High-precision molybdenum isotope analysis by negative thermal ionization mass spectrometry

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ABSTRACT

Procedures for the separation, purification, and high-precision analysis of mass-independent isotopic variations in molybdenum (Mo) using negative thermal ionization mass spectrometry are reported. Separation and purification of Mo from silicate and metal matrices are achieved using a two-stage anion exchange chromatographic procedure. Molybdenum is ionized as the MoO_3^- species using a double filament assembly. The MoO_3^- ion beams are collected using Faraday cup detectors equipped with a mixed array of amplifiers utilizing 10^{11} and $10^{12}\,\Omega$ resistors, which allows for *in situ* measurement and correction of oxygen isobars. The long-term external reproducibility of $^{97}Mo/^{96}Mo$, the most precisely measured Mo isotope ratio, is ±5.4 ppm (2SD), based on the repeated analyses of the *Alfa Aesar Specpure®* Mo plasma standard and using $^{98}Mo/^{96}Mo$ for fractionation correction. The long-term external reproducibilities of $^{92}Mo/^{96}Mo$, $^{94}Mo/^{96}Mo$, $^{95}Mo/^{96}Mo$, and $^{100}Mo/^{96}Mo$ are ±107, 37, 23, and 32 ppm (2SD), respectively. With this precision, smaller differences in Mo isotopic compositions can be resolved than have been previously possible.

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1. Introduction

The molybdenum (Mo) isotopic system is uniquely suited to address current issues in cosmochemistry from the origin of isotopic heterogeneity in the solar nebula to the diversity of planetary bodies. Though the cosmochemical applications for Mo isotopes are the primary focus of this study, the application of mass-dependent Mo isotope effects as indicators of paleoredox conditions has been the focus of most Mo isotope studies in geochemistry (*e.g.*, [1–3]). In cosmochemistry, "mass-independent" nucleosynthetic Mo isotope anomalies, which have been observed in a variety of cosmochemical materials, including at the bulk meteorite scale, have been used primarily to evaluate the extent of mixing and/or thermal processing in the solar nebula, and to test genetic relations amongst solar system materials (*e.g.*, [4–7]). The use of Mo as a genetic tracing tool is important for the elucidation of nebular and planetary processes, including the characterization of the nebular feeding zones of planetary bodies. By merging groups or incorporating ungrouped or anomalous meteorites into existing groups, the accretionary histories and evolution of meteorite parent bodies can be further developed. As a corollary, by demonstrating that certain solar system objects are unrelated, the parent bodies' evolutionary histories can be clarified.

Molybdenum has been previously analyzed by thermal ionization mass spectrometry in both positive (P-TIMS – *e.g.*, [8–11]) and negative mode (N-TIMS – [12,5,6,13]). Molybdenum isotopes in cosmochemical and terrestrial materials have also been measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (*e.g.*, [14,15,4,7,16]). The current state-of-the-art precision (2SD) of the measured $^{97}Mo/^{96}Mo$ isotope ratio is ±13 ppm by N-TIMS [13] and ±21 ppm by MC-ICP-MS [13]. Although the method of Nagai and Yokoyama [13] produces high-precision Mo isotope ratios, 1000 ng–4000 ng of Mo were used in their study. This requires large sample masses of up to 4 g for some chondritic meteorites. Due to the valuable nature of cosmochemical materials, it is desirable to use as little material as possible.

In an effort to increase the resolving power of the Mo isotopic system when ≤1000 ng of Mo are available, we developed procedures for the separation, purification, and high-precision analysis of Mo using a *Thermo-Fisher Triton Plus* N-TIMS at the University of Maryland. Using N-TIMS has the advantage of more stable signal intensities and lower likelihood of isobaric interferences, as opposed to P-TIMS and MC-ICP-MS. In addition, the sensitivity of N-TIMS is typically higher than that of P-TIMS for elements that form negative ions or oxyanions, such as Mo [17,18]. The method, however, requires correction for interferences from oxides containing

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the heavier oxygen isotopes (*e.g.*, [17]). One recent advance in the application of N-TIMS is the *in situ* measurement of certain oxygen isobars, which provides the opportunity to monitor the variability in the oxygen isotopic composition during analysis [19–24,13,25]. This study incorporates the use of $10^{12}\,\Omega$ resistors to measure and correct for oxygen isobars.

The methods presented here are primarily applicable to the measurement of mass-independent nucleosynthetic effects, but may also be adapted to double-spike methods for the determination of mass-dependent stable isotope effects. To demonstrate the utility of these procedures, the Mo isotopic compositions of standards, a gravimetrically prepared spike-standard mixture, the iron meteorites Toluca and Skookum, and the chondrite Allegan are reported.

2. Sample preparation

Iron meteorite samples were cut into 0.3–2 g pieces using a water-cooled Leco "Vari-cut" saw with a 12.7 cm diamond wafering blade. All iron meteorite pieces were mechanically abraded with different pieces of carborundum paper for each sample, and sonicated in ethanol three times to remove adhering rust, fusion crust, or saw blade contamination. All acids used for digestion and ion exchange chromatography were sub-boiling distilled with a quartz still (HCl and HNO_3) or a *Savillex Teflon*® still (HF) in-house. High-purity water used for dilutions and cleaning was produced using a *Milli-Q* water purification system (deionized to a resistivity of 18.2 M$\Omega\cdot$cm). Iron meteorite samples were digested using 30–40 ml of 8 M HCl in *Savillex Teflon*® beakers which were heated at 130–140 °C on a hotplate for at least 48 h. The chondrite sample (Allegan) was powdered in an agate mortar and pestle, and digested in 30 ml of a concentrated $HF:HNO_3$ mixture in 5:1 proportions. The Allegan solution was evaporated to a sludge, 5 ml of concentrated HNO_3 was added to dilute the remaining HF, and then 5 ml of concentrated HCl was added and evaporated twice to dissolve fluorides that are insoluble in HNO_3. Chondrite and iron meteorite samples were dried to a sludge, and 3 ml of concentrated HNO_3:HCl in 2:1 proportions was added to the samples and heated at 100 °C overnight or 115 °C for at least one hour in an effort to drive Mo to its highest oxidation state (MoVI). This step was used in an attempt to mitigate loss of Mo during ion exchange due to the presence of multiple valences of Mo on the column. The acid phase was evaporated to a sludge, at which point, 6 M HCl was added and dried to sludge twice to remove traces of HNO_3. Then 1 M HF was added and dried to sludge twice, and finally the samples were taken into the 1 M HF loading solution. At this point, some Mo was likely reduced to a lower oxidation state, but the successive additions of HCl and HF were necessary to ensure that the loading solution was the correct molarity of HF, with minimal traces of HCl and HNO_3.

The separation and purification of Mo from natural samples utilized a two-stage anion exchange chromatography method adapted from Pietruszka et al. [26], Scheiderich et al. [27], and Nagai and Yokoyama [28] (Table 1). *Eichrom* AG 1 × 8 200–400 mesh resin was pre-cleaned using reagent grade 1 M HCl and 6 M HCl, followed by quartz-distilled 6 M HCl and 1 M HCl, added in succession with *Milli-Q* water between stages of cleaning. The primary column generally follows the same procedure as the primary column of Nagai and Yokoyama [28]. Disposable *Biorad Poly-Prep* columns with 2 ml resin bed volume capacity were loaded with 1.4 ml of resin, which was further cleaned using the procedures outlined in Table 1. Samples were loaded in 1 ml of 1 M HF for each column, with 1 column per ∼100 mg of iron meteorite and ∼300 mg of chondrite. Major elements were eluted in an additional 3 ml of 1 M HF; Zr, Ru, Ti, and Hf were eluted in 6 ml of 9 M HCl–0.05 M HF; W was eluted in 12 ml of 9 M HCl–1 M HF; and Mo was collected in 10 ml of 6 M HNO_3–3 M

HF. Before the addition of 6 M HNO_3–3 M HF, 1.5 ml of Milli-Q H_2O was added to the column to prevent the formation of *aqua regia* in the column.

