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

Hou, QingHua; Zhou, Lian; Gao, Shan; Zhang, Ting; Feng, Lanping; Yang, Lu

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6   QingHua Hou[1], Lian Zhou*[1], Shan Gao[1], Ting Zhang[1], Lanping Feng[1] and Lu Yang*[2]

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8   1: State Key Laboratory of Geological Processes and Mineral Resources, China University

9   of Geosciences, Wuhan, 430074, China

10   2: Chemical Metrology, Measurement Science and Standards, National Research Council

11   Canada, Ottawa, Ontario, Canada K1A 0R6

12   Correspondence author: zhcug@163.com and lu.yang@nrc-cnrc.gc.ca

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Abstract: First absolute determination of Cu isotope ratio in NIST SRM 3114 is performed based a regression mass bias correction model with 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, and a value of +0.18±0.04 ‰ (2SD, n=5) was obtained for $\delta^{65}Cu$ 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 $\delta^{65}Cu$ value relative to NIST 976 make it suitable as a new candidate reference material for Cu isotope ratio measurements. In addition, a protocol is described for the accurate and precise determination of $\delta^{65}Cu$ 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% (2 SD, 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 $\delta^{65}Cu$ 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

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39   Copper has two stable isotopes, ^{63}Cu and ^{65}Cu, with relative abundances of 69.17% and

40   30.83%, respectively.[1,2] As an important ore-forming element, copper exists widely in

41   different geological systems and is active in ore-forming and rock-forming processes.[3]

42   Therefore, copper isotopes can be a useful geochemical tracer and play an important role in

43   the study of sources of Cu in the ore-forming process and mechanism.[4-6] Copper isotopes

44   have also been used as a new tracer in the study of the evolution of the Earth's environment,

45   geosphere and biosphere interactions, and other aspects of the formation mechanism of the

46   deposit.[7,8] It is of great significance to obtain high precision and accuracy copper isotope

47   data.   Significant variations of copper isotope composition have been reported in nature.

48   Walker et al.[1] and Shields et al.[2] used thermal ionization mass spectrometry (TIMS) to

49   investigate the distribution of Cu isotopes in natural samples. Modern advances in

50   multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) have allowed

51   high precision isotope ratio measurements, and the relative precision of the isotope ratio

52   measurements can be as low as 10 ppm, comparable to that of TIMS.[9,10] Moreover,

53   MC-ICPMS benefits from simple and robust sample introduction, high sample throughput,

54   and high mass resolution. The advantages above have generated a renewed research interest

55   in copper isotopes.[11,12]

56   MC-ICPMS suffers from large mass bias which needs to be properly corrected for the

57   accurate isotope ratio measurements. For Cu isotope ratio measurements, various mass bias

58   correction models can be employed, such as the direct standard-sample bracketing (SSB)

59   model,[13] the combined SSB with internal mass bias correction model and regression mass

60   bias correction model. The SSB approach is capable of correcting instrumental mass bias

61   providing analyte and sample matrix are matched between the standard and the sample.

62   However, it does not account for the short-term fluctuations in mass bias between

63   bracketing standards. Recent studies[14-19] have reported use of a combined SSB with internal

64   mass bias correction model whereby a standard with known analyte ratio is used to calibrate

65   the ratio of the internal standard; this calibrated ratio of the internal standard is then used to

66   calibrate the analyte ratio in the sample. The advantage of this correction model is that the

67   short-term fluctuations in mass bias between bracketing standards are corrected. As

68   demonstrated in these studies, [14-19] precision of analyte ratio has improved at least twofold by

69   using the combined SSB with internal standard when compared to the direct SSB.

70   Previously published Cu isotope data are reported relative to the reference material of

71   NIST SRM 976, which is certified for isotope amount ratios.[20-23] Unfortunately, the NIST

72   SRM 976 is no longer available, thus alternative reference materials with known isotopic

73   composition are in urgent need for the Cu isotope ratio study in various scientific fields.

74   Ideally, the new reference material is calculated against NIST SRM 976 in order to have

75   comparative data from different research labs. For example, the reference materials

76   ERM-AE633 and ERM-AE647 from IRMM (Institute for Reference Materials and

77   Measurements, Belgium) were calibrated against the NIST SRM 976 for δ^{65}Cu.[22] Liu et al.

78   [24] also used the GSB from the National Standard Substances of China as a new Cu standard,

79   where the average δ^{65}Cu$_{GSB}$ Cu solutions is +0.44±0.04 (2SD; n=32) relative to NIST 976.

80   In this study, NIST 3114 copper standard solution was selected as a candidate Cu

81   reference material and its absolute isotope amount ratio was determined by MC-ICPMS

82   using a state-of-the-art regression mass bias correction model based on the utilization of

83   temporal drift between the measured Cu and Ga isotope ratios in their log space without any

84   untestable assumptions.[10] Isotopic reference material NIST SRM 994 Ga with known

85   isotopic composition was used as the calibrant for the absolute determination of Cu isotope

86   ratio. Cu isotope ratio of several common geological reference materials were determined

87   relative to the new characterized reference material (NIST SRM3114) using the combined

88   SSB and internal normalization method with internal standard of Ga. These geological

89   reference materials were subjected to ion exchange column separation of Cu from

90   geological and Fe-rich matrices prior to MC-ICPMS measurements.

