purified digests). These matrix elements not only potentially generate polyatomic interferences such as $^{23}Na^{40}Ar^{+}$, $^{23}Na_2{}^{16}O^{1}H$, $^{23}Na_2{}^{18}O^{1}H^{+}$ $^{47}Ti^{16}O^{+}$, $^{46}Ti^{16}O^{1}H^{+}$, $^{49}Ti^{16}O^{+}$, $^{48}Ti^{16}O^{1}H^{+}$on ^{63}Cu and ^{65}Cu, but also induce matric effects, which could bias the final results. Thus the effects of Na, Fe, Co and Ti on $\delta^{65}Cu$ were investigated by examining 0.2 μg g^{-1} Cu standard solutions of NIST SRM 3114 in the presence of various amounts of Na, Fe, Co and Ti, relative to a pure 0.2 μg g^{-1} Cu standard solution of SRM 3114. Measured intensities for Ga isotopes in the 2% HNO_3 solution and in the purified Cu fractions (prior to spike with Ga internal standard) were at background levels of <0.0001 V, confirming insignificant polyatomic interferences of $^{40}Ar^{29}Si^{+}$ and $^{40}Ar^{15}N^{16}O^{+}$ on ^{69}Ga and ^{71}Ga.

Figure 3 shows the effect of Na on $\delta^{65}Cu$. It is evident that when concentration ratio of Na/Cu is less than 0.5, no significant effect on the $\delta^{65}Cu$ is presented. In this study, the measured concentration ratios of Na/Cu in purified digests were found to be less than 0.05, therefore the influence of Na^{+} on the final Cu isotope ratios can be neglected.

The matrix effects of Fe and Co on $^{65}Cu/^{63}Cu$ ratio measured are presented in Figure 4. No significant effect on $\delta^{65}Cu$ during the tested range of concentration ratio of Fe/Cu from 1 to 20, as shown in Figure 4a. Since the measured concentration ratios of Fe/Cu in purified digests were less than 15, thus the influence of Fe on the final Cu isotope ratio can be neglected. Unlike iron, the effect of Co on $\delta^{65}Cu$ became significant when Co/Cu ratio increased to 1. Since the Co/Cu ratio was found to be less than 0.02 in the purified digests, confirming no significant effect on the final δ^{65}Cu values.

The residual Ti content in the range of 0-1.0 for concentration ratio of Ti/Cu was found in the purified digests. Based on the relative isotope abundance of Ti, polyatomic interferences of $^{47}Ti(7.44\%)^{16}O^+$ and $^{46}Ti(8.25\%)^{16}O^1H^+$ on ^{63}Cu; $^{49}Ti(5.41\%)^{16}O^+$ and $^{48}Ti(73.72\%)^{16}O^1H^+$ on ^{65}Cu would induce the measured δ^{65}Cu value towards to heavier value. As shown in Figure 5a, measured δ^{65}Cu values in SRM 3114 solutions spiked with various amounts of Ti increased significantly as Ti concentration increased. Since the residual Ti contents in the purified geological digests have significant effect on δ^{65}Cu, correction for such interferences remains essential. Instead of performing a second chemical separation, the bracketing standard SRM 3114 solution was doped with same amount of Ti as in the purified geological digests. As shown in Figure 5b, accurate δ^{65}Cu can be obtained when matrix is matched for Ti for both the sample and the bracketing standard. Thus for the determination of δ^{65}Cu in purified geological digests, each bracketing standard solution of SRM 3114 was doped with same amount of Ti in each purified digest to achieve accurate δ^{65}Cu measurements.

Results for geological reference materials. A total process blank of 2 ng was found for Cu, typically less than 1–2% of Cu found in the purified geological sample digests. Nevertheless, intensities of all measured isotopes obtained from the process blank were subtracted from those of all samples. Results for Cu isotope ratios in five geological reference materials are summarized in Table 3. Based on the δ^{65}Cu value of +0.18±0.02‰ (2SD, n=6) for NIST

3114 relative to NIST SRM 976 calculated earlier, final results for δ^{65}Cu in the geological reference materials were converted relative to SRM 976 for comparison. The δ^{65}Cu values for basaltic reference materials (BCR-2, BHVO-2 and BIR-1a) as well as for an andesite (AGV-2) and a granodiorite (GSP-2) spanned in a rather narrow range between 0.01 and 0.26‰ relative to NIST SRM 976. All results are in good agreement with previously determined Cu isotope ratio data of these reference materials[35-39], confirming the accuracy of the proposed method.

