High-precision Copper and Zinc Isotopic Measurements in Igneous Rock Standards Using Large-geometry MC-ICP-MS

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ABSTRACT

In this study, Cu and Zn isotopic measurements were optimized using a large-geometry high-resolution multiple collector inductively coupled plasma mass spectrometer. A single-column anion-exchange separation of Cu and Zn from igneous rocks was performed using a strong anion resin AG-MP-1M. The Cu and Zn isotopic compositions were calibrated by a sample–standard bracketing method, while a Cu internal element spike was also used to correct for mass bias in the Zn measurements. A series of experiments were developed to evaluate the influence of various parameters on the isotopic measurements of Cu and Zn. Acid molarity, matrix (Na, Ti, Mg, and Ni), and residual HF and HCl could significantly affect the accuracy and precision of the results. The long-term external precision was better than ± 0.04‰ (2SD) for both the δ^{65}Cu and δ^{66}Zn. The Cu and Zn isotopic compositions of all igneous rock standards measured in this study agree well with previously published data within uncertainties.

INTRODUCTION

Copper has two natural isotopes, ^{63}Cu and ^{65}Cu, whose abundances are 69.17% and 30.83%. Zinc has five natural isotopes, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn, with abundances of 49.17%, 27.73%, 4.04%, 18.45%, and 0.61%, respectively. In the past decade, with the development of multiple collector inductively coupled plasma mass spectrometers (MC-ICP-MS), several high precision Cu and Zn isotopic analysis methods have been developed (1-4). The isotopes of these two elements have also been widely used in various scientific disciplines, including cosmochemistry (5-7), geochemistry (8-10), mineral resources (11, 12), oceanographic and environmental studies (13), biology (6, 14), and medical science (15, 16). The extent of mass-dependent stable isotope fractionation is inversely proportional to the temperature and the atomic mass (17, 18). As a result, meaningful measurements of variation in Cu or Zn isotopic composition in high temperature geological processes require a highly precise and accurate methodology.

Chromatographic separation and mass spectrometry are two significant aspects controlling the precision and accuracy of the isotopic results. Cu and Zn are generally purified by ion-exchange chromatography in 6–10 N HCl medium on macro-porous resin AG-MP1 (1-3, 19). For more pure elution of Cu or Zn, the whole procedure is often repeated (20, 21). Another method to purify Zn is to employ the strong complexation of Zn with bromide, such as with more dilute acids (HBr/HNO_3 media) on micro-columns (0.1 µL) of anion-exchange resin (22-24). The mass spectrometric calibration often adopts a sample-standard bracketing method. Cu and Zn can be used as an internal standard for each other. Ga can also be used as the internal standard for Cu (2). At present, the routine analytical precision for both the Cu and Zn isotopes is about 0.05‰, no matter which kind of improvement is adopted (2-4, 13, 23).

For the precise measurement of Cu and Zn isotopic compositions in various igneous rocks, the authors developed an efficient chemical purification procedure and optimized mass spectrometric analysis. The elements Cu and Zn were separated from an igneous rock matrix by single-column anion exchange chromatography using a strong anion resin, AG-MP-1M. Various analytical factors that potentially affect the quality of isotopic analysis were also evaluated, such as matrix effect, residual HF or HNO_3, acid molarity, and concentration mismatch. As a result, long-term external reproducibility of better than ± 0.04 ‰ (2SD) for both δ^{65}Cu and δ^{66}Zn measurements was achieved. In addition, the Cu and Zn isotopic compositions of six igneous rock standards were measured simultaneously, and their values were found to agree well with previously published data within uncertainties.

EXPERIMENTAL

Samples and Reagents

Six powdered igneous rock reference materials (basalt: BHVO-2, BIR-1a, and BCR-2; andesite: AGV-2; granodiorite: GSP-2; diabase W-2a) from the United States Geological Survey (USGS) were analyzed for

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Cu and Zn isotopic compositions. An isotopic reference material, IRMM-3702, was purchased from Thermo Fisher Scientific Inc. (Tewksbury, MA, USA). Two element standard reference materials, NIST SRM 3114 and NIST SRM 683, from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), were used as Cu and Zn isotopic calibration standards, respectively. Two pure standard solutions, Alfa Cu (Alfa Aesar 13867) and Alfa Zn (Alfa Aesar 13835) from Thermo Fisher Scientific Inc. (Tewksbury, MA, USA) were used for routine tuning. AG-MP-1M strong anion exchange resin (100–200 mesh; chloride form) and empty polypropylene columns [#7311550, 9 cm high, 2 mL bed volume (0.8 × 4 cm), 10 mL reservoir, including end caps and tip closures] from Bio-Rad Laboratories Inc. (Hercules, CA, USA) were used for the chemical purification procedure.

All chemical procedures were prepared in laminar flow hoods (Class 100) in a cleanroom (Class 1000) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). For minimizing total procedural blanks, a Savillex® DST-1000 acid purification system was used to purify the acids (HCl, HNO_3 and HF). All Savillex® Teflon® vials and FEP bottles were soaked in 5 mol L^{-1} HNO_3 at ~ 120 °C for 24 hours, rinsed with deionized water (18.2 MΩ.cm) three times, then soaked in purified 5 mol L^{-1} HNO_3 for 24 hours, and subsequently in deionized water for six hours, and again rinsed with deionized water three times before final drying.