91   **Experimental Section**

92   **Instrumentation**

93   All Cu isotope measurements were carried out on a MC-ICPMS (Neptune Plus, Thermo

94   Finnigan Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes

95   and Mineral Resources, Wuhan, China. This instrument is equipped with nine Faraday cups

96   and a combination of cyclonic and Scott-type spray chambers with a MCN50 PFA

97   self-aspirating nebulizer (Elemental Scientific, Omaha, NE, USA) operating at 50 μl min^{-1}

98   was used for Cu isotope ratio measurements at the low-resolution mode. Optimization of the

99   Neptune was performed as recommended by the manufacturer, and typical operating

100   conditions are summarized in Table 1. The gain on each Faraday cup was monitored daily to

101   ensure correction for its efficiency.

102   A quadrupole ICPMS from Agilent Technologies (Yokogawa, Japan) was used for

103   semi-quantitative analysis of matrix element concentrations in rinse and eluate fractions. A

104   LabTech hot plate (EG20A plus, Suzhou Science Instrument Co., China) was used for the

105   evaporation of sample solutions. Electric constant temperature drying oven (DHG-9203A,

106   Shanghai Jing Hong Laboratory Instrumengt Co., China) was used for the acid digestion of

107   geological samples.

108   **Reagents and Materials**

109   Nitric and hydrofluoric acids were purified in-house prior to use by sub-boiling

110   distillation of reagent grade feedstock in a DST-1000 acid purification system (Savillex,

111   Eden Prairie, USA), and hydrochloric acid used to load sample was prepared by dilution of

112   Suprapur® grade ortho-Phosphoric acid (Merck KGaA., Darmstadt, Germany) with DI water.

113   High purity deionized water (DIW) 18 M Ω was obtained from a Milli-Q water system

114   (Millipore Corp., Billerica, MA, USA). All lab wares, including Savillex® containers and

115   disposable plastics, were cleaned in concentrated reagent-grade acids and deionized H_2O

116   prior to use.

117   The candidate reference material NIST 3114 Cu and the internal standard of NIST

118   SRM 994 Ga were purchased from the National Institute of Standards and Technology

119   (Gaithersburg, MD, USA). Gallium metal isotopic reference material, NIST SRM 994, is

120   certified for $^{69}Ga/^{71}Ga=1.50676\pm0.00039$ (U, at 95% condidence interval), determined by

121   thermal-ionization mass spectrometry. A 2000 µg g^{-1} stock solution of NIST SRM994 was

122 prepared by quantitative dissolution of Ga in concentrated nitric acid with heating and then

123 diluted with DIW. A 100 μg g^{-1} standard solution of copper was prepared by dilution of a

124 high-purity Cu solution of 1000 mg l^{-1} Cu (copper ICP standard, Merck KGaK, Darmstadt,

125 Germany batch Cu011017) in 2% nitric acid. An in-house Cu stock solution of 10,040 μg

126 g^{-1} was prepared by quantitative dissolution of an Alfa Aesar Puratronic$^{®}$ Cu wire (Alfa

127 Aesar, Karlsruhe, Germany; batch 23·16498C) in HNO$_3$. A 200 ng g^{-1} Cu (Alfa Cu A)

128 solution was prepared by dilution of the 10,040 μg g^{-1} Cu stock in 2 % HNO$_3$ solution.

129 Another Alfa Aesar Cu stock solution (Alfa Cu B) of 1000 μg g^{-1} was prepared by

130 quantitative dissolution of Puratronic$^{®}$ Cu wire (batch 04·1792K) in HNO$_3$ and diluted with

131 DIW. GSB Cu standard was obtained from the Isotope Geochemistry Laboratory of the

132 China University of Geosciences, Beijing, China.

133 Five geological reference materials of BCR-2, BHVO-2 and BIR-1a (basalts), AGV-2

134 (andesite) and GSP-2 (granite) purchased from United States Geological Survey (Reston,

135 VA, USA) were used as test samples for Cu isotope ratio measurements.

136 **Sample preparation and analysis of NIST SRM3114 Cu standard for absolute Cu**

137 **isotope ratio**

138 The absolute isotope ratio of Cu standard (NIST 3114) was measured following an early

139 method described by Yang et al.[10], using a regression mass bias correction model with Ga as

140 calibrant. Replicate solutions of 200 ng g^{-1} Cu were prepared by diluting the Cu stock

141 solution in 2% HNO$_3$ followed by spiking with the gallium standard solution, yielding a mass

142 fraction of 200 ng g^{-1} for Ga. Samples were introduced into the plasma in a self-aspiration

143   mode at a flow rate of 50 µL min^{-1}. Intensities of Cu and all other measured isotopes of

144   interest (see below) obtained from a blank solution of 2% HNO_3 were subtracted from those

145   of all samples. A static run was employed to collect ^{63}Cu, ^{65}Cu, and ^{69}Ga and ^{71}Ga isotopes

146   simultaneously using the Faraday cup configuration shown in Table 1. A total of 15

147   measurements were made on each sample solution and the duration of each session of

148   measurements was about 5-6 h. Data acquisition parameters are summarized in Table 1.

