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Development of Copper Isotope Reference Materials for High Precision Copper Isotope Analysis by Laser Ablation Inductively Coupled Multi-collector Mass Spectrometry

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Copper isotopic studies from a wide spectrum of ore-forming systems (volcanogenic massive sulfide, porphyry, skarn, hydrothermal, and supergene) have demonstrated that the Cu isotope ratios ($^{65}Cu/^{63}Cu$) of Cu-bearing minerals provide important insights into the genesis of magmatic and hydrothermal Cu mineral deposits,1 and they can be used as a potentially powerful tool for exploration and evaluation of Cu mineral deposits.2 The advent of laser ablation inductively coupled plasma multi-collector mass spectrometry (LA-MC-ICP-MS), with its ability to provide rapid and cost-effective, spatially resolved, in-situ Cu isotope analysis of individual Cu-bearing mineral phases, provided a promising new technique for highly precise measurements of Cu isotope ratios among Cu minerals However, due to significant matrix effects that occur during determination of Cu isotope ratio measurements by LA-MC-ICP-MS analysis using nanosecond lasers,3 sample-standard-sample bracketing (SSB) with matrix-matched calibration standards is required to achieve accurate results with a precision of better than 0.14 ‰ (2s.d.). More importantly, the hitherto commonly used Cu-metal NIST SRM976 standard is no longer being produced. The lack of suitable calibration standards has limited the widespread use of LA-MC-ICP-MS for in-situ Cu isotope analysis of native Cu. Thus, there is a clear need for well characterised reference materials suitable for in situ Cu isotope measurement. In this contribution, we investigated the suitability of new available reference materials including SSC-1, SSC-3, SSC-4 Cu rods and CUPD-1 Cu anode from CANMET, Canada, as Cu isotope reference materials for LA and solution nebulization (SN) Cu isotope analysis. The Cu isotope ratio measurements were performed using LA and SN MC-ICP-MS at the Geological Survey of Canada (GSC). The system consisted of a Neptune Plus MC-ICP-MS coupled to a Teledyne Photon Machines Analyte G1 excimer laser ablation system. The $^{66}Zn/^{64}Zn$ of the Zn isotope standard SRM683 in combination with SSB were used to correct for instrumental mass bias. Aliquots of the pure copper reference materials were dissolved to produce 1000 to 4000 μg mL-1 stock solutions. The Cu isotopic compositions $\delta^{65}Cu_{SRM976}$ and precision (2s.d.) of SSC-1, SSC-3, SSC-4 and CUPD-1 determined using SN-MC-ICP-MS with SRM976 as calibrator were 0.03±0.03‰ (n=30), 0.04±0.02‰ (n=30), 0.05±0.03‰ (n=30) and 2.15±0.04‰ (n=30) respectively. The Cu isotopic compositions $\delta^{65}Cu_{AE633}$ and precision (2s.d.) of SSC-1, SSC-3, SSC-4 and CUPD-1 determined independently using ERM AE633 as calibrator were 0.20±0.05‰ (n=30), 0.04±0.02‰ (n=30), 0.03±0.02‰ (n=30) and 2.14±0.03‰ (n=30) respectively. The Cu isotopic compositions δ65CuSRM976 and precision (2s.d.) of the quality control standard ERM AE647 determined using SRM976 and AE633 as calibrators were 0.20±0.04‰ (n=24) and 0.20±0.05‰ (n=62). The Cu isotopic compositions $\delta^{65}Cu_{SRM976}$ and precision (2s.d.) of the quality control materials AE647 and Romil Cu determined using the newly developed reference material CUPD-1 were 0.18±0.06‰ (n=20) and 0.17±0.06‰ (n=20). The measured Cu isotope ratios for the new reference materials using two different calibration standards are identical at the 95% confidence level. The values of measured Cu isotope ratios for the quality control standards also agree well the accepted values4. The measured Cu isotopes of the new reference materials by LA-MC-ICP-MS analysis were used to examine the Cu isotope homogeneity of the reference materials, and evaluate the achievable precision and accuracy of in-situ Cu isotope measurements of native copper. The LA analyses were accomplished in a Helium atmosphere and the ablation aerosol is then mixed with a dry Zn aerosol before being delivered to the MC-ICP-MS. The spot size of 43 µm and a low laser repetition rate (2 Hz) were employed to minimise down-hole laser-induced isotopic fractionation. A plug of glass wool (ca. 40 mg) in the sample delivery tubing was also used to preferentially filter particles (>0.5 µm) too large to be quantitatively volatilised in the ICP, which can result in severe isotopic fractionation.3 One of the new reference materials was used to correct for additional biases and to calibrate the analyses relative to SRM976. The homogeneity test of the new reference materials using a Normal distribution quantile-quantile plot shows that the quantile points for the determined Cu isotope ratios yielded a straight line with a correlation coefficient of 0.97 to 0.99. The homogeneity of the new four reference materials was further assessed using the mean square weighted deviation (MSWD). The determined MSWD for SSC1, SSC-3, SSC-4 and CUPD-1 was 0.80 (n=34), 0.96 (n=35), 0.69 (n=44) and 3.1 (n=28) respectively. The results indicate that the measured Cu isotope ratios from the new reference materials closely approximate single normally-distributed populations, and the new reference materials are homogeneous at 43 µm within the level of analytical uncertainty of the measurement techniques. The significantly higher MSWD for CUPD-1 suggests excess data-point scatter that is unaccounted for by the quoted analytical uncertainty. The Cu isotopic compositions $\delta^{65}Cu_{SRM976}$ and precision (2s.d.) of SSC-1, SSC-4 and CUPD-1 determined using SSC-3 as calibrator were 0.03±0.08‰ (n=34), 0.02±0.06‰ (n=44) and 2.12±0.10‰ (n=28) respectively. The Cu isotopic composition $\delta^{65}Cu_{SRM976}$ of SSC-3 and precision (2s.d.) determined using SSC-1 as calibrator was 0.03±0.08‰ (n=34). The Cu isotope composition of each new reference materials by LA agree well with SN analyses at the 95% confidence level with an acceptable range of precision (2s.d.) of ≤ 0.10‰. The suitability and chemical purity of the newly developed Cu isotope reference materials will be further studied. The developed copper isotope reference material can potentially serve as calibration and quality control standards for in-situ and SN Cu isotope analysis.

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