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

Emily A. Worsham^{a*}, Richard J. Walker^a, and Katherine R. Bermingham^a

^aDepartment of Geology, University of Maryland, College Park, Maryland, 20742 USA

*Corresponding Author Details:

Emily A. Worsham

eworshal@umd.edu

Phone: 423-360-3891

Key words: molybdenum isotope; thermal ionization mass spectrometry; N-TIMS; oxide correction; $10^{12} \Omega$ resistor; oxygen isotope

Abstract

Procedures for the separation, purification, and high-precision analysis of mass independent isotopic variations in Mo using negative thermal ionization mass spectrometry are reported. Separation and purification of Mo from silicate and metal matrices is 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 $^{97}\text{Mo}/^{96}\text{Mo}$, 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 $^{98}\text{Mo}/^{96}\text{Mo}$ for fractionation correction. The long-term external reproducibilities of $^{92}\text{Mo}/^{96}\text{Mo}$, $^{94}\text{Mo}/^{96}\text{Mo}$, $^{95}\text{Mo}/^{96}\text{Mo}$, and $^{100}\text{Mo}/^{96}\text{Mo}$ 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.

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., Barling et al., 2001; Siebert et al., 2003; Anbar et al., 2001). 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., Dauphas et al., 2002; Yin et al., 2002; Becker and Walker, 2003; Burkhardt et al., 2011). 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., Lu and Masuda, 1992; Turnlund et al., 1993; Wieser and De Laeter, 2000, 2009) and negative mode (N-TIMS – Giussani et al., 1995; Yin et al., 2002; Becker and Walker, 2003; Nagai and Yokoyama, 2016). Molybdenum isotopes in cosmochemical and terrestrial materials have also been measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (e.g., Lee and Halliday, 1995; Dauphas et al., 2001; Dauphas et al., 2002; Burkhardt et al., 2011; Burkhardt et al., 2014). The current state-of-the-art precision (2SD) of the measured $^{97}\text{Mo}/^{96}\text{Mo}$ isotope ratio is ± 13 ppm by N-TIMS (Nagai and Yokoyama, 2016) and ± 21 ppm by MC-ICP-MS (Burkhardt et al., 2011). Although the method of Nagai and Yokoyama (2016) 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 (Heumann et al., 1995; Wieser et al., 2007). The method, however, requires correction for interferences from oxides containing the heavier oxygen isotopes (e.g., Heumann et al., 1995). One recent advance in the application of N-TIMS is the *in situ* measurement of certain oxygen isobars, which can account for variability in the oxygen isotopic composition during analysis (Liu et al., 1998; Luguet et al., 2008; Aggarwal et al., 2009; Chatterjee and Lassiter, 2015; Chu et al., 2015; Bermingham et al., 2016; Nagai and Yokoyama, 2016; Trinquier et al., 2016). 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 to 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

82 abraded with different pieces of carborundum paper for each sample, and sonicated in ethanol
83 three times to remove any adhering rust, fusion crust, or saw blade contamination. All acids used
84 for digestion and ion exchange chromatography were sub-boiling distilled with a quartz still
85 (HCl and HNO₃) or a *Savillex Teflon*[®] still (HF) in-house. High purity water used for dilutions
86 and cleaning was produced using a *Milli-Q* water purification system (deionized to a resistivity
87 of 18.2 MΩ·cm). Iron meteorite samples were digested using 30-40 ml of 8M HCl in *Savillex*
88 *Teflon*[®] beakers which were heated at 130-140 °C on a hotplate for at least 48 hours. The
89 chondrite sample (Allegan) was powdered in an agate mortar and pestle, and digested in 30 ml of
90 a concentrated HF/HNO₃ mixture in 5:1 proportions. The Allegan solution was evaporated to a
91 sludge, 5 ml of concentrated HNO₃ was added to dilute the remaining HF, and then 5 ml of
92 concentrated HCl was added and evaporated twice to dissolve fluorides that are insoluble in
93 HNO₃. Chondrite and iron meteorite samples were dried to a sludge, and 3 ml of concentrated
94 HNO₃:HCl in 2:1 proportions was added to the samples and heated at 100 °C overnight or 115
95 °C for at least an hour in an effort to drive Mo to its highest oxidation state (MoVI). This step
96 was used in an attempt to mitigate loss of Mo during ion exchange due to the presence of
97 multiple valences of Mo on the column. The acid phase was evaporated to a sludge, at which
98 point, 6M HCl was added and dried to sludge twice to remove traces of HNO₃. Then 1M HF was
99 added and dried to sludge twice, and finally the samples were taken into the 1M HF loading
100 solution. At this point, some Mo was likely reduced to a lower oxidation state, but the successive
101 additions of HCl and HF were necessary to ensure that the loading solution was the correct
102 molarity of HF, with minimal traces of HCl and HNO₃.

103 The separation and purification of Mo from natural samples utilized a two-stage anion
104 exchange chromatography method adapted from Pietruszka et al. (2006), Scheiderich et al.