149   **Geological sample preparation and analysis**

150   Sample preparation was carried out in a metal-free clean room fitted with an

151   HEPA-filtered air supply and laminar low benches. 50 mg sub-samples were dissolved in 3

152   ml HF/HNO_3 (1:1) at 190°C for 48h in Teflon beakers. The contents were evaporated to

153   dryness on a hot plate at 105°C. 1 mL of HNO_3 was added to each sample and then

154   evaporated to dryness to completely remove HF. 1 ml of 8.5 N HCl + 0.03% H_2O_2 solution

155   was added to each beaker. All beakers were placed in an oven and heated at 120°C for 10h.

156   Contents were then evaporated to dryness on a hot plate at 105°C.   0.25ml 8.5N HCl+0.03%

157   H_2O_2 solution was added to each beaker and the contents were evaporated to dryness. This

158   process was repeated three times to ensure that all cations were converted to chloride species.

159   The final residues were redissolved in 8 ml 8.5 N HCl+0.03% H_2O_2 for the purification of Cu

160   using anion exchange resin.

161   Copper was separated from the matrix using new type of anion exchange AG MP-1M

162   Bio-Rad resin (100–200 mesh) and followed a protocol by Maréchal et al.[11] (1999) with

163   some modifications. Instead of 7 N HCl used by Maréchal et al. 8.5 N HCl was used in this

164   study for more efficient separation of Cu from matrix elements, especially Co. The resin

165   was first cleaned by sequentially leaching twice with 10 mL of 2N HNO_3 and twice with 10

166   mL 2N HCl, respectively.[25, 26] Columns containing 1 ml of AG MP-1M resin were cleaned

167   and preconditioned using acidic solutions as detailed in Table 2. Most matrix elements (e.g.

168   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

169   eluted in the following 8 ml 8.5 N HCl, leaving Co, Fe and Zn retained on the resin. These

170   eluents containing Cu were evaporated to dryness on a hot plate at 105°C and redissolved in

171   0.1 ml concentrated HNO_3 and diluted to 4 ml with DIW.

172   0.5 ml of purified Cu fractions were taken and diluted to 4 ml in 2% HNO_3 (v/v), and

173   were measured by ICP-MS (POEMS III ICP-MS) for total Cu concentrations to check the

174   recovery of column separation for each sample. The remaining purified Cu fractions in 2%

175   HNO_3 were spiked with Ga standard solution, yielding a concentration of 200 ng g^{-1}.

176   Solutions of SRM 3114 in 2% HNO_3 containing similar concentrations of Cu as in the

177   purified BCR-2, BHVO-2, BIR-1a, AGV-2and GSP-2 solutions were prepared, respectively,

178   and spiked with Ga to yield a concentration of 200 ng g^{-1}. Samples and standards were

179   introduced into the plasma in the following sequence: SRM 3114 – sample – SRM 3114.

180   Intensities of all measured isotopes obtained from a blank solution of 2 % (v/v) HNO_3 were

181   subtracted from standards and intensities of all measured isotopes obtained from process

182   blank were subtracted from all samples. Data acquisition parameters are summarized in

183   Table 1. Four replicate measurements or more of each sample solution were performed.

184   **Results and Discussion**

Absolute Cu isotope ratio measurements in NIST SRM 3114.

185

186   For the absolute determination of Cu isotope ratio in NIST SRM 3114, the log-linear

187   regression mass bias correction model was used to measure isotope ratio of Cu in this study,

188   in a manner similar to that used in previous studies of Cu[11], Fe[27, 28], Hg[29, 30], Ge[10], Ag[31] and

189   In[31] isotopes. This model is based on monitoring the temporal drift in the simultaneous

190   isotopic ratio measurements where the intercept and slope of the constructed log-linear

191   regressions between the observed (uncorrected) isotope ratio of the measurand $r^{Cu}_{65/63}$ and

192   the calibrant $r^{Ga}_{69/71}$ forms the basis for calibration of Cu isotope ratio. The major

193   of the regression model over the traditional exponential correction model is that the

194   regression approach is free of the requirement for identical fractionation behavior between

195   the element pairs.[10, 32] Additionally, the regression model is not hampered by the untestable

196   assumption regarding the very nature of the fractionation (linear, exponential, etc.).

197   Equation 1 forms the basis for the Cu isotope ratio calibration with Ga as the calibrant: [10, 18]

198
$$\ln r^{Cu}_{65/63} = \underbrace{\ln R^{Cu}_{65/63} - \frac{\ln K^{Cu}_{65/63}}{\ln K^{Ga}_{69/71}} \ln R^{Ga}_{69/71}}_{\text{intercept, } a} + \underbrace{\frac{\ln K^{Cu}_{65/63}}{\ln K^{Ga}_{69/71}} \cdot \ln r^{Ga}_{69/71}}_{\text{slope, } b} \qquad (1)$$

199   Note that Equation 1 is a logarithmic rearrangment of the expressions of

200     $R^{Cu}_{65/63} = K^{Cu}_{65/63} \cdot r^{Cu}_{65/63}$ and $R^{Ga}_{69/71} = K^{Ga}_{69/71} \cdot r^{Ga}_{69/71}$, where K is the isotope ratio correction

201   factor that links the measured isotope ratio (r) with the mass bias corrected isotope ratio (R).