Digestion of Samples

According to the Cu and Zn concentrations in the samples, about 10-30 mg (containing ~1 µg Cu or Zn) of sample powder was weighed into 7 mL Savillex® Teflon® vials, mixed with 1 mL HF and 1 mL HNO_3, then put on a hotplate at 120 °C for 24 hours. Afterwards, these solutions were evaporated to dryness at 120 °C, then added an additional 1 mL of concentrated HNO_3 twice to remove HF completely. Subsequently, 2 mL aqua regia (1.5 mL HCl + 0.5 mL HNO_3) was added to digest the residues (120 °C for 48 hours). After complete digestion, 1 mL HCl was added and then evaporated to dryness. For chemical purification, the residue in these samples was dissolved with 1 mL of 8 mol L^{-1} HCl + 0.001% H_2O_2.

Chromatographic Separation of Cu and Zn

The chromatography procedure was modified according to the works by Maréchal et al. (19) and Liu et al. (3). A 1 mL sample solution was loaded on a 2 mL pre-cleaned AG-MP-1M resin. After elution of the matrix elements (e.g., K, Ca, Na, Mg, Al, Ti, Cr, Ni, and Mn) with 9 mL 8 mol L^{-1} HCl + 0.001% H_2O_2, an amount of 28 mL 8 mol L^{-1} HCl + 0.001% H_2O_2 was used for collecting Cu. Then, Fe and Co were eluted with 12 mL 0.5 mol L^{-1} HCl, and Zn was collected after addition of 10 mL 0.5 mol L^{-1} HNO_3 (Table I). The elution curves of the intermediate-acid igneous rock sample (AGV-2) suggested that Cu and Zn could be separated from other matrix elements in turn (Figure 1). The final Cu and Zn elution solution was evaporated to dryness and converted to nitrate by re-addition and re-evaporation of 0.5 mL purified HNO_3 and 0.5 mL Milli-Q™ water twice, respectively. Finally, these samples were re-dissolved in 2% HNO_3 for isotopic analysis.

TABLE I
Chromatographic Separation Procedures of Cu and Zn
(2 mL AG-MP-1M resin, 0.8 cm diameter × 4 cm length)

Eluent	Volume (mL)	Purpose
Milli-Q water and 0.5 mol L^{-1} HNO_3	10	Clean resin
8 mol L^{-1} HCl + 0.001% H_2O_2	9	Condition resin
8 mol L^{-1} HCl + 0.001% H_2O_2	1	Load sample
8 mol L^{-1} HCl + 0.001% H_2O_2	9	Remove matrix
8 mol L^{-1} HCl + 0.001% H_2O_2	28	Elute Cu
0.5 mol L^{-1} HCl	12	Elute Fe
0.5 mol L^{-1} HNO_3	10	Elute Zn

Mass Spectrometry

Copper and zinc isotopic ratios were measured using a Nu Plasma 1700 MC-ICP-MS (Nu Instruments, Wrexham, UK) at the China University of Geosciences (Wuhan). The instrument is a large-geometry double-focusing mass spectrometer, employing a 943 mm radius, 70° sector electrostatic analyzer, followed by a 750 mm radius, and a 70° laminated magnet. The natural dispersion of the instrument, excluding any Quad lens effects, is approximately 1700, which is three times bigger than that of normal geometry MC-ICP-MS instruments (25). This instrument is equipped with a Cetac ASX-112FR automatic sampler (CETAC Technologies, Omaha, NE, USA), a ~100 µL min^{-1} Glass Expansion nebulizer (Glass Expansion, Pocasset, MA, USA) and standard cones. The two natural Cu isotopes (^{63}Cu and ^{65}Cu) and four Zn isotopes (^{64}Zn, ^{66}Zn, ^{67}Zn, and ^{68}Zn), whose m/z were 63, 64, 65, 66, 67, and 68, were collected with L4, L3, L2, Ax (C), H2 and H4 Faraday cups, respectively. For monitoring the interference of ^{64}Ni on ^{64}Zn,

^{60}Ni was also collected with an L6 Faraday cup. All Faraday amplifiers used 10^{11} Ω resistors.

The measurements were performed in wet plasma and low-resolution mode. A 200 ng g^{-1} Cu solution and a 300 ng g^{-1} Zn solution, which produced about 4~5 V signal for ^{63}Cu and ~ 4 V for ^{64}Zn, were used for routine tuning and analyses. Each isotopic analysis included the integration of 25 cycles, with 8 seconds per cycle. Before normal measurements, all the concentrations of the samples and standards were pre-analyzed using the mass spectrometer, and diluted to a unified concentration.

All of the mass spectrometry parameters are listed in Table II. The reference materials NIST SRM 976 and JMC-Lyon 3-0749L are regarded as the primary standard of the Cu and Zn isotopes, respectively. The Cu isotope data are reported in standard δ–notation in per mil relative to NIST SRM 976: $\delta^{65}Cu = [(^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{NIST976} - 1] \times 1000$. The Zn isotope ratios are reported in standard δ–notation in per mil relative to JMC-Lyon 3-0749L: $\delta^{X}Zn = [(^{X}Zn/^{64}Zn)_{sample}/(^{X}Zn/^{64}Zn)_{JMC\text{-}Lyon} - 1] \times 1000$, where X = 66, 67, and 68. The conversion details have been discussed in references (1, 2).