(2010), and Nagai and Yokoyama (2014) (**Table 1**). *Eichrom* AG 1X8 200-400 mesh resin was pre-cleaned using reagent grade 1M HCl and 6M HCl, followed by quartz-distilled 6M HCl and 1M 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 (2014). 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 1M 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 1M HF; Zr, Ru, Ti, and Hf were eluted in 6 ml of 9M HCl-0.05M HF; W was eluted in 12 ml of 9M HCl-1M HF; and Mo was collected in 10 ml of 6M HNO₃-3M HF. Before the addition of 6M HNO₃-3M HF, 1.5 ml of *Milli-Q* H₂O 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 x 2.4 cm. The secondary column was filled to the base of the reservoir with *Eichrom* AG 1X8 200-400 mesh resin (~300 µl). The resin bed was then cleaned using 0.01M HCl, 1M HCl, and 6M HCl. Prior to loading, samples were dissolved in 2:1 HNO₃:HCl and heated overnight or for one hour, as was done prior to the primary column. Again, 6M HCl was added and dried to remove traces of HNO₃ twice, and then the sample was taken up into 0.5 ml of 6M HCl to be loaded onto the column. Four ml of 6M HCl was added to the column to elute remaining impurities, such as Fe, Ni, and Co, followed by 1 ml of 0.01M HCl-0.1M HF to remove remaining Fe, followed by 3 ml of 0.01M HCl. Molybdenum was then

collected in 12.5 ml of 1 M HCl (**Table 1**). This column, including the oxidation stage with 2:1 HNO₃: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. 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 ²³Na and ²⁷Al, and the ratios of these signals to the corresponding ⁹⁸Mo signals were typically 0.02-2 (²³Na/⁹⁸Mo) and 0.2-1 (²⁷Al/⁹⁸Mo). Other species typically had signal ratios, relative to ⁹⁸Mo, 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. (2016) 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,

150 indicate that fractionation that occurred during the column chemistry was effectively corrected
151 for.

152 Loss of Mo primarily occurred in the primary column in the loading stage where some
153 Mo was eluted with the Fe. Because the yield for the secondary column was typically 80-100%,
154 and matrix was largely absent at this stage, it is likely that the matrix was the complicating factor
155 in the primary column. The breakthrough of Mo in the primary column was mitigated by loading
156 in 1M HF, as opposed to the 0.4M HCl-0.5M HF loading solution used by Nagai and Yokoyama
157 (2014). The partition coefficient between the resin and the acid phase (K_d) for Mo is relatively
158 low in 0.4M HCl-0.5M HF compared to 1M HF ($K_d = 45$ in 0.4M HCl-0.5M HF vs. $K_d = 573$ in
159 1M HF - Nagai and Yokoyama 2014). These authors chose not to use 1M HF due to the high K_d
160 values they measured for Zr and Hf, but we observed that these elements were efficiently
161 separated from Mo in the primary and secondary columns. Although Fe does not occupy anion
162 exchange sites in 1M HF, overloading the column may reduce the tendency of Mo to stick to the
163 resin when Fe is present. The sample sizes loaded onto each primary column were small in order
164 to minimize the effect of Fe on the behavior of Mo on the column. Alternatively, the presence of
165 redox-sensitive Fe or other major elements may change the valence of Mo, resulting in the
166 persistence of mixed valence states in the primary column. One way to mitigate this possible
167 effect is to load the column using H_2O_2 or another oxidizing agent to better control the oxidation
168 state of Mo (and Fe) (e.g., Bandi et al., 1961), but this is yet to be incorporated into methods
169 described here.

170 After the completion of the chromatographic procedures, the purified sample was taken
171 into solution in 2:1 concentrated HNO_3 :HCl and dried to remove resin-derived organics. This
172 step was repeated seven times for each sample. Following the last addition of 2:1 HNO_3 :HCl,

concentrated HCl was added and dried three times to remove traces of HNO₃. Samples were then dissolved in 6M HCl to load onto filaments.

3. Mass Spectrometry

3.1. Sample loading procedure

Samples and standards were loaded onto outgassed Re filaments. The 99.99% pure Re ribbon used for this study was 0.76 mm wide and 0.030 mm thick and was purchased from the *H. Cross Company*. Rhenium filaments were outgassed at 4.2 A for 40 minutes at least 24 hours before loading. A double filament assembly was found to increase signal intensity and duration of the ionization of Mo, compared to single filaments, in agreement with Turnlund et al. (1993) and Giussani et al. (1995). Further, we found that the double filament assembly provided better control of the ionization of Mo than was achieved with single filaments. The ionization of Mo on single filaments typically would reach a point where the growth of the signal and temperature became exponential without manual heating. Soon after, both the signal and temperature would reach a maximum and then the signal would decrease precipitously. The use of an ionization filament and evaporation filament prevented the exponential growth by providing a non-direct heat source, which dramatically improved signal duration and stability. Further, Mo isotopes ionized on single filaments were often fractionated more quickly and more intensely than Mo that was ionized using a double filament assembly. This phenomenon was reflected by the absolute range in the fractionation factor, β , in the exponential law which was used for fractionation correction, discussed below. Over the course of a given analysis, β had an absolute

range up to ~ 0.5 for single filament analyses, but a range of < 0.3 for most double filament analyses, which were also ~ 3.5 times longer in duration.