202   As evident from Figure 1, the measured drift of the $r^{Cu}_{65/63}$ and $r^{Ga}_{69/71}$ isotope ratios

203   shows well-defined log-linear relationship over a measurement session of 5-6 h in

204   accordance with the Equation 1. The corresponding intercept (a) and slope (b) of the

205 log-linear regression are calculated using the least squares regression and these values are

206 then used to obtain the mass-bias corrected Cu isotope ratio, by algebraic rearrangement of

207 Equation 1:

208 $$R^{Cu}_{65/63} = \left(R^{Ga}_{69/71}\right)^{b} \cdot e^{a} \tag{2}$$

209 In this work, the NIST certified value[33] of $1.50676(39)_{95\%}$ was used for $R^{Ga}_{69/71}$ to obtain

210 the mass bias corrected $R^{Cu}_{65/63}$. Although Equation 2 resembles the traditional exponential

211 mass-bias correction in its appearance, the underlying logic is significantly different.[10, 14]

212 This "regression" approach is capable of generating accurate ratio data as demonstrated in

213 previous studies,[10,15,29,34] however, it suffers from poor precision due to the need for linear

214 regression to generate the slope and intercept, which are subsequently used to calculate a

215 mass bias corrected analyte ratio. To reduce the uncertainty associated with this process, the

216 number of measurement sessions should be increased.[16] During a six-month period between

217 December 2013 and June 2014, many sets of isotope ratio log-linear regressions were

218 acquired for ^{65}Cu/^{63}Cu vs ^{69}Ga/^{71}Ga, each yielding the respective intercept and slope. Of

219 these, 37 high-quality sets exhibiting a coefficient of determination larger than 0.999

220 ($R^2 \geq 0.999$) were selected for calculation of the final results. The mass bias corrected Cu

221 isotope ratio of 0.4470±0.0013 (2SD, n=37) was obtained.

222 **Comparison of SRM 3114 to other Cu standards.**

223 As mentioned above, previously published Cu isotope data are reported relative to the

224 reference material of NIST SRM 976, which is certified for isotope amount ratios.[24, 35-39]

225 Unfortunately, this reference material is no longer available. In order to compare result of

226 Cu isotope ratios generated from different research labs, it is essential to compare Cu

227 isotope ratio value in SRM3114 to other Cu standards or internationally accepted common

228 standard material. Delta notation (δ) for the Cu isotope ratio is thus employed relative to the

229 SRM3114 in accordance with:

230 $$\delta^{65}Cu = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \qquad (3)$$

231 To correct mass bias, a combined standard sample bracketing and internal normalization

232 method (C-SSBIN) is undertaken in this study. Ga is used as the internal standard and added

233 to both sample and standard solutions, a variation of the methodology as typically used for

234 other isotope systems. [14-19] To the best of our knowledge, this is the first report of

235 implementing this C-SSBIN mass bias correction model with use of Ga as the internal

236 standard for the determination of Cu isotope ratios. The obtained absolute value of

237 0.4470±0.0013 (2SD, n=37) for $^{65}Cu/^{63}Cu$ in SRM 3114 was used to calculate mass bias

238 corrected ratios of $^{69}Ga/^{71}Ga$ in two adjacent bracketing standard solutions of SRM 3114 in

239 accordance with Equation 1 of Russell's law:[40, 41]

240 $$R^{i/j} = r^{i/j} \cdot \left(\frac{m_j}{m_i}\right)^f \qquad (4)$$

241 where r and R are the measured and true isotope ratios, respectively, m_i and m_j are nuclide

242 masses of the isotopes of interest which can be found elsewhere,[42] and f is the mass bias

243 factor. Their average value of $^{69}Ga/^{71}Ga$ was then used to calculate mass bias corrected Cu

244 isotope ratio in the sample. Note that the Ga internal standard in the sample serves as the

245 mass-bias correction proxy to allow for correction of time-dependent variation of the mass

246 bias. Therefore the absolute value of the Ga isotope ratio is not needed. Even though the

247   value obtained for the Ga isotope ratio may be biased due to the limitations of the employed

248   mass-bias correction model (e.g., assumption of $f^{Cu} = f^{Ga}$), this bias is largely negated in the

249   second step of the calibration (Ga→Cu). This mass bias correction model is only fully valid

250   if matrix and concentration matching is fully attained.

251   Results from measurements of an Alfa Cu standard solution relative to NIST SRM

252   3114 using direct SSB (Fig. 2a) and C-SSBIN (Fig. 2b) mass bias correction models,

253   respectively, are presented in Figure 2. The results were acquired over a period of four days.

254   Values of 0.22±0.05‰ (2SD, n=10) and 0.20±0.01‰ (2SD, n=10) for $\delta^{65}Cu$ in Alfa Cu

255   relative to NIST 3114 standard were obtained with use of direct SSB and C-SSBIN for

256   mass bias correction, respectively. An approximately five-fold improvement in precision of

257   determination of $\delta^{65}Cu$ was obtained with the use of the proposed C-SSBIN mass bias

258   correction approach compared to those solely with the SSB approach.   Thus the C-SSBIN

259   mass bias correction approach was used for all subsequent measurements.

