

Natural Molybdenum Isotope Fractionation Determined by Double-Spike MC-ICP-MS Mo Isotope Ratio Measurements

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Using multicollector ICP mass spectrometry with a $^{100}\text{Mo}/^{97}\text{Mo}$ double spike, we demonstrate mass dependant molybdenum isotope fractionation in ion exchange column separation as well as natural fractionation between chondritic, iron meteoritic and terrestrial samples.

The addition of a double spike before molybdenum separation circumvents problems related to analytically induced isotope fractionation. In addition, this method provides precise molybdenum concentrations. The $\text{H}_2\text{SO}_4/\text{HCl}$ anion exchange chromatography showed a 90% Mo yield. It proved successful in purifying molybdenum from silicate and metal matrixes (chondritic and iron meteorites).

Molybdenum masses 92 through 100 were measured simultaneously by multicollector ICP-MS (Nu instruments). Three dimensional data reduction assuming exponential laws for instrumental and for external fractionation was carried out online. Mass ratios 98/96, 98/95, 98/94, and 98/92 were used to constrain isotopic fractionation. This multi ratio approach provides a consistency check and thus eliminates errors due to unresolved isobaric interferences. In addition, Ruthenium was monitored on mass 99. In the case of iron-meteorites trace amounts could be detected and were corrected for. 2s external standard reproducibility of the different ratios range from 0.05-0.08 permille. The weighted mean and error of up to four ratios result in even tighter constrains.

Molybdenum isotope fractionation induced by chromatography was tested for by collecting unspiked Mo fractions eluded successively from the column. Subsequently spiked 10% fractions showed deviations of up to 1 permille on $^{98}\text{Mo}/^{95}\text{Mo}$. As this procedure involves Mo-complexes, it must be assumed, that cation-exchange chromatography will lead to even larger fractionation. Standard aliquots spiked before the column procedure show no fractionation. This

demonstrates that incomplete recovery should not impair analytical results (c.f Russell et al., 1978).

Taking the reproduced and consistent Molybdenum isotopic composition of two chondritic meteorites (Utzenstorf, Switzerland; Klausenburg, Siebenbuergen) as referenced, hydrothermal molybdenite from Huanglongpu, China (HLP-5, by courtesy of H. Stein; Stein et al., 1997) shows significantly lighter isotopic composition (0.23 permille per atomic mass unit (amu)).

An unexpected result was the lighter and slightly varying Mo isotopic composition (between 0.12 and 0.15 permille per amu) of three different iron meteorites (Brownfield, Texas; Canyon Diabolo, Arizona; Odessa, Texas; all meteoritic samples by courtesy of O. Eugster). This may point to previously unresolved (Wetherill, 1964) redox-dependant light Mo isotope enrichment in core formation processes. This is supported by the fact that lighter Mo isotopes are enriched in the iron meteorite with the lowest Mo concentration. Further studies of this effect may constrain redox conditions of core formation in planetisimals.

In view of the highly resolvable variations observed, molybdenum isotope determination by double spike technique and MC-ICP-MS has great potential to provide constraints on a wide variety of geological and cosmochemical problems.

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