About 400-1000 ng Mo for samples and 1000 ng Mo for standards were loaded onto the evaporation filament in two ~0.5 µl aliquots, and dried at 0.6 A. Before the first aliquot was dry, the second was added so that distinct reservoirs of Mo did not form. The avoidance of distinct reservoirs was found to improve the ionization of Mo on single filaments in the early stages of the development of these procedures. For samples, once the deposit was dried, the current was increased slowly from 0 to ~2 A until a faint red glow was observed or until the sample transitioned from cloudy white to a colorless or bronze-colored deposit with a black rim. This was done to remove any remaining organics not eliminated by successive additions of 2:1 HNO₃:HCl prior to loading. Care was taken not to heat the filament beyond a dull glow because the sample can burn off. Ten micrograms of 5 µg/µl La(NO₃)₃ in 1M HNO₃ were then added as an electron emitter to reduce the work function of Re and promote the ionization of MoO₃⁻ (e.g., Heumann et al., 1995; Becker and Walker, 2003). The La(NO₃)₃ activator was dried at 0.6 A, but because the solution does not dry completely, the current was then increased from 0 to ~2 A until the solution was observed to boil to dryness. Ten micrograms of La(NO₃)₃ was also added to the ionization filament, using the same drying procedure.

As this loading procedure was developed, variables such as the type of loading solution, the type and amount of activator, the filament assembly, and the placement of activator on the ionization and/or evaporation filaments were systematically varied in order to optimize the ionization of Mo to facilitate stable, long lasting signals. It was found that loading Mo in a chloride form in HCl led to better ionization than when Mo was loaded in HBr or in HNO₃. In agreement with Nagai and Yokoyama (2016), the optimal activator was found to be La(NO₃)₃,

although we also trialed $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{NO}_3)_2$, and a mixture of La and Gd. Nagai and Yokoyama (2016) also found that a ratio of 5:1 La:Mo was most effective. The results of the initial work with single filaments in this study are consistent with this conclusion, though the optimal ratio of La:Mo for double filaments appears to be higher. Initially, 1 μg of Mo was loaded onto the evaporation filament and 5 μg of $\text{La}(\text{NO}_3)_3$ was loaded only onto the ionization filament, but it was found that adding an additional 5 μg of $\text{La}(\text{NO}_3)_3$ on top of the sample or standard improved ionization. However, when this was done, the problem of exponential growth and subsequent rapid decrease of the Mo signals that was observed with single filaments persisted. When the amount of $\text{La}(\text{NO}_3)_3$ was doubled on both the ionization and evaporation filaments, the temperature of the filaments and the ionization of Mo were better controlled, and, thus, more stable and long-lived.

The loading blank using this loading procedure was ~ 1 ng. It was suspected that the Mo was primarily sourced from the Re ribbon, as Mo was not observed in the $\text{La}(\text{NO}_3)_3$ activator when it was examined by ICP-MS. Because Mo was not eliminated by outgassing, and Mo and Re are chemically similar, Mo may be bound in the structure of the Re ribbon. The effect of the loading blank on the measured isotope ratios was examined using different size loads of the gravimetrically prepared spike-standard mixture (400-1000 ng), and was observed to be negligible.

3.2. Instrumental setup and measurement routine

A Thermo-Fisher Triton Plus solid source mass spectrometer was used to measure the Mo isotopic compositions of samples and standards. The instrument was equipped with nine

239 Faraday cups, seven of which were used to measure Mo isotopes. A gain calibration of the
240 Faraday cup detectors was performed each day. Liquid nitrogen was added to a cryopump each
241 day to maintain a stable working vacuum. Using a variable leak valve, high-purity oxygen was
242 bled into the source can to attempt to promote the formation and ionization of MoO_3^+ . The O_2
243 partial pressure was $\sim 1.73 \times 10^{-7}$ mbar above the baseline pressure with liquid nitrogen, such that
244 the total pressure in the source can was typically $2.0 - 2.4 \times 10^{-7}$ mbar. Using single filaments,
245 standards were also analyzed with no O_2 bled into the source, and with total pressures up to $4 \times$
246 10^{-7} mbar. With double filaments, total pressures up to 7.4×10^{-7} mbar were tested. This testing
247 did not definitively show that Mo ionization correlates with the amount of O_2 that is used. For
248 their single filament method, Nagai and Yokoyama (2016) observed that best results were
249 obtained without bleeding O_2 into the source.