260   GSB Cu standard was measured against the SRM 3114 using the C-SSBIN for mass

261   bias correction, and a value of +0.27±0.02‰ (2SD, n=6) for $\delta^{65}Cu$ was obtained, in

262   agreement with the value of +0.26±0.04‰ (2SD, n=5) measured by the Isotope

263   Geochemistry Laboratory of the China University of Geosciences, Beijing, China. Liu et

264   al.[24] reported a value of +0.44±0.04‰ (2SD, n=32) for $\delta^{65}Cu_{GSB}$ in GBS Cu relative to

265   NIST SRM 976. Based on these results, $\delta^{65}Cu$ value of +0.18±0.02‰ (2SD, n=6) for NIST

266   3114 is thus calculated, relative to NIST SRM 976.

267   Since the NIST SRM3114 is available and with the absolute Cu isotope ratio

268   determined, we recommend the use of this material over the SRM 976 for future Cu

269   isotopic studies. Based on the study by Moeller et al.[22] wherein $\delta^{65/63}$Cu isotope ratio of

270   NIST SRM 976 was determined against ERM-AE633 and ERM-AE647 Cu reference

271   standards, respectively, and values of -0.01 ± 0.05‰(2SD,n=40) and value of -0.21 ±

272   0.05‰(2SD,n=60) were obtained, respectively. Alternatively, two Cu standards,

273   ERM-AE633 and ERM-AE647, can also be used as new certified reference materials for

274   future Cu isotopic studies. Regardless of which Cu standard is selected, we strongly

275   recommend report final Cu isotope ratio data relative to NIST SRM976 by using available

276    $\delta^{65/63}$Cu values between these four Cu standards of NIST SRM976, SRM3114, IRMM

277   ERM-AE633 and ERM-AE647 for calculations, in order to obtain comparable results from

278   different research labs.

279   **Matrix separation.**

280   As noted earlier, the CSSBIN mass bias correction model requires matrix matching

281   between the sample and the standard solutions to ensure accuracy. Since it is practically

282   impossible to match all matrix elements between a sample (e.g. geological samples) and a

283   standard solution, separation of the matrix elements is the method of choice. It is widely

284   recognized that non-quantitative recovery of analyte during such a process may result in

285   isotope fractionation,[43-44] and quantitative recovery (above 95 %) of analyte is thus required

286   to ensure accurate results. Recovery was checked for every geological sample by ICP-MS

287   and 100 ± 2% (2 SD, n=15) recoveries were obtained for these samples.

288   The collected Cu fractions in 2% HNO_3 solution were examined for semi-quantitative

289 analysis to check the efficiency of matrix separation. Concentrations of concomitants were

290 significantly reduced and only a few matrix elements (i.e., Na, Fe, Co and Ti) remained at

291 levels greater than 0.01 (expressed as ratio of individual matrix element concentration to the

292 Cu concentration in the purified digests). These matrix elements not only potentially

293 generate polyatomic interferences such as $^{23}Na^{40}Ar^+$, $^{23}Na_2^{16}O^1H$, $^{23}Na_2^{18}O^1H^+$ $^{47}Ti^{16}O^+$,

294 $^{46}Ti^{16}O^1H^+$, $^{49}Ti^{16}O^+$, $^{48}Ti^{16}O^1H^+$ on ^{63}Cu and ^{65}Cu, but also induce matric effects; both could

295 bias the final results. Thus the effects of Na, Fe, Co and Ti on $\delta^{65}Cu$ were investigated by

296 examining NIST SRM 3114 0.2 $\mu g\ g^{-1}$ Cu standard solutions in the presence of varying

297 amounts of Na, Fe, Co and Ti, relative to a pure SRM 3114 0.2 $\mu g\ g^{-1}$ Cu standard solution.

298 Measured intensities for Ga isotopes in the 2% HNO_3 solution and in the purified Cu

299 fractions (prior to spike with Ga internal standard) were at background levels of <0.0001 V,

300 confirming insignificant polyatomic interferences of $^{40}Ar^{29}Si^+$ and $^{40}Ar^{15}N^{16}O^+$ on ^{69}Ga and

301 ^{71}Ga.

302   Figure 3 shows the effect of Na on $\delta^{65}Cu$. It is evident that when concentration ratio of

303 Na/Cu is less than 0.5 no significant effect on the $\delta^{65}Cu$ was presented. In this study, the

304 measured concentration ratios of Na/Cu in purified digests were found to be less than 0.05,

305 therefore the influence of Na^+ on the final Cu isotope ratios can be neglected.

306   The matrix effects of Fe and Co on $^{65}Cu/^{63}Cu$ ratio measured are presented in Figure 4.

307 No significant effect on $\delta^{65}Cu$ during the tested range of concentration ratio of Fe/Cu from

308 1 to 20, as shown in Figure 4a. Since the measured concentration ratios of Fe/Cu in purified

309 digests were less than 15, thus the influence of Fe on the final Cu isotope ratios can be

310   neglected. Unlike iron, the effect of Co on δ^{65}Cu became significant when Co/Cu ratio

311   increased to 1. Since the Co/Cu ratio was found to be less than 0.02 in the purified digests,

312   confirming no significant effect on the final δ^{65}Cu values.