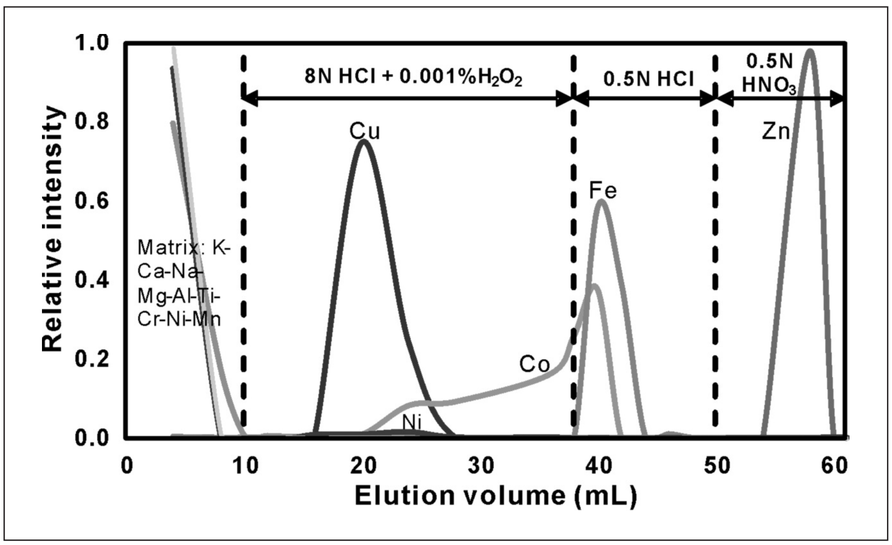

Fig. 1. Elution curves of Cu and Zn purification procedures of intermediate-acid igneous rock (AGV-2).

RESULT AND DISCUSSION

Calibration Method and Precision

A sample-standard bracketing (SSB) method was utilized to correct for instrumental mass fractionation and drifting, using the standards NIST SRM 3114 (2) for Cu and NIST SRM 683 (1) for Zn. Element-doping as an external standard was also commonly adopted to correct for instrumental mass bias during Cu (2, 19, 26) or Zn (19) isotopic analysis. In this study, trace amounts of Ni were found in the Cu eluent but did not affect the measurement of the Cu isotopes (see section 'Effects of Elemental Matrix'). But when Zn or Ni was used as an internal standard during Cu isotopic analysis, the residual Ni interfered with the testing of the internal standards and gave a wrong result. There was no Ni or Cu detected in the Zn eluent. Here, the Cu isotopic ratios were measured by the single SSB method, while Cu-doping as an internal standard was adopted during Zn isotopic analysis.

The reproducibility of the Cu and Zn isotopic ratios was evaluated based on the repeated measurement of Alfa Cu, IRMM3702, BHVO-2, and BCR-2 over two years. The external reproducibility of $\delta^{65}Cu_{NIST976}$ and $\delta^{66}Zn_{JMC\text{-}Lyon}$ was for both better than ± 0.04‰ (2SD) (Figure 2).

TABLE II
Instrumental Operating Conditions for Cu and Zn Isotopic Measurements

MC-ICP-MS	Nu Plasma 1700		Nebulizer		Glass Expansion, ~ 100 µL min^{-1}	
Cooling Gas	Ar, 13 L min^{-1}		Cones		Standard cones	
Auxiliary Gas	Ar, 0.95 L min^{-1}		Mass resolution		Low resolution	
Nebulizer Gas	Ar, 29.5 Psi		Sensitivity		^{63}Cu, ~20 V ppm^{-1}; ^{64}Zn, ~14 V ppm^{-1}	
RF Power	1300 W		Oxide		$^{140}Ce^{16}O/^{140}Ce$, ~ 2.5 %	

Cup configuration	L6	L4	L3	L2	Ax	H2	H4
m/z	60	63	64	65	66	67	68
Isotopes	^{60}Ni	^{63}Cu	^{64}Zn, ^{64}Ni	^{65}Cu	^{66}Zn	^{67}Zn	^{68}Zn

Atomic Spectroscopy
Vol. 40(6), Nov./Dec. 2019

Effects of Acid Molarity and Concentration Mismatch

Previous studies have shown that acid molarity and concentration mismatch of samples and standards will affect Cu or Zn isotopic analysis (1, 3). The effect of acid molarity on Cu and Zn isotopic analysis was evaluated by changing the acid molarity of the samples (Alfa Cu and Alfa Zn were used here, respectively) at the constant acid molarity of the standards (2% HNO_3) and the same Cu or Zn concentration. The results suggest that high acid concentration would lead to a heavy isotopic composition for Cu and Zn. But with Cu as the internal standard, the effect of acid molarity exerted on the Zn isotope would decrease (Figure 3). The effect of concentration on Cu and Zn isotopic analysis was evaluated by changing the concentrations of the samples (Alfa Cu and Alfa Zn were used in this study, respectively) at the constant concentration of the standards and the same acid molarity. The results were completely different from previous studies (3), which held the opinion that an imperfect Cu concentration match (>10%) could affect the accuracy of the Cu isotopic measurements quite considerably. In this study, even if the imperfect Cu concentration match was more than 60%, accuracy of the Cu isotopic measurements still kept constant (Figure 4). The result of the Zn isotope was like the Cu isotope, and the Cu-internal standard correction did not show a significant improvement in the results of the concentration mismatch.