250 The heating protocol for the filaments was consistent for all standards and samples.
251 Because of the close proximity of the two filaments, the ionization and evaporation filaments
252 were initially slowly heated to avoid warping the Re ribbon. The ionization filament was heated
253 first at 50 mA/min to 1000 mA, then at 20 mA/min to 1700 mA, and then at 10 mA/min to 1930
254 mA, in order to gently warm the evaporation filament. When the ionization filament reached
255 1700 mA, the evaporation filament was heated at 30 mA/min to 500 mA, then at 20 mA/min.
256 Both filaments were continuously heated, with the rate gradually being decreased during the
257 heating procedure until the ionization and evaporation filaments were heated at 0.1 mA/min and
258 0.1-0.2 mA/min, respectively. Once the ionization filament reached ~ 1930 mA and the
259 evaporation filament reached ~ 630 mA, a mV-level signal was typically registered on the
260 Faraday cups. During the warm-up of samples and standards, the intensity of the signal usually
261 went through periods during which it decreased substantially until the evaporation filament

reached 1200-1500 mA. The peak shapes during this period were also usually asymmetrical, likely due to overlapping peaks from ribbon-derived Mo that was not equilibrated with the sample or standard. After the evaporation filament heating current surpassed 1200-1500 mA and the intensity of the signal on $^{98}\text{Mo}^{16}\text{O}_3^-$ ($m/z \sim 146$) reached 400 mV, the peak shape typically became symmetrical for samples and standards. Once the signal intensity reached 800 mV to 1000 mV on $^{98}\text{Mo}^{16}\text{O}_3^-$, the analyses were started. This signal intensity typically corresponded to a current of 1650-1800 mA and 2080-2150 mA applied to the evaporation filament and ionization filament, respectively. At the beginning of analyses for samples, the signal often decreased for the duration of ~ 50 -100 ratios, but would then stabilize or begin to grow. During a single analysis, lasting ~ 13 h, the typical signal intensity for $^{98}\text{Mo}^{16}\text{O}_3^-$ ranged between 1000 mV and 1600 mV.

Molybdenum was measured as $^x\text{MoO}_3^-$ in a static single-line measurement routine. Seven Faraday cup detectors, which were electronically connected to amplifiers equipped with $10^{11} \Omega$ resistors, were used to collect the $^x\text{MoO}_3^-$ beams, with $^{96}\text{Mo}^{16}\text{O}_3^-$ in the center cup ($m/z \sim 144$ – **Table 2**). An additional Faraday cup (H4) was electronically connected to an amplifier equipped with a $10^{12} \Omega$ resistor. This detector was used to collect the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ beam, which was used for the *in-situ* oxide correction. Later in the development of the analytical method, the L3 cup and a $10^{12} \Omega$ resistor were used to collect the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2$ beam, as discussed below. The amplifiers equipped with $10^{11} \Omega$ resistors were electronically rotated to remove amplifier bias using the virtual amplifier capability of the *Triton*.

Although Zr tends to form positive ions (e.g., Sahoo and Masuda, 1997), and Ru, which forms negative trioxides, does not ionize on Re filaments at the running temperature of Mo (Birmingham et al., 2016), potential minor isobaric interferences from Zr and Ru were

monitored by scanning the low and high masses surrounding the mass range of $^x\text{MoO}_3^-$ (140-148) using the electron multiplier. No interferences were observed corresponding to Zr or Ru. Further, no unaccounted-for signals (those not associated with MoO_2^- and MoO_4^-) were observed to be greater than ~ 10 -200 cps, excluding a ~ 1000 cps peak at mass 155 which we attribute to LaO^- . Therefore, no corrections for isobaric interferences from species in the MoO_3 mass range were applied, excluding oxide corrections.

The procedures for incorporating the use of $10^{12} \Omega$ resistors into the measurement routine were adapted from Koornneef et al. (2013), Liu and Pearson (2014), and Trinquier et al. (2016). Baseline measurement times of 1200 s, with a 30 s settling time, and idle times of 15 s were used. Due to the longer settling time of the $10^{12} \Omega$ resistor, compared to $10^{11} \Omega$ resistors, and the lower signal intensity of the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species (2-4 mV), the optimal time over which the isotope ratio measurements were initially integrated was 67.109 s. Much of the data for the standards and samples were, therefore, collected using two 67.109s integrations such that the isotope ratio measurements were integrated over a total of 134.218 s. It was subsequently determined, however, that this integration time was unnecessarily long, so it was halved and the number of ratios was doubled from standard 35 onward (**Table 3**). No difference in the measured ratios was evident with the long vs. short integration times, but the internal statistics improved slightly with the shorter integration times. Measurements were taken in 50 blocks with 10 cycles/block for a total of 500 ratios. Baselines were measured every 10 blocks and the pilot mass $^{96}\text{Mo}^{16}\text{O}_3$ was centered and automatically focused every 2 blocks.

3.3. Fractionation correction

The isotope ratios were oxide corrected, as described below, and then fractionation corrected for natural and instrumental mass-dependent fractionation using the exponential law (Russell et al., 1978). Instrumental mass-dependent fractionation in thermal ionization is largely due to the preferential evaporation of the lighter isotopes. Traditionally, the normalizing ratio of $^{98}\text{Mo}/^{96}\text{Mo}$ has been used (Dauphas et al., 2002; Burkhardt et al., 2011), where $^{98}\text{Mo}/^{96}\text{Mo} \equiv 1.453171$ (Lu and Masuda, 1994). The exponential law is commonly used to correct a given isotope ratio (R_y^x) by normalizing to a second ratio (R_y^w) of two stable and non-radiogenic isotopes (Russell et al., 1978), where:

$$R_{wy}^{xy} = (R_y^x \times M_y^x)^{-\beta}$$

and R_{wy}^{xy} is the fractionation corrected ratio, R_y^x is the oxide-corrected, measured ratio, M_y^x is the isotope mass ratio of the isotopes being fractionation corrected, and β is the fractionation factor:

$$\beta = \frac{\ln(R_y^w / R_{y \text{ Accepted}}^w)}{\ln(M_y^w)}$$

where R_y^w is the measured, oxide-corrected ratio, $R_{y \text{ Accepted}}^w$ is the accepted value ($^{98}\text{Mo}/^{96}\text{Mo} = 1.453171$), and M_y^w is the mass ratio of the isotopes used for normalization. Because Mo is measured as a trioxide, the molecular mass ratios were used in addition to the isotope mass ratios (e.g., 140/144 vs. 92/96). These results are compared below (**Table 4**). The molecular mass was required to fractionation correct the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species because it has no corresponding isotope mass, as ^{100}Mo is the heaviest Mo isotope.

3.4. Oxide corrections

Because Mo was measured as a trioxide, the intensity measured for each $^x\text{MoO}_3^-$, except the lowest mass $^{92}\text{MoO}_3^-$, must be corrected for isobaric interferences from the heavier oxygen isotope trioxides of lower mass Mo isotopes (**Table 2**). For example, $^{94}\text{Mo}^{16}\text{O}_3^-$ at mass 142 must be corrected for the interference caused by $^{92}\text{Mo}^{18}\text{O}^{16}\text{O}_2^-$ at mass 142. Other oxide species which generate significant interferences are $\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$, $\text{Mo}^{17}\text{O}_2^{16}\text{O}^-$, $\text{Mo}^{18}\text{O}_2^{16}\text{O}^-$, $\text{Mo}^{18}\text{O}^{17}\text{O}^{16}\text{O}^-$, $\text{Mo}^{17}\text{O}_3^-$, and $\text{Mo}^{17}\text{O}_2^{18}\text{O}^-$. Additional species ($\text{Mo}^{17}\text{O}^{18}\text{O}_2^-$ and $\text{Mo}^{18}\text{O}_3^-$) were also formed, but in such low abundance that they do not generate significant interferences (Yin, 1995). The relative abundances of the oxide species were calculated as in Creaser et al. (1991) and Harper and Jacobsen (1996) using the isotopic composition of oxygen.

Oxide corrections commonly have been applied using a single oxygen isotopic composition, such as that from Nier (1950) ($^{17}\text{O}/^{16}\text{O} = 0.0003749$ and $^{18}\text{O}/^{16}\text{O} = 0.0020439$), for every sample or standard. However, systematic variations in the isotope ratios from standard to standard are likely due to variability in the oxygen isotopic composition, as has been the case for other measurements of Mo by N-TIMS (Nagai and Yokoyama, 2016) and for measurements of Os, B, W, and Ru by N-TIMS (e.g., Liu et al. 1998; Luguet et al. 2008; Aggarwal et al., 2009; Touboul and Walker, 2012; Bermingham et al., 2016; Trinquier et al., 2016). Therefore, $10^{12} \Omega$ resistors were installed in order to measure $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$, and later $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2$, from which the oxygen isotope composition can be calculated. The $10^{12} \Omega$ resistor reduces the signal to noise ratio and is most advantageous for signals between ~5 and 20 mV (e.g., Koornneef et al., 2013), which is on the order of the typical signal intensity for $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ (2 - 4 mV). The ratio of the intensities of $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2 / ^{100}\text{Mo}^{16}\text{O}_3$ divided by 3 gives the $^{18}\text{O}/^{16}\text{O}$ ratio. By dividing by 3, the different permutations that ^{18}O can be configured in a trioxide are accounted for (Yin, 1995).

The methods for measuring oxygen *in situ* were adapted from Liu et al. (1998) and Luguet et al. (2008). In agreement with Liu et al. (1998) and Luguet et al. (2008), the $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios were observed to increase over the course of a run, and the average $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratio was found to vary from standard to standard (**Table 3**) and sample to sample. Because of the changing oxygen isotope ratio within analyses, the oxide correction was done for each cycle (referred to as *line by line* oxide correction). Data were also corrected using the oxygen isotopic composition of Nier (1950) (*Nier* oxide correction), the measured oxygen isotopic composition averaged over the entire run (*measured single value* oxide correction), and the line by line oxygen correction with “fractionation corrected” $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ (*line by line (FC)* oxide correction).

For the *measured single value*, *line by line*, and *line by line (FC)* oxide corrections, the data reduction required two-iterations (Luguet et al., 2008). The first was to correct the measured $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2^-$ intensity for the interference from $^{98}\text{Mo}^{18}\text{O}_2^{16}\text{O}^-$ using the oxygen isotopic composition of Nier (1950), termed the first-order oxide correction. The second iteration used the average oxide-corrected $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ intensity for the *measured single value* oxide correction, or the oxide-corrected $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ intensities for each line for the *line by line* oxide correction to calculate the $^{18}\text{O}/^{16}\text{O}$ ratio(s). For the *line by line (FC)* oxide correction, the oxide-corrected $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ was fractionation corrected as described above.

The $^{17}\text{O}/^{16}\text{O}$ was calculated from the $^{18}\text{O}/^{16}\text{O}$ ratio using the slope of the terrestrial fractionation line (TFL, **Fig. 2**). The $^{17}\text{O}/^{16}\text{O}$ was also measured *in situ* from standard 35 onward. However, the signal intensity for the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2$ species was at the limit of the effective range of the $10^{12}\Omega$ resistor (< 2 mV), and the internal precision of these measurements was not as precise as the measurement of $^{18}\text{O}/^{16}\text{O}$. A $10^{13}\Omega$ resistor, with a lower effective range (~ 0.3 -20

mV – Koornneef et al., 2014), may be advantageously employed to measure this species, but this has not yet been tested. Only negligible differences in the external reproducibility of the 14 standards were observed when the oxide correction was done using the calculated vs. measured $^{17}\text{O}/^{16}\text{O}$, although the absolute values of the Mo isotope ratios were different (**Table 5**). To be consistent and to characterize the long-term external reproducibility, only Mo isotope data that was oxide corrected using the calculated $^{17}\text{O}/^{16}\text{O}$ is reported here.

4. Results and discussion

The standard data for all Mo isotopes using the preferred data reduction method is shown in **Table 3** and **Figure 1**. The external reproducibilities of the standards for the $^{97}\text{Mo}/^{96}\text{Mo}$ measurement, which is the Mo isotope ratio that is measured to the best statistical precision, using the various oxide and fractionation correction methods are compared in **Table 4**. The magnitudes of the oxide interferences for each Mo isotope are presented in **Table 6**. The results for spike-standard mixtures and samples are reported in μ notation (**Tables 7** and **8**), which gives the deviation of $^x\text{Mo}/^{96}\text{Mo}$ of a sample relative to the average $^x\text{Mo}/^{96}\text{Mo}$ of the repeated analyses of the *Alfa Aesar* Mo plasma standard over a given period of time, in parts per million. For example, for $\mu^{97}\text{Mo}$:

$$\mu^{97}\text{Mo}_{\text{sample}} = \left[\frac{\left(\text{Mo } \frac{97}{96}\right)_{\text{sample}}}{\left(\text{Mo } \frac{97}{96}\right)_{\text{standard}}} - 1 \right] \times 10^6$$

The best external reproducibility (2SD) for all oxide (except *Nier*, as described below) and fractionation correction methods (molecular vs. isotope mass) was obtained for ^{97}Mo because it is bracketed by the normalizing ratio isotopes.

4.1 Oxide corrections comparison and molecular vs. isotopic fractionation correction

The average $^{18}\text{O}/^{16}\text{O}$ measured for standards was 0.002060 ± 0.000020 (2SD, $n = 48$), which is within uncertainty of the ratio reported by Nagai and Yokoyama (2016) (0.002064 ± 0.000005 , $n = 21$). The long-term external reproducibility of $^{97}\text{Mo}/^{96}\text{Mo}$ using the *Nier*, *measured single value*, *line by line*, and *line by line (FC)* oxide corrections and the molecular mass fractionation correction were ± 66 ppm, 15 ppm, 5.4 ppm, and 23 ppm, respectively (**Table 4**). For the *Nier* oxide correction, ^{95}Mo had the best precision of the Mo isotopes (40 ppm). This effect is likely because the $^{95}\text{MoO}_3^-$ beam has the smallest oxide interference compared to the other Mo isotope beams, especially $^{97}\text{MoO}_3^-$ and $^{100}\text{MoO}_3^-$ (**Table 6**). Therefore, the difference between the *Nier* (1950) and measured oxygen isotopic compositions was magnified with the *Nier* oxide correction on $^{97}\text{MoO}_3^-$, compared to $^{95}\text{MoO}_3^-$. All oxide corrections using the *in situ* measured oxygen isotopic composition resulted in improved precision relative to the *Nier* oxide correction, demonstrating that the variability of the oxygen isotopic composition between analyses adversely affects precision. Further, better precision for $^{97}\text{Mo}/^{96}\text{Mo}$ resulted from using the *line by line* correction vs. the *measured single value* correction, which demonstrates that the variability of the oxygen isotopic composition within a single analysis also affects external precision. The *line by line (FC)* correction exhibits worse external reproducibility for most Mo isotopes, including $^{97}\text{Mo}/^{96}\text{Mo}$, relative to the non-fractionation corrected *line by line* method.

This is likely because the fractionation correction using the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species does not sufficiently account for oxygen isotope fractionation that originates in the tank from which O_2 is bled into the source can, or during formation of the trioxide (Luguet et al., 2008). Therefore, the preferred oxide correction method is the *line by line* correction.

The fractionation correction of Mo using the isotope mass, as opposed to the molecular mass, gives a long-term external reproducibility of 6.7 ppm for $^{97}\text{Mo}/^{96}\text{Mo}$. The reason for the difference between the two methods is unclear; however, the discrepancy may indicate that Mo forms the molecular trioxide before evaporation on the filament fractionates Mo. Thus, using the molecular mass for fractionation correction provides a more accurate correction.

The best external reproducibility for $^{97}\text{Mo}/^{96}\text{Mo}$ was obtained using the *line by line* oxide correction and the fractionation correction using the molecular mass. Using these correction methods, the long-term external reproducibility (2SD) over 13 months of periodic measurement campaigns (**Fig. 1** and **Table 3**, $n = 48$) was ± 107 ppm for ^{92}Mo , 37 ppm for ^{94}Mo , 23 ppm for ^{95}Mo , 5.4 ppm for ^{97}Mo , and 32 ppm for ^{100}Mo . The short-term external reproducibility for one ~2 week period ($n = 8$) was ± 112 , 37, 17, 3.7, and 28 ppm for ^{92}Mo , ^{94}Mo , ^{95}Mo , ^{97}Mo , and ^{100}Mo , respectively. The internal precision (2SE) was typically < 4 ppm for ^{97}Mo . The findings that a line by line oxide correction and fractionation correction using the molecular mass produce the most precise measurements of the Mo isotope ratios is in agreement with Nagai and Yokoyama (2016), who used a single filament assembly and measured both $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ from the $^{100}\text{Mo}^{17}\text{O}^{16}\text{O}_2$ and $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species using $10^{11} \Omega$ resistors. However, the external reproducibility of $^{97}\text{Mo}/^{96}\text{Mo}$ reported in this study is improved by a factor of ~2.4 relative to Nagai and Yokoyama (2016), the precision of $^{100}\text{Mo}/^{96}\text{Mo}$ is roughly equivalent to slightly better on the short term, and the other isotope ratios are less precise (by a factor of ~2.3).

The methods reported here produce more or equivalently precise ratios for the heavy Mo isotopes and less precise ratios for the lighter Mo isotopes, relative to Nagai and Yokoyama (2016). The reason for this is unknown, but may be related to the differences in fractionation of Mo on single vs. double filaments and/or to the measurement vs. calculation of the oxygen isotope ratios. Nagai and Yokoyama (2016) reported an absolute range in the fractionation factor, β , of ~ 0.6 , similar to the range we obtained using single filaments. As noted above, the range in β over the course of an analysis is ~ 0.3 for double filaments. Therefore, if fractionation of Mo isotopes were the dominant cause for the difference in precision between this study and Nagai and Yokoyama (2016), one might expect that more strongly fractionated measurements would have poorer precision on the light Mo isotopes. This is because the light Mo isotopes are evaporated more readily than the heavier isotopes and are farther in atomic mass units from the normalizing ratio, which could cause the fractionation correction to be inadequate. However, this is not observed, likely because Mo fractionation is coupled with the effects of the fractionating oxygen isotope composition, since the trioxides evidently form before Mo is fractionated by evaporation.

The magnitude of the oxide correction is largest on ^{97}Mo and ^{100}Mo , and the contribution of ^{18}O to the total oxide interference signal becomes larger relative to ^{17}O from ^{95}Mo to ^{100}Mo (**Table 6**). Because this study utilized a $10^{12}\Omega$ resistor to measure the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species, the variance of the $^{18}\text{O}/^{16}\text{O}$ ratio may be better accounted for relative to measurements using $10^{11}\Omega$ resistors (Nagai and Yokoyama, 2016). Therefore, the oxide correction applied here for ^{97}Mo and ^{100}Mo , which is larger in magnitude than for other isotopes, may be more accurate, resulting in higher precision for these isotope ratios.

It is possible that some of the low mass Mo isotopes (i.e., ^{95}Mo and ^{96}Mo – **Table 6**) are less accurately corrected, and therefore less precise, because the contribution of species incorporating ^{17}O is larger on these isotopes than on the heavier Mo isotopes. Because ^{96}Mo is affected by this, and because the data are normalized to ^{96}Mo , the effect of an inaccurate correction on ^{96}Mo may be magnified on ^{94}Mo and ^{92}Mo , which are far from the normalizing ratio in terms of atomic mass units. The low mass Mo isotopes are measured less precisely in this study when both the measured $^{17}\text{O}/^{16}\text{O}$ and the calculated $^{17}\text{O}/^{16}\text{O}$ are used for the oxide correction. This may be because of the lower internal precision of the $^{17}\text{O}/^{16}\text{O}$ measurements or that the canonical TFL slope is not the optimal slope by which to calculate $^{17}\text{O}/^{16}\text{O}$ in this system. Bermingham et al. (2016) and Trinquier (2016) found that the oxygen isotopic compositions of RuO_3^- and U^+/UO_2^+ , respectively, do not always fractionate along the canonical TFL slope (i.e., $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O} = 0.52$ or $^{18}\text{O}/^{16}\text{O}$ vs. $^{17}\text{O}/^{16}\text{O} = 0.0954$). Instead, for RuO_3^- , which is run in negative mode like Mo, oxygen fractionation may result from mixing isotopically distinct reservoirs of oxygen from the oxygen tank and from the filament.

