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Comment

Comment on: "Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry" [N.H. Gale, A.P. Woodhead, Z.A. Stos-Gale, A. Walder, I. Bowen, Int. J. Mass Spectrom. 184 (1999) 1]

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In the original publication Gale and co-workers pointed out that TIMS $^{63}Cu/^{65}Cu$ isotope ratio measurements of good run-to-run reproducibility were reported in literature ($\pm 0.06\%$ at the 2σ level, $n = 6$) but experimental details are not available [1].

Hereby the missing details are given. "A triple rhenium filament ion source was used. A drop of solution containing 20 μg copper was electroplated on each degassed sample filament. A pure platinum wire serving as an anode was dipped into the solution and a dc was passed through for 30 s. The ionization and sample filaments were slowly heated to 5.2 and 1.0 A, respectively, yielding a stable 3×10^{-13} A $^{63}Cu^{+}$ ion current. Thirty-six ratios were collected for one sample. The relative standard deviations for six samples measured in the single and double collector mode of operation were 0.041% and 0.031%, respectively." This procedure has also been published recently elsewhere [2].

At this occasion two further points of interest about

Table 1
Summary of selected Cu isotope ratio precision data

Method	Material	$^{63}Cu/^{65}Cu$	Precision (%)	Reference
TIMS	NIST-SRM 976	2.2440	0.047[a]	[3]
TIMS	Lab. Reagent	2.2548[b]	0.031	[1]
TIMS	NIST-SRM 976	2.2448	0.031	[4]
TIMS	NIST-SRM 976	2.2447	0.035	Original study
MC-ICP-MS	NIST-SRM 976	2.2443	0.0076	Original study
TOF-ICP-MS	N.A.	N.A.	0.031[c]	[5]

[a] See text.
[b] Not corrected for fractionation.
[c] Best reported value (Cu concentration 500 μg/L, acquisition time 30 s per replicate).

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copper isotope ratio measurement should be noted. In the original study Gale et al. also used multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), reporting precision of 0.0076% for the $^{63}Cu/^{65}Cu$ isotope ratio. Table 1 summarizes selected data for Cu isotope ratio measurements, including very recent data by Vanhaecke et al. who evaluated the performance of an axial time-of-flight (TOF) ICP-MS [5]. Furthermore, copper isotope measurements are extremely sensitive to cationic (Na, Ti, V and Cr) and anionic (sulfate, phosphate and chloride) impurities, introducing isobaric polyatomic interferences at $m/z = 63$ and 65 [6].

It should be noted that the precision quoted in [1],[4],[5] and Gale's work represents the relative standard deviation of the grand mean (i.e. the mean of the measured sample means), whereas the NIST value ([3]) indicates the overall limits of error including also allowances for the effects of known sources of possible systematic error. Therefore the measurement precision is better than the quoted value in Table 1 and [3].

References

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