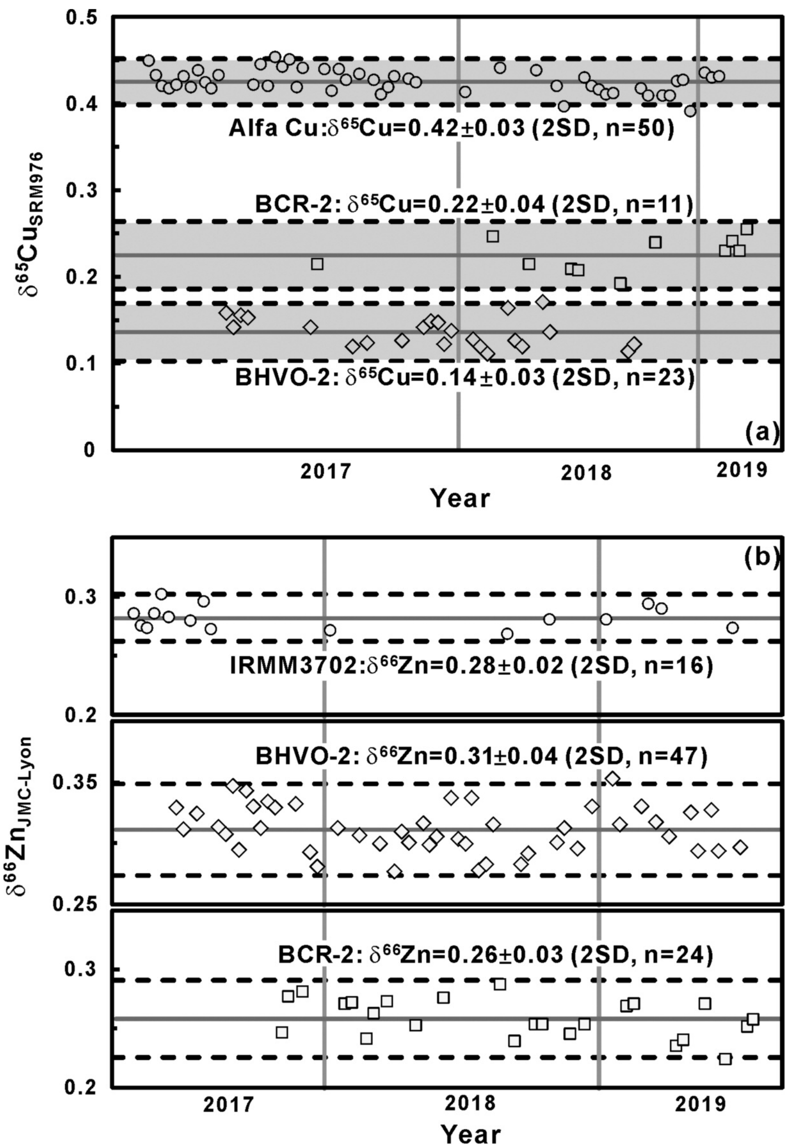

Fig. 2. Long-term (more than two years) analyses of the mono-element standard solutions (Alfa Cu and IRMM3702, and the USGS geological reference materials BCR-2 and BHVO-2). The long-term external precisions of $\delta^{65}Cu_{NIST976}$ and $\delta^{66}Zn_{JMC\text{-}Lyon}$ were each better than ± 0.04‰ (2SD).

Effect of Concentrations on Precision

As mentioned above, the precision of the Cu and Zn isotopic measurements was not sensitive to the imperfect concentration match. There are many samples with extremely low Cu and Zn content in nature (27), so it is important to understand the limits of low concentrations in which suitable precision can also be achieved. The concentrations in the samples and standards (Alfa Cu and Alfa Zn were used here, respectively) were changed to the same concentration and acid molarity between the samples and standards. The results suggest that even at the concentration as low as 100 ppb, the precision is still acceptable (Figure 5) (~ ±0.05‰) (2SD), consistent with the published report of the isotope geochemistry of zinc and copper (28). As the concentration increases, the accuracy gets better and better, which can meet different requirements of different samples.

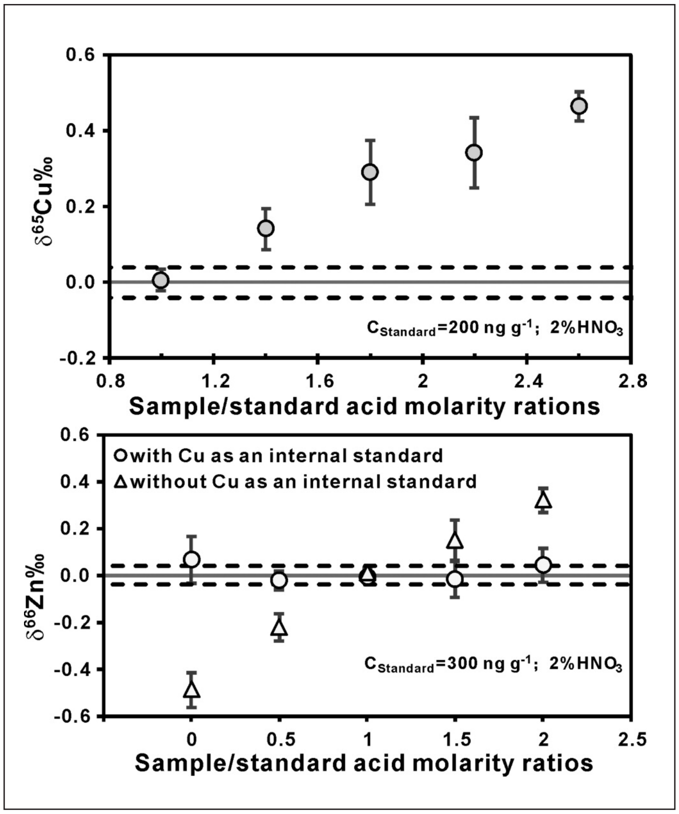

Fig. 3. Influence of acid molarity on Cu and Zn isotopic measurements.