313   The residual Ti content in the range of 0-1.0 for concentration ratio of Ti/Cu was found in

314   the purified digests. Based on the relative isotope abundance of Ti, polyatomic

315   interferences of ^{47}Ti(7.44%)^{16}O$^+$ and ^{46}Ti(8.25%)^{16}O^{1}H$^+$ on ^{63}Cu; ^{49}Ti(5.41%)^{16}O$^+$ and

316   ^{48}Ti(73.72%)^{16}O^{1}H$^+$ on ^{65}Cu would induce the measured δ^{65}Cu value towards to heavy

317   value. As shown in Figure 5a, measured δ^{65}Cu values in SRM 3114 solutions spiked with

318   various amount of Ti increased significantly as Ti concentration increased. Since the

319   residual Ti content in the purified geological digests has significant effect on δ^{65}Cu values,

320   correction for such interferences remains essential. Instead of performing a second

321   chemical separation, the bracketing standard SRM 3114 solution was doped with same

322   amount Ti as in the purified geological digests instead. As shown in Figure 5b, accurate

323   δ^{65}Cu can be obtained when matrix is matched for Ti for both sample and bracketing

324   standard. Thus for the determination of δ^{65}Cu in purified geological digests, bracketing

325   standard solutions of SRM 3114 were doped with same amount of Ti to achieve accurate

326   δ^{65}Cu measurements.

327   **Results for geological reference materials.**

328   The total process blank of 2 ng was found for Cu, typically less than 1–2% of Cu

329   contained in the purified geological sample digests. Nevertheless, intensities of all measured

330   isotopes obtained from the process blank were subtracted from those of all samples. Results

331 for Cu isotope ratios in five geological reference materials are summarized in Table 3. Based

332 on the δ^{65}Cu value of +0.18±0.02‰ (2SD, n=6) for NIST 3114 relative to NIST SRM 976

333 calculated earlier, final results for δ^{65}Cu in the geological reference materials were

334 converted relative to SRM 976 for comparison. The δ^{65}Cu values for basaltic reference

335 materials (BCR-2, BHVO-2 and BIR-1a) as well as for an andesite (AGV-2) and a

336 granodiorite (GSP-2) spanned in a rather narrow range between 0.01 and 0.26‰ relative to

337 NIST SRM 976. All results were in good agreement with previously determined isotope

338 amount ratio data of the reference materials[35-39], confirming the accuracy of the proposed

339 method.

Conclusion

341   A precise and accurate method is presented the first time for absolute Cu isotope ratio

342 measurements in NIST SRM3114 wherein isotopic ratio was calibrated using a regression

343 mass bias correction model with NIST SRM 944 Ga as the calibrant. A value of

344 0.4470±0.0013 (2SD, n=37) for ^{65}Cu/^{63} ratio was obtained for the NIST SRM3114. A

345 value of +0.18±0.04 ‰ (2SD, n=5) for δ^{65}Cu in NIST SRM 3114 was obtained relative to

346 NIST 976. Based on above values, NIST SRM 3114 is recommeded to be a candidate

347 reference material for future Cu isotopic studies.

348   Moreover, an accurate and precise method has been developed for the determination of

349 Cu isotope ratio in geological samples by MC-ICPMS using a modified mass bias

350 correction approach comprising a combined standard-sample bracketing and internal

351 normalization. To the best of our knowledge, this is the first report of implementing this

352 C-SSBIN mass bias correction model with use of Ga as the internal standard for the

353 determination of Cu isotope ratios. An approximately five-fold improvement in precision of

354 determination of $\delta^{65}Cu$ was obtained with the use of the proposed C-SSBIN mass bias

355 correction approach compared to those solely with the SSB approach. The proposed

356 method is expected to have applications for Cu isotope ratio measurements in study of

357 hydrothermal ore-forming processes, paleo-oceanography, and biological processes.

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447   **Table 1.** MC-ICPMS Operating Conditions

	Instrument Settings
reflected 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

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459 **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$_2$O$_2$	2
Sample loading	8.5 N HCl+0.03% H$_2$O$_2$	1
Matrix elution	8.5 N HCl+0.03% H$_2$O$_2$	4
Cu elution	8.5 N HCl+0.03% H$_2$O$_2$	8

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

comment	δ^{65}Cu relative to SRM 3114	δ^{65}Cu relative to SRM 976	reported	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]

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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 calibrating copper isotope ratio via the $R^{Ga}_{69/71}$ 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. (a) Direct SSB mass bias correction approach; (b) Proposed C-SSBIN mass bias correction approach.

Figure 3. The effect of Na on $\delta^{65}Cu$ measured in NIST SRM 3114 Cu standard solutions spiked with different amounts of Na.

Figure 4. Assessment of effect of Fe (a) and Co (b) contents on $\delta^{65}Cu$ measurements. The errors (2SD) were calculated based on four times replicate measurements.

