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.

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 $^{66}_{64}$Zn/$^{68}_{66}$Zn ($R_{Zn}$).

In the initial experiments described here, $^{63}_{63}$Cu/$^{65}_{65}$Cu ($R_{Cu}$) was determined in an in-house standard and in a sample of malachite dissolved in HNO₃. The internal precision of individual ratio measurements was ± 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 $\alpha_{Cu}/\alpha_{Zn}$ 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 $\alpha_{Cu}/\alpha_{Zn}$.

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 $\alpha_{Cu}/\alpha_{Zn}$, Cu was isolated from both the standard and the sample using anion exchange chromatography, and analysed by MC-ICP-MS. Chemically purified and
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 ± 0.05‰ for each δ determination. Repeat analyses yield ΔCu_malachite = 2.81 ± 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 δCu 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 90Zr/91Zr (R_{Zr}). Using this method, 95Mo/97Mo (R_{Mo}) has been determined in an in-house Mo standard, and in a gravimetrically-prepared standard enriched in 95Mo.

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 δ97Mo 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 δ97Mo = -3.42 ± 0.15‰ (2σ). This value is indistinguishable from the gravimetric prediction of δ97Mo = -3.44‰. We expect that this approach will be useful in searching for fractionations of Mo isotopes in nature.

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References