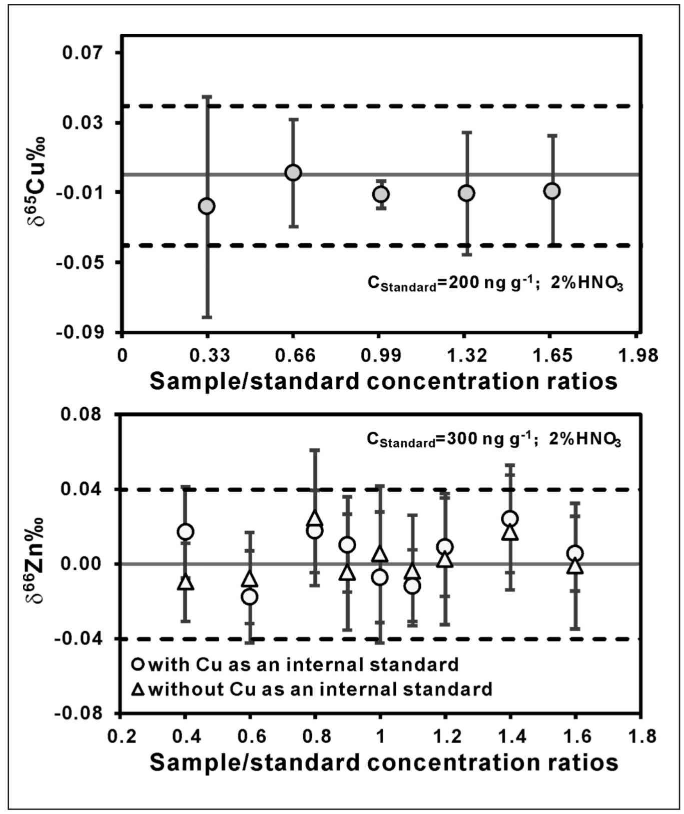

Fig. 4. Influence of concentration mismatch on Cu and Zn isotopic measurements.

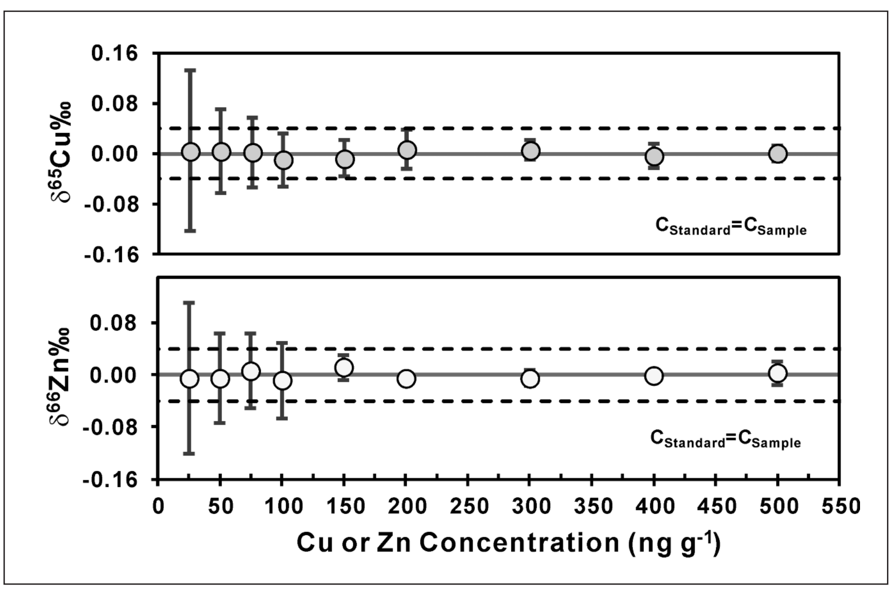

Fig. 5. Accuracy of Cu and Zn isotopes at different concentrations.