To test for this possibility during analysis of Mo isotopes, a ^{97}Mo - ^{100}Mo double spike was measured, such that sufficiently intense signals were generated for the $^{100}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ (2-4 mV) and $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2^-$ species (10-20 mV) using $10^{12}\Omega$ resistors (**Fig. 2**). For the longer of the two analyses, the slope of $^{18}\text{O}/^{16}\text{O}$ vs. $^{17}\text{O}/^{16}\text{O}$ was 0.1128 ± 0.015 (2SD), which is marginally higher than the canonical slope of 0.0954. This indicates that mixing of two isotopically distinct reservoirs of oxygen may result in an inaccurate calculation of $^{17}\text{O}/^{16}\text{O}$ when using the TFL. This effect is evidently minor, however, as the standard data that was oxide corrected using the measured $^{17}\text{O}/^{16}\text{O}$ produces nearly identical precision. Alternatively, the mixing effect may simply not be observed when $^{17}\text{O}/^{16}\text{O}$ is measured using $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ when its signal intensity is

< 2 mV. Because the effective range of $10^{13}\Omega$ resistors includes signals of < 2 mV, future methods using a $10^{13}\Omega$ resistor to measure the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ or $^{100}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ species and a $10^{12}\Omega$ or $10^{13}\Omega$ resistor to measure the $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2^-$ will likely be necessary to optimize the precision on all the Mo isotope ratios. It is also worth noting that the intensity of the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ species is higher than the $^{100}\text{Mo}^{17}\text{O}^{16}\text{O}_2^-$ species, due to the larger abundance of ^{92}Mo , and it requires no first-order oxide correction. Thus, the use of the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2$ species to calculate the $^{17}\text{O}/^{16}\text{O}$ ratio is advantageous.

In addition to the in-run oxygen isotopic compositions of the double spikes, the average measured oxygen isotopic composition of the standards for which $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ were measured is shown in **Figure 2** (UMD mean O). The oxygen isotopic composition of the spikes and the standards are similar to the mean oxygen isotopic composition reported by Nagai and Yokoyama (2016). The UMD mean O is not similar to the Nier (1950) value, or the value recommended by IUPAC. This dissimilarity suggests that the use of the Nier (1950) value for the first-order correction may be inappropriate. However, when the UMD mean O is used for the first-order correction instead, the precision of each ratio and the absolute isotope ratios, excluding $^{92}\text{Mo}/^{96}\text{Mo}$ are within ~1-2 ppm of those calculated with the Nier (1950) value.

4.2 Gravimetrically prepared spike-standard mixture

To test the accuracy of the methods described above, an isotopically-enriched mixture was analyzed in the same way as samples and standards using the *line by line* oxygen correction and molecular mass fractionation correction. The mixture was gravimetrically prepared using a ^{97}Mo -enriched spike (Oak Ridge National Lab) and the *Alfa Aesar* Mo plasma standard. The

concentration of the ^{97}Mo -enriched spike solution was calibrated prior to preparing the mixture. Once the spike and standard were combined in the appropriate proportions, the mixture was allowed to equilibrate on a hotplate at $\sim 120^\circ\text{C}$ overnight. The mixture was then evaporated to dryness and 2:1 $\text{HNO}_3\text{:HCl}$ was added and dried one time. Finally, the mixture was taken into solution in 6M HCl to load onto the filaments. The predicted “anomaly” for the mixture was $\mu^{97}\text{Mo} = +16.7$. Repeated measurements of the spike-standard mixture yielded $\mu^{97}\text{Mo} = +15.4 \pm 2.9$ (2 SD, $n = 7$), which is in excellent agreement with the predicted value (**Table 7, Fig. 1**). The very good reproducibility indicates that over short-term, differences in $\mu^{97}\text{Mo} < 10$ ppm may be resolved.

It was suspected that Mo derived from the Re ribbon resulted in relatively large Mo signals that interfered with Mo signals from the samples and standards. To test for this, five of the analyses of the spike-standard mixture were for loads of ~ 1000 ng and two of the analyses were for loads of ~ 400 ng Mo. The smaller loads showed $\mu^{97}\text{Mo}$ values within uncertainties of the larger loads, so any effect of the loading blank was not reflected in the measurements. Further, any differences in fractionation behavior caused by the different amounts of Mo on the filament were not evident. These data show that the measurement procedure and data reduction provide accurate and precise data that can be routinely used to resolve differences in $\mu^{97}\text{Mo}$ of $\sim 10\text{-}15$ ppm.

4.3 Natural samples

Data for natural samples are shown in **Table 8** and **Figure 3**. One piece of Toluca and Allegan were digested and processed using the methods described above. Two other pieces of

Toluca and two pieces of Skookum were processed during the development of the method using different chemical separation procedures; resulting in variable yields for some samples (see **Table 8** for details).

The Mo yield for the three digestions of Toluca ranged from ~15-55 %. The yield for one Toluca digestion was low (15%), potentially due to loss of Mo during the loading stage of the primary column using the 0.4M HCl-0.5M HF loading solution as described above. The yields for the two digestions of Skookum were similar at around 45%. The $\mu^{97}\text{Mo}$ values obtained for the three digestions of Toluca with variable yields are within uncertainty of one another and the *Alfa Aesar* Mo standard. The $\mu^{97}\text{Mo}$ for Toluca is not within uