Determination of Cu and Mo isotope fractionations in natural materials using MC-ICP-MS

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Fractionations of transition metal isotopes in nature have seldom been studied because of analytical difficulties. Here, we describe a simple analytical approach to study natural fractionations of Cu and Mo isotopes. This methodology should be useful for novel research in trace metal geochemistry, environmental chemistry and bioinorganic chemistry.

Methodology

Our aim is to determine the deviations (δ) in the isotopic compositions of Cu and Mo between samples and standards, using the VG Plasma54 multiple-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS) at the University of Rochester. MC-ICP-MS systems are well-suited to this research because they feature high ionization efficiency for all transition metals, simple sample introduction, simultaneous collection of multiple ion beams for precise determination of isotope ratios, and no fractionation of the sample reservoir during analysis (Halliday et al., 1995). As a result, the largest source of uncertainty in isotopic analyses by MC-ICP-MS is the variability of instrumental mass bias with time.

We can correct for this effect if we take advantage of another unique characteristic of MC-ICP-MS: The minimal variation in instrumental mass bias among different elements over a limited mass range (Hirata, 1996). As a result, if samples and standards are 'spiked' with an element of similar mass to the element of interest, the magnitude of mass bias, α, can be determined by comparing the measured isotopic composition of the spike element to the 'true' value. The measured composition of the element of interest is then corrected using α and the appropriate mass fractionation law.

This 'elemental spike' method, analogous to use of an isotopic 'double spike', has proven useful in precise and accurate determination of Pb isotopic compositions (Longerich et al., 1987; Hirata et al., 1996). For fractionation studies, the use of elemental spikes avoids some of the complexities of a double spike. It also facilitates isotopic analysis of elements with fewer than four stable isotopes.

Significantly, δ values do not depend on α being identical for the element of interest (α_i) and the spike element (α_s). Although differences in α produce inaccuracies in isotope ratio determinations, such errors cancel in the δ notation as long as α_i/α_s is constant. Similarly, inaccuracy in the 'true' value of the spike element will not affect δ, as long as the isotopic composition of the spike is identical in samples and standards.

Cu Isotopes

For Cu isotopic studies, samples and standards are doped with Zn from an in-house standard, following the procedure of Maréchal et al. (1997). The magnitude of mass bias is determined from measurement of the ratio $^{66}Zn/^{68}Zn$ (R_{Zn}).

In the initial experiments described here, $^{63}Cu/^{65}Cu$ (R_{Cu}) was determined in an in-house standard and in a sample of malachite dissolved in HNO_3. The internal precision of individual ratio measurements was $\sim \pm 0.0020$ (% std err).

To assess the validity of the elemental spike method, data are plotted in Fig. 1 as $\ln(R_{Cu})$ vs. $\ln(R_{Zn})$, without mass bias correction. A linear relationship is expected if α_{Cu}/α_{Zn} is constant. Data from samples with different true R_{Cu} should fall along parallel lines. As seen in Fig. 1, a linear relationship exists for both the Cu standard and the malachite sample. The slight deviations from linearity and parallelism may reflect small variations in α_{Cu}/α_{Zn}.

The unambiguous offset between the standard and sample data sets is consistent with a difference in true R_{Cu}. To eliminate the possibility that this offset is the result of isobaric interferences or matrix effects on α_{Cu}/α_{Zn}, Cu was isolated from both the standard and the sample using anion exchange chromatography, and analysed by MC-ICP-MS. Chemically purified and
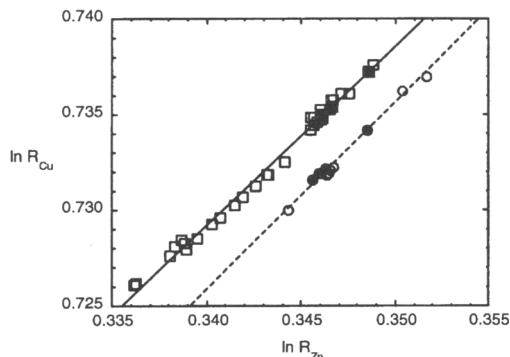
FIG. 1. R_{Cu} *vs* R_{Zn} for Cu standards (squares) and malachite (circles). Filled symbols are samples from which Cu has been extracted by anion exchange chemistry. Error bars are smaller than the symbols.

FIG. 2. External precision of $\delta^{65}Cu_{malachite}$, based on replicate determinations. All uncertainties are $\pm$ 2σ.

unpurified materials fall on the same trends (Fig. 1). This also demonstrates that there is no fractionation of Cu isotopes in the separation chemistry.

By alternating measurements of the sample and the standard, and using the exponential law of Russell *et al.* (1978), we attain a precision of $\pm$ 0.05‰ for each δ determination. Repeat analyses yield $\delta^{65}Cu_{malachite}$ = 2.81 $\pm$ 0.11‰ (Fig. 2). These results confirm the existence of natural variations in the isotopic composition of Cu (Shields *et al.*, 1965; Maréchal *et al.*, 1997), and demonstrate the utility of MC-ICP-MS for $\delta^{65}Cu$ determination.

Mo Isotopes

We have developed a similar method to study the fractionation of Mo isotopes, using Zr as the elemental spike. Mass bias is measured using $^{90}Zr/^{91}Zr$ (R_{Zr}). Using this method, $^{95}Mo/^{97}Mo$
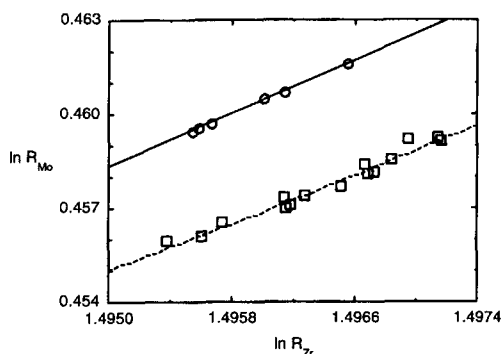
(R_{Mo}) has been determined in an in-house Mo standard, and in a gravimetrically-prepared standard enriched in ^{95}Mo.

In Fig. 3, we plot $\ln(R_{Mo})$ *vs* $\ln(R_{Zr})$ for both standards. As with Cu and Zn, a linear relationship is seen for both sets of data, with only minor deviations from linearity and parallelism.

The precision of our method for measuring $\delta^{97}Mo$ can be assessed by comparing the δ value expected from gravimetry to the measured δ after mass bias correction. Based on repeat analyses of both standards, we find $\delta^{97}Mo$ = −3.42 $\pm$ 0.15‰ (2σ). This value is indistinguishable from the gravimetric prediction of $\delta^{97}Mo$ = −3.44‰. We expect that this approach will be useful in searching for fractionations of Mo isotopes in nature.

Acknowledgements

FIG. 3. R_{Mo} *vs* R_{Zr} for isotopically-normal Mo standards (squares) and ^{95}Mo-enriched standards (circles). Error bars are smaller than the symbols.
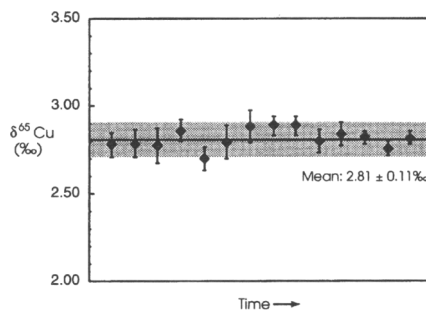
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