Effect of Depth of Sample Solution

In this study, it was found that the position of the sampling probe could also affect the analytical accuracy. When the entrance of the sampling probe is about 3 mm down to the bottom of the sample tube, the Cu isotope tended to change with the depth differences between the sample and the standard solutions. When the depth ratio of sample to standard (H_{sample}/$H_{standard}$) was lower than 0.3 or more than 2.8, the δ^{65}Cu positively increased with this ratio. When this ratio was between 0.3 to 2.8, then the measured Cu isotopic composition did not change (Figure 6). This phen-menon can be attributed to different pressure at different solution depth. When the distance between the entrance of the sampling probe and the bottom of the

Atomic Spectroscopy
Vol. 40(6), Nov./Dec. 2019

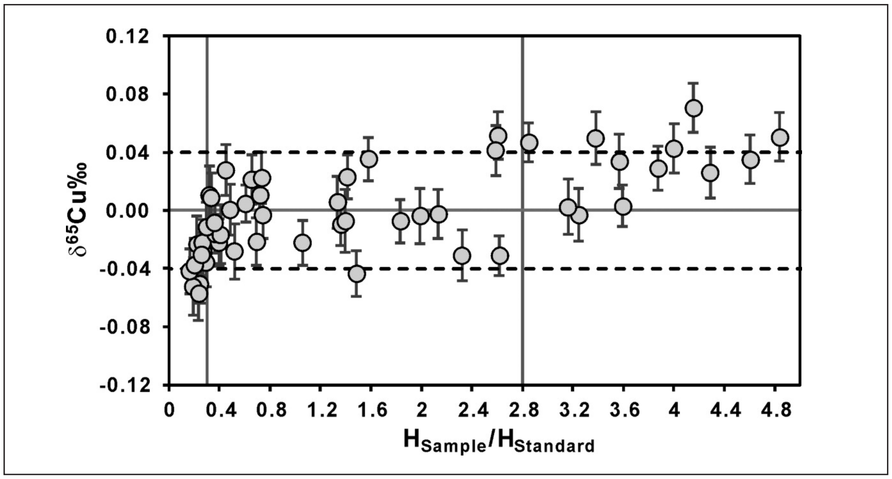

Fig. 6. Copper isotopes vary with the liquid level.

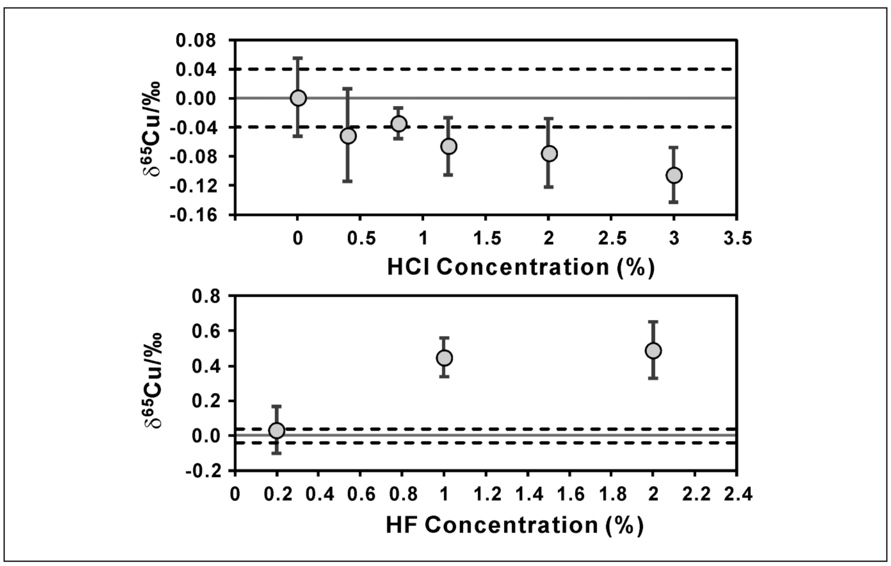

Fig. 7. Copper isotopes vary with the content of residual HCl and HF.

sample tube was more than 5 mm, this phenomenon was unobservable.

Effect of Residual Acid

A large amount of HCl and HF was used in the sample digestion and the chromatographic separation of Cu and Zn. Therefore, evaluation of the effect of residual HCl and HF in the elution was very important. The HCl or HF molarity of the samples (Alfa Cu) was changed at the constant acid molarity of the standards (HNO_3 = 2%) and the same Cu concentration (200 ng g^{-1}). The result suggests that HCl would lead to a lighter isotopic composition for Cu, and HF would lead to a heavier Cu isotope (Figure 7).

Effect of Elemental Matrix

In this study, seven matrix elements (Na, Co, Ti, Mg, Al, Fe, and Ni) were quantitatively assessed for their possible effect on the Zn and Cu isotopic measurements with their mass fractions varied in the sample solutions. Different concentrations of these elements were added to the constant samples at the constant standards (Alfa Cu and Alfa Zn were used, respectively). The potential molecular spectral interferents for Cu isotopic analysis include $^{47}Ti^{16}O$, $^{23}Na^{40}Ar$ on ^{63}Cu, $^{25}Mg^{40}Ar$ and $^{47}Ti^{18}O$ on ^{65}Cu, and for the Zn isotopic analysis include $^{48}Ti^{16}O$ on ^{66}Zn, ^{64}Ni on ^{64}Zn. The $\delta^{65}Cu$ values are sensitive to the Ti, Na, and Mg amounts in the sample solutions (Figure 8 a&b). The influence of Na on Cu isotopic analysis towards a light isotopic composition is likely due to the $(^{23}Na^{40}Ar)^+$ interference on the lighter isotope of Cu (^{63}Cu) (3). Excess Ti and Mg will lead to a heavier Cu isotope, because the $^{25}Mg^{40}Ar$ and $^{47}Ti^{18}O$ could interfere with ^{65}Cu. Because Cu is the internal standard for Zn, the $\delta^{66}Zn$ values are also sensitive to Ti, Na, and Mg in the sample solutions (Figures 8 a&b) and show an opposite trend with the Cu isotope. ^{64}Ni affects the ^{64}Zn directly, even a little bit (2 ppm) of Ni will lead to a light isotope for Zn (Figure 8 a&b). Other elements (Co, Al, and Fe) have no obvious influence on the Cu and Zn isotopes.

Accuracy

In this study, six igneous rock reference materials BHVO-2, BCR-2, BIR-1a, AGV-2, GSP-2, and W-2a were extensively digested and analyzed along with routine samples. International standards and repeated samples were analyzed to test the accuracy of the whole analysis procedure. The uncertainty of repeated samples was better than ± 0.04‰ (2SD) for both $\delta^{65}Cu$ and $\delta^{66}Zn$. The results of these standards are consistent with the recommended values reported in previous studies within uncertainties (Table III).

CONCLUSION

A method for high-precision Cu and Zn isotope analysis using sample standard bracketing on the

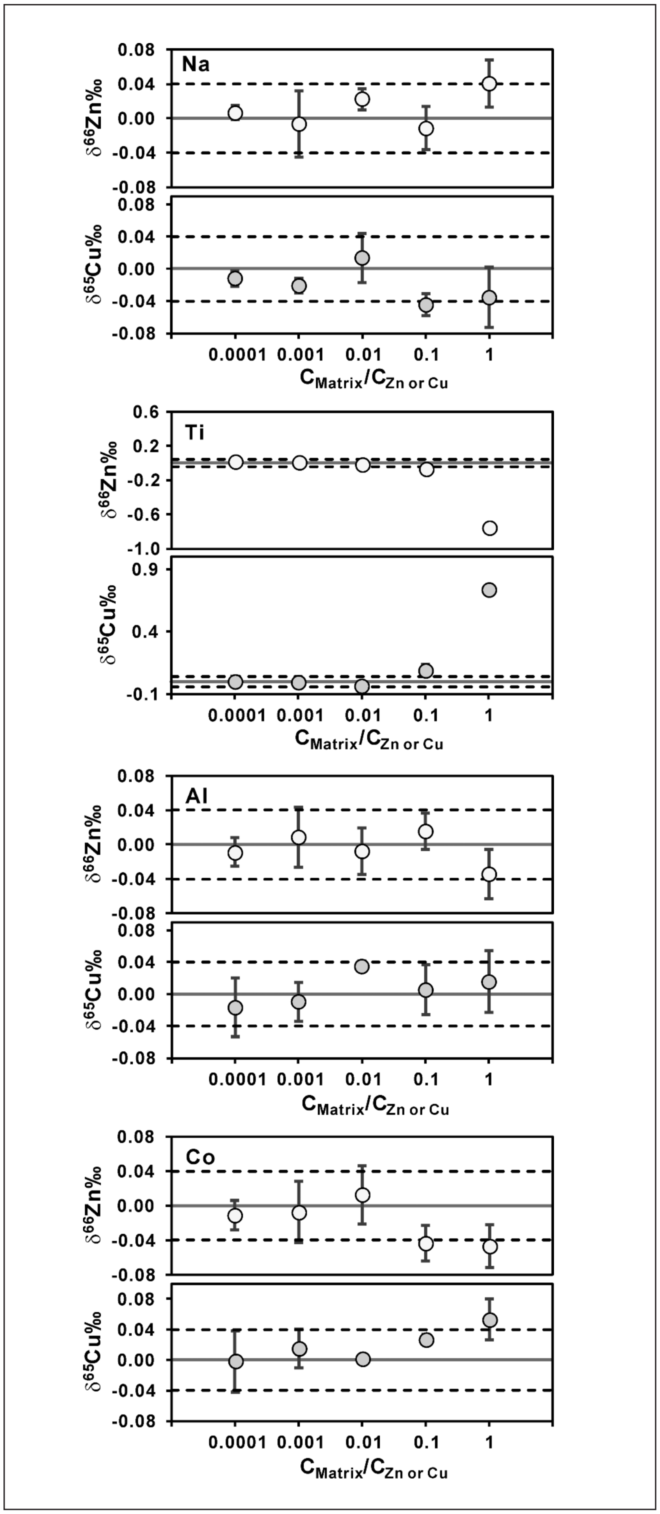

Fig. 8(a). Cu or Zn isotopic variations of Alfa Cu or Alfa Zn standard solutions spiked with different amounts of Na, Ti, Al, and Co relative to the unspiked Cu or Zn solution.