Figure 5. The effect of Ti concentration on $\delta^{65}Cu$. a: SRM 3114 solutions containing 0.2 µg g^{-1} Cu spiked with different amount 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 amount of Ti measured against themselves, respectively.
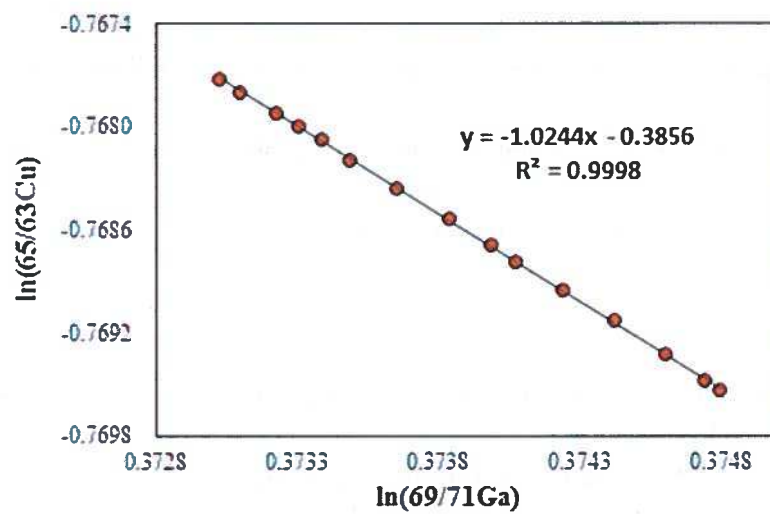
498   Fig.1

y = -1.0244x - 0.3856
R² = 0.9998

ln(65/63Cu) [vertical axis]
ln(69/71Ga) [horizontal axis]

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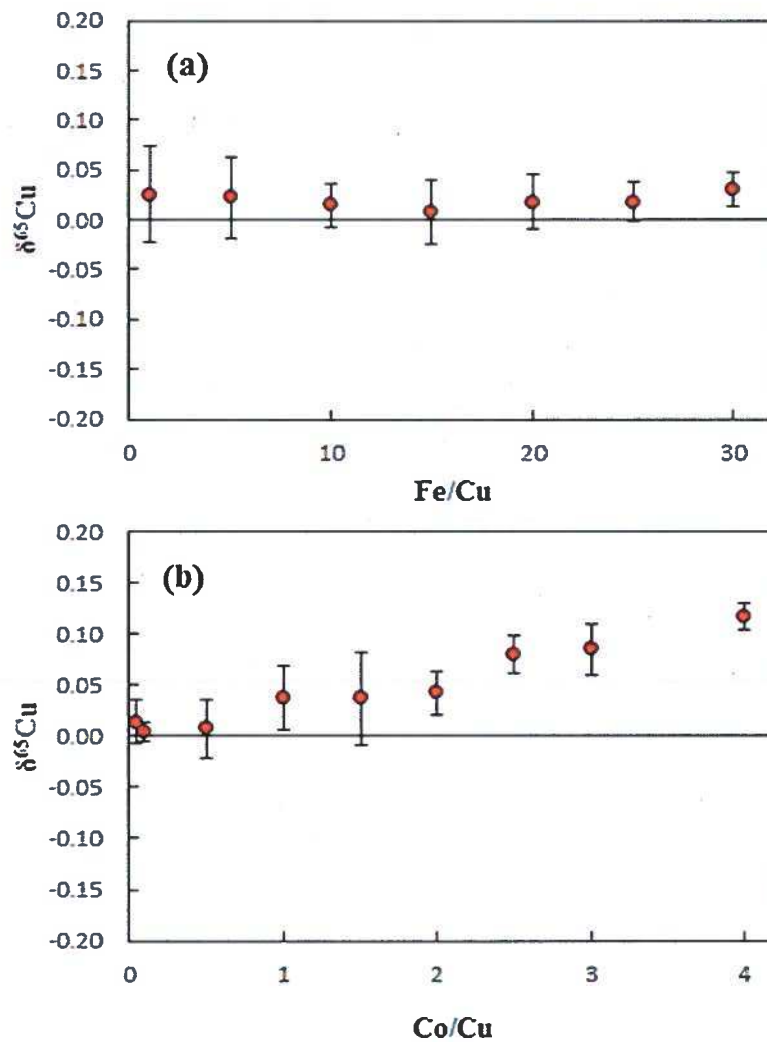
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518   Fig.2