The secondary column was a small version of the anion column described by Pietruszka et al. (2006), and was used to further purify the Mo. The columns used for this study were made with *Teflon*® heat-shrink tubing and were fitted with *Teflon*® frits. The resin bed for these columns had dimensions of 0.4 × 2.4 cm. The secondary column was filled to the base of the reservoir with *Eichrom* AG 1 × 8 200–400 mesh resin (∼300 μl). The resin bed was then cleaned using 0.01 M HCl, 1 M HCl, and 6 M HCl. Prior to loading, samples were dissolved in 2:1 HNO_3:HCl and heated overnight or for one hour, as was done prior to the primary column. Again, 6 M HCl was added and dried to remove traces of HNO_3 twice, and then the sample was taken up into 0.5 ml of 6 M HCl to be loaded onto the column. Four ml of 6 M HCl was added to the column to elute remaining impurities, such as Fe, Ni, and Co, followed by 1 ml of 0.01 M HCl-0.1 M HF to remove remaining Fe, followed by 3 ml of 0.01 M HCl. Molybdenum was then collected in 12.5 ml of 1 M HCl (Table 1). This column, including the oxidation stage with 2:1 HNO_3:HCl, was repeated once to improve sample purity. Molybdenum purity and yield was monitored qualitatively using a *Thermo-Fisher Element 2* single-collector ICP-MS prior to loading onto filaments for analysis. Occasional above-background signals on masses corresponding to Na, Al, V, Mn, Zn, and Sn were observed; some of which may have been generated by gas species from the plasma. The largest and most variable signals were observed for [23]Na and [27]Al, and the ratios of these signals to the corresponding [98]Mo signals were typically 0.02-2 ([23]Na/[98]Mo) and 0.2-1 ([27]Al/[98]Mo). Other species typically had signal ratios, relative to [98]Mo, significantly less than ∼0.2. The occurrences of these non-analyte species were not correlated with poor ionization of Mo.

Three total analytical blanks were determined for these procedures. Each blank used either one, three, or four primary columns, and resulted in blanks of 0.92, 1.3, and 2.8 ng of Mo, respectively. The total analytical blank using one primary column is, therefore, estimated to be ∼0.9 ± 0.3 ng (2SD). These blanks were sufficiently low to be negligible for the quantities of Mo used for the analyses reported.

The total yield for the chemistry described above was ∼50–65%. It is possible that the sub-optimal recovery of Mo resulted in mass-dependent fractionation of the Mo isotopes. However, the Mo isotopic compositions reported here were fractionation corrected for mass-dependent isotope effects that occurred naturally and/or that resulted from the column chemistry. Although Rizo et al. [29] showed that fractionation correction of mass-dependently fractionated materials can result in apparent mass-independent anomalies in W isotopes, the agreement of the Mo data reported here with those of previous studies, as discussed below, indicate that fractionation that occurred during the column chemistry was effectively corrected for.

Loss of Mo primarily occurred in the primary column in the loading stage where some Mo was eluted with the Fe. Because the yield for the secondary column was typically 80–100%, and matrix was largely absent at this stage, it is likely that the matrix was the complicating factor in the primary column. The breakthrough of Mo in the primary column was mitigated by loading in 1 M HF, as opposed to the 0.4 M HCl–0.5 M HF loading solution used by Nagai and Yokoyama [28]. The partition coefficient between the resin and the acid phase (K_d) for Mo is relatively low in 0.4 M HCl–0.5 M HF compared to 1 M HF (K_d = 45 in 0.4 M HCl–0.5 M HF *vs.* K_d = 573 in 1 M HF – Nagai and Yokoyama [28]. These authors chose not to use 1 M HF due to the high K_d values they measured for Zr and Hf, but we observed that Zr was efficiently separated from Mo in the primary and secondary columns. Hafnium was not monitored by