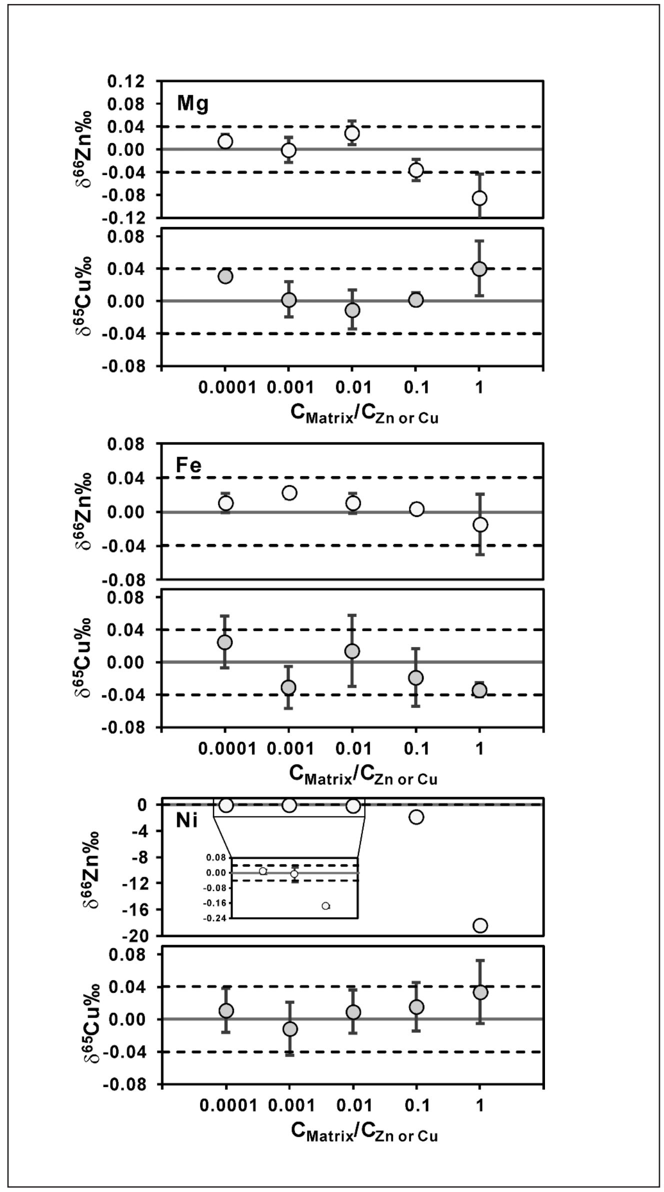

Fig. 8(b). Cu or Zn isotopic variations of Alfa Cu or Alfa Zn standard solutions spiked with different amounts of Mg, Fe, and Ni relative to the unspiked Cu or Zn solution.

large-geometry MC-ICP-MS is presented. Cu and Zn were separated from the matrix through a single column using the strong anion resin AG-MP-1M. Although Na, Ti, Mg, and Ni can significantly affect the results of the Cu and Zn isotopes, these elements and other matrixes could be removed efficiently. To obtain more accurate data, the acid molarity of the sample should be kept consistent with those in standard materials and ensure that no HF or HCl remains during its digestion process. Although the results of this study indicate that the Cu and Zn iso-

TABLE III
Copper and Zinc Isotopic Composition of Igneous Rock Standards

Sample Type	Cu (μg/g)[a]	Zn (μg/g)[a]	$\delta^{65}Cu_{SRM976}$[b]	2SD[d]	$\delta^{66}Zn_{JMC\text{-}Lyon}$ /‰[c]	2SD[d]	$\delta^{67}Zn_{JMC\text{-}Lyon}$ /‰[c]	2SDd	$\delta^{68}Zn_{JMC\text{-}Lyon}$ /‰[c]	2SD[d]	N[e]	References
BHVO-2	135	102	0.14	0.03	0.31	0.04	0.51	0.18	0.63	0.10	47	This study
			0.12	0.04	0.28	0.09						Ref. (28)[f]
BIR-1a	125	70	0.01	0.03	0.24	0.04	0.39	0.17	0.49	0.10	17	This study
			0.02	0.10	0.26	0.10						Ref. (28)[f]
BCR-2	18	128	0.22	0.04	0.26	0.03	0.41	0.11	0.51	0.07	24	This study
			0.17	0.12	0.25	0.08						Ref. (28)[f]
AGV-2	50	88	0.04	0.04	0.28	0.04	0.44	0.16	0.57	0.07	19	This study
			0.04	0.10	0.29	0.06						Ref. (28)[f]
W-2a	114	77	0.14	0.02	0.22	0.03	0.37	0.11	0.45	0.04	7	This study
					0.22	0.05			0.46	0.08		Ref. (1)
			0.11	0.02								Ref. (3)
GSP-2	44	110	0.29	0.04	1.05	0.04	1.51	0.19	1.73	0.11	19	This study
					1.07	0.06	1.53	0.11	1.74	0.10		Ref. (1)
			0.30	0.04								Ref. (3)

[a] The contents of Cu and Zn are from reference (29).
[b] The $\delta^{65}Cu$ reported as per mil deviation of the $^{65}Cu/^{63}Cu$ ratio from the SRM976 standard.
[c] The $\delta^{66}Zn$, $\delta^{67}Zn$, and $\delta^{68}Zn$ reported as per mil deviation of the $^{66}Zn/^{64}Zn$, $^{67}Zn/^{64}Zn$, and $^{68}Zn/^{64}Zn$ ratio from the JMC-Lyon standard.
[d] Two times the standard deviation.
[e] N represents the times of full replicates of the same sample (dissolution from different aliquots of same powder).
[f] The recommended values from reference (28) are summarized from previously published data.

topes are not very sensitive to concentration matching, the concentrations of the samples and standards suggest that they do match each other.

Based on repeated measurements of the standard solutions and the reference materials, the long-term external precisions of $\delta^{65}Cu$ and $\delta^{66}Zn$ were better than ± 0.04‰ (2SD). The Cu and Zn isotopic compositions of six igneous rock standards, including basalt, andesite, granodiorite, and diabase, were measured. All Cu and Zn isotopic data obtained in this study agree with previously published values within uncertainty.

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