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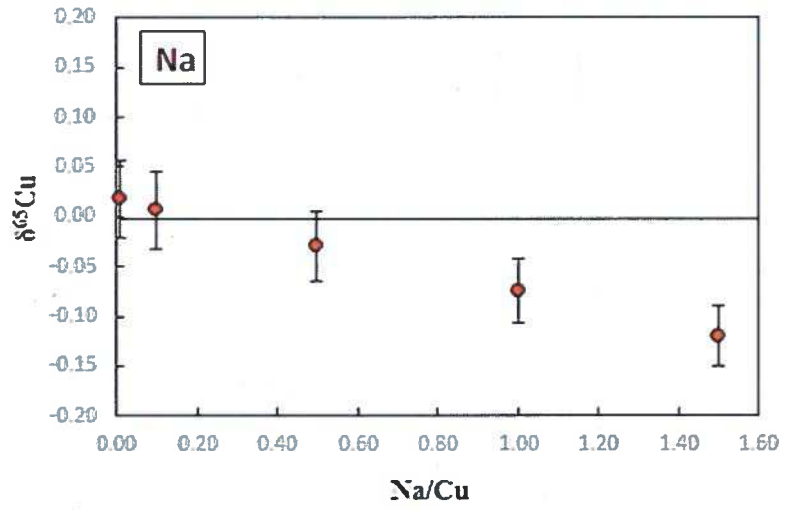526
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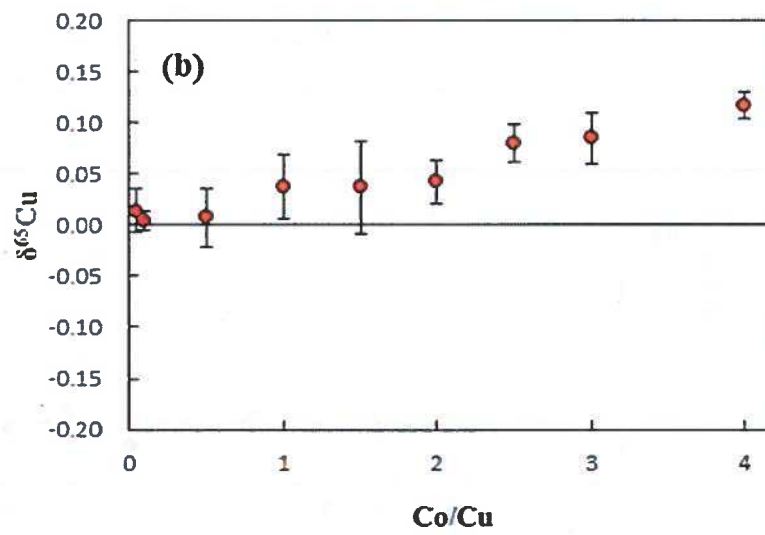536

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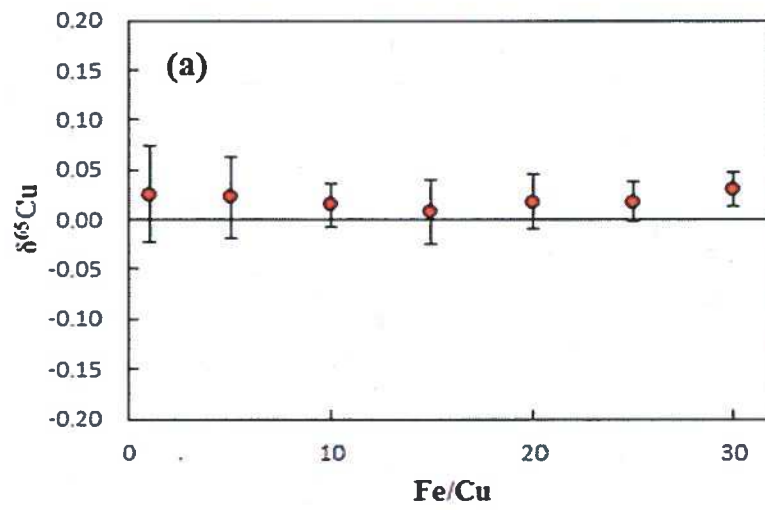
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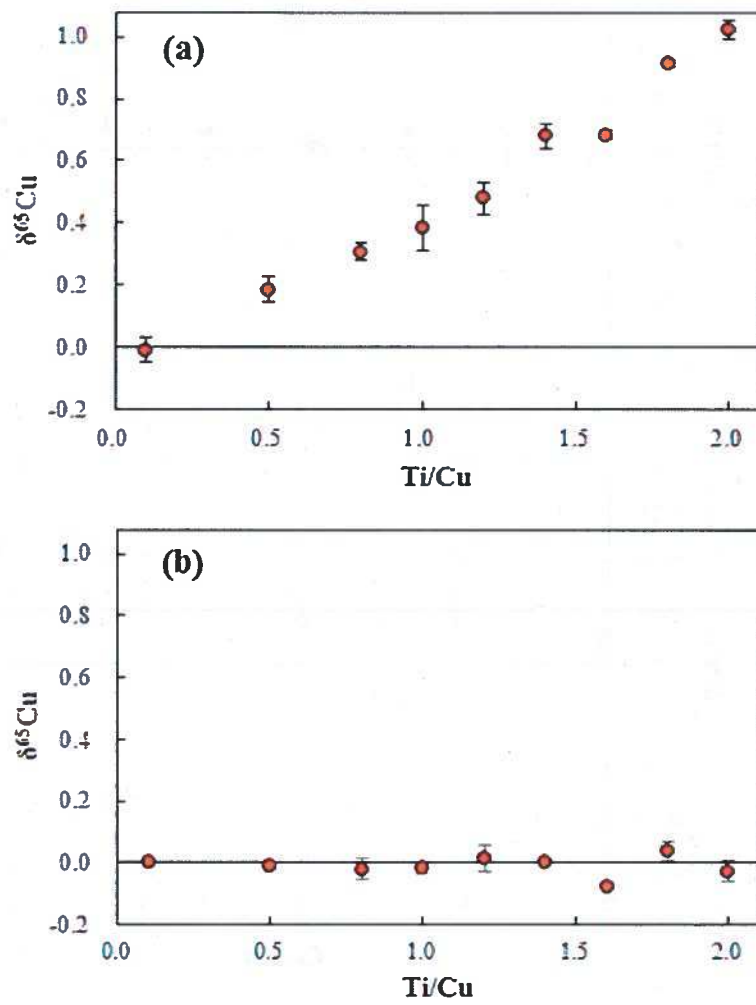553

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562   Fig.5

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