Conclusion

A method is presented the first time for the absolute determination of Cu isotope ratio in NIST SRM3114, wherein isotopic ratio was calibrated using the regression mass bias correction model with NIST SRM 944 Ga as the calibrant. A value of 0.4470±0.0013 (2SD, n=37) for ^{65}Cu/^{63} ratio was obtained for the NIST SRM3114 with a value of +0.18±0.04 ‰ (2SD, n=5) for δ^{65}Cu in NIST SRM 3114 relative to NIST 976. Based on above values, NIST SRM 3114 is recommeded to be a candidate reference material for future Cu isotope ratio studies.

Moreover, an accurate and precise method has been developed for the determination of Cu isotope ratio in geological samples by MC-ICPMS using the modified mass bias correction approach comprising standard-sample bracketing and internal normalization. To the best of our knowledge, this is the first report of implementing this C-SSBIN mass bias correction model with use of Ga as the internal standard for the determination of Cu isotope ratio. An approximately five-fold improvement in precision of determination of δ^{65}Cu was obtained with use of the proposed C-SSBIN mass bias correction approach compared to that obtained solely using the SSB approach. The proposed method is expected to have applications for Cu isotope ratio measurements in study of hydrothermal ore-forming processes, paleo-oceanography, and biological processes.

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Table 1. MC-ICPMS Operating Conditions

	Instrument Settings
Forward power	1183W
plasma gas flow rate	16.0 L Ar min^{-1}
auxiliary gas flow rate	0.95 L Ar min^{-1}
carrier gas flow rate	1.030 L Ar min^{-1}
Sample cone (H)	Nickel, 1.1 mm (orifice)
Skimmer cone (X)	Nickel, 0.88 mm (orifice)
lens settings	Focus: -880V; X deflection: 0.21 V; Y deflection: -0.41 V; Shape: 202V V; Rot Quad 1: 3.00 V; Foc Quad 1: -19.89 V; Rot Quad 2: 5.78V; Source Offset: 1.00 V; Focus Offset: 50.00 V
	Data Acquisition Parameters
Faraday cup configuration	L4 (^{63}Cu), L2 (^{65}Cu), C (^{67}Zn), H2 (^{69}Ga), H4 (^{71}Ga)
Zoom Optics	Focus Quad: 0 V and Dispersion Quad: 0 V
Mass resolution, $m/\Delta m$ at 5 and 95%	~300
sensitivity	13 V for ^{63}Cu at 200 ng/g
blank signal (2% HNO_3)	3 mV for ^{63}Cu
signal integration time	4.194 s
No. of integrations, cycles, blocks	1, 10, 5

Table 2. Column separation procedure using AG MP-1M Bio-Rad resin.

Separation steps	Volume of elute and acid type	Volume/ml
Cleaning	2N HNO_3, 2N HCl	10×2，10×2
Conditioning	8.5N HCl+0.03% H_2O_2	2
Sample loading	8.5 N HCl+0.03% H_2O_2	1
Matrix elution	8.5 N HCl+0.03% H_2O_2	4
Cu elution	8.5 N HCl+0.03% H_2O_2	8

Table 3. Results (mean, 2SD) for geological reference materials

Sample name	**δ^{65}Cu relative to SRM 3114**	**δ^{65}Cu relative to SRM 976**	**reported[a]**	**Sources**
BCR-2	0.00±0.04(n=20)	0.18±0.04(n=20)	0.22±0.05	Bigalke et al(2010a)[35]
			0.22±0.04	Liu et al(2014)[24]
			0.18 ± 0.09	Bigalke et al(2011)[36]
			0.16±0.04	Tang et al.(2012)[37]
BHVO-2	-0.05±0.04(n=9)	0.13±0.04(n=9)	0.10±0.07	Moynieret et al.(2010[21]
			0.15±0.05	Liu et al(2014) [24]
AGV-2	-0.10±0.03(n=6)	0.08±0.03(n=6)	0.05±0.04	Liu et al(2014) [24]
			0.10±0.10	Weinstein et al. (2011)[38]
BIR-1a	-0.17±0.06(n=4)	0.01±0.06(n=4)	0.00±0.05	Liu et al(2014) [24]
			0.027±0.019	Tang et al.(2012) [37]
GSP-2	0.08±0.04(n=7)	0.26±0.04(n=7)	0.30±0.04	Liu et al(2014) [24]
			0.25±0.03	Bigalke et al(2010a)[35]
			0.35±0.06	Bigalke et al(2010b)[39]

a: The reported values δ^{65}Cu were calculated relative to SRM 976.

Figure Captions

Figure 1. Temporal drift of the copper and gallium isotope ratios during a 6h measurement session. The log-linear regression plot is the basis for calibration of copper isotope ratio via the $R^{\mathrm{Ga}}_{69/71}$ certified reference value (NIST SRM 994).

Figure 2. Comparison of two mass bias correction models for the determination of ^{65}Cu/^{63}Cu ratio in Alfa Cu standard, error bars are 2SD. (a) Direct SSB mass bias correction approach; (b) Proposed C-SSBIN mass bias correction approach.

Figure 3. The effect of Na on δ^{65}Cu measured in NIST SRM 3114 Cu standard solutions spiked with different amounts of Na, error bars are 2SD. C-SSBIN mass bias correction approach was used.

Figure 4. Assessment of effects of Fe (a) and Co (b) contents on δ^{65}Cu measurements, error bars are 2SD. The errors (2SD) were calculated based on four times replicate measurements. C-SSBIN mass bias correction approach was used.

Figure 5. The effect of Ti concentration on δ^{65}Cu, error bars are 2SD. a: SRM 3114 solutions containing 0.2 µg g^{-1} Cu spiked with different amounts of Ti relative to the pure SRM 3114 0.2 µg g^{-1} Cu solution; b: SRM 3114 solutions containing 0.2 µg g^{-1} Cu and

different amounts of Ti measured against themselves, respectively. C-SSBIN mass bias correction approach was used.

Fig.1

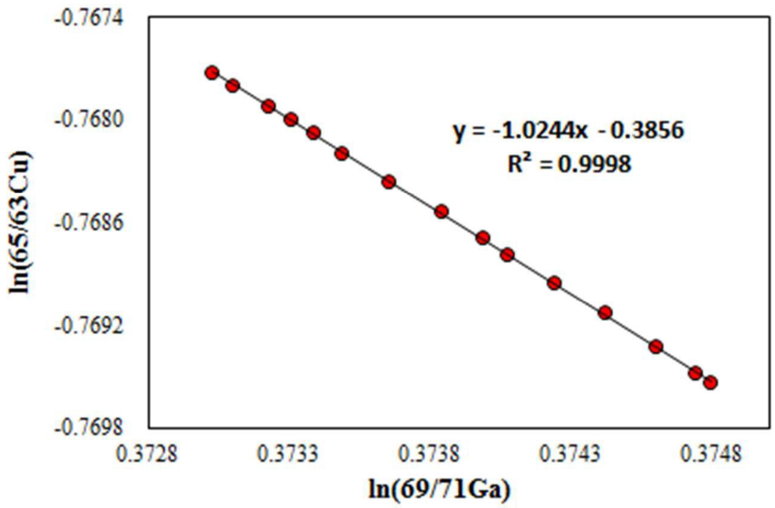
-0.7674
-0.7680
-0.7686
-0.7692
-0.7698
0.3728
0.3733
0.3738
0.3743
0.3748
ln(65/63Cu)
ln(69/71Ga)
y = -1.0244x - 0.3856
R² = 0.9998

Fig.2

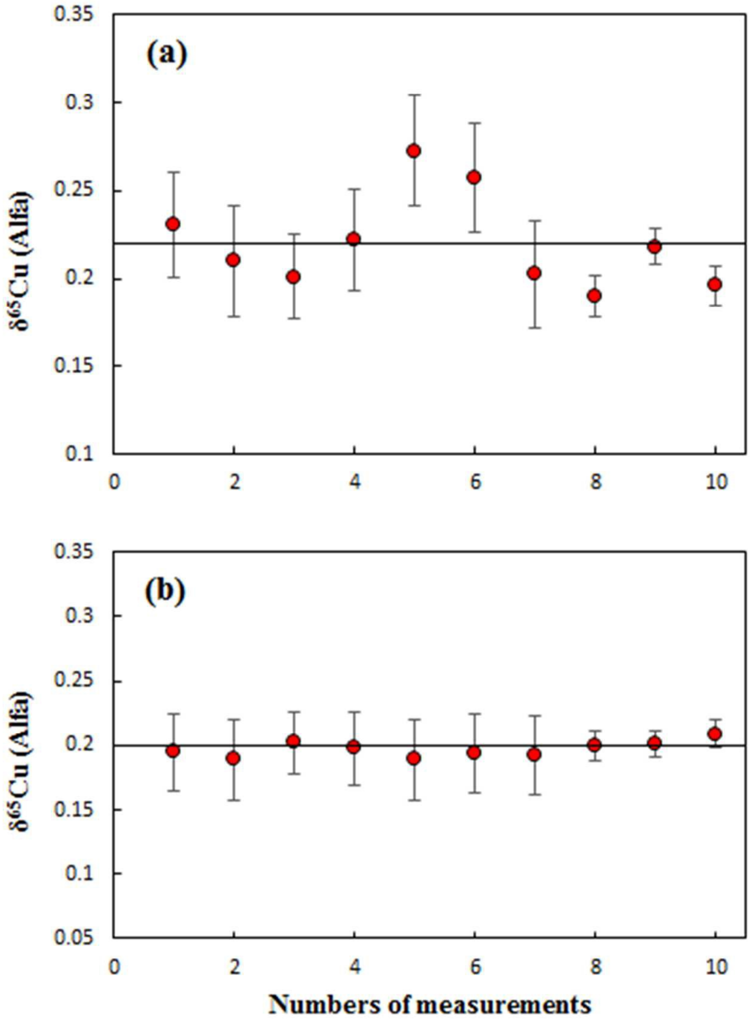
(a)
δ65Cu (Alfa)
0.35
0.3
0.25
0.2
0.15
0.1
0
2
4
6
8
10
(b)
δ65Cu (Alfa)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
2
4
6
8
10
Numbers of measurements

Fig.3

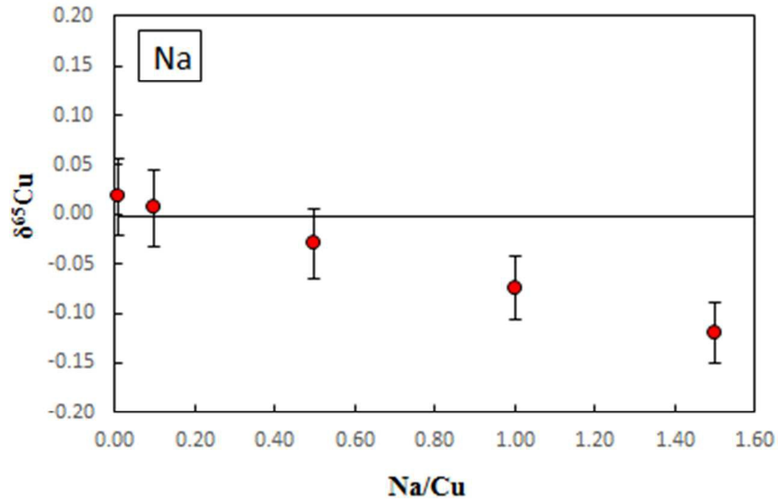
Na
δ65Cu
Na/Cu
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60

Fig.4

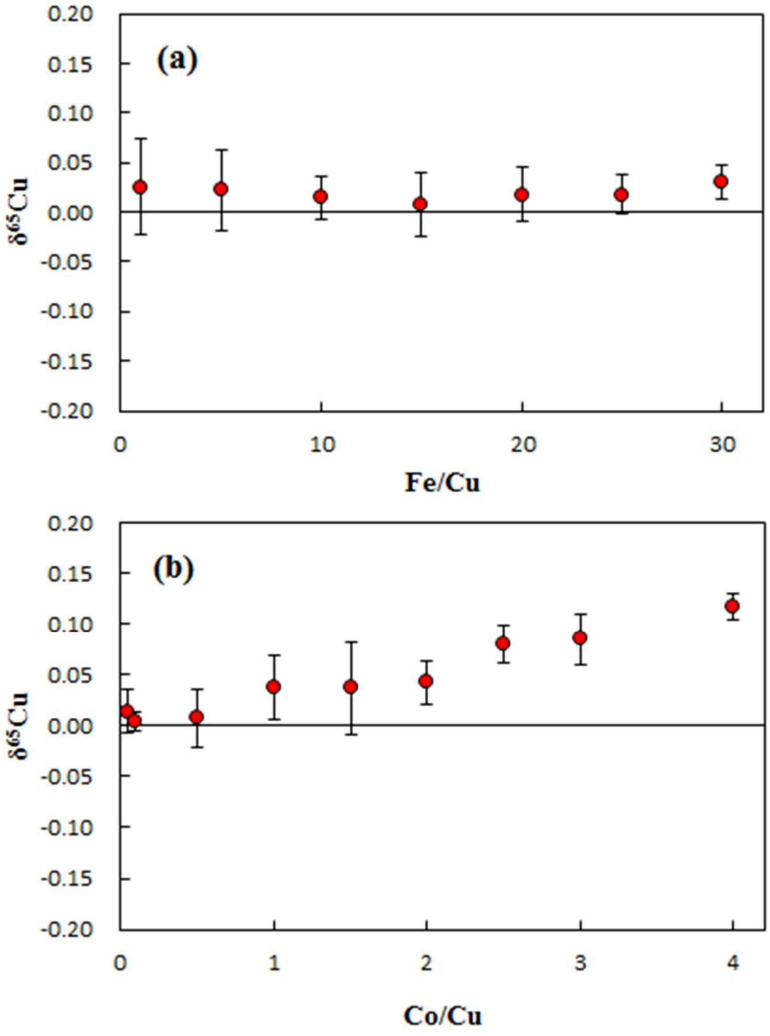
(a)
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
δ65Cu
0
10
20
30
Fe/Cu
(b)
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
δ65Cu
0
1
2
3
4
Co/Cu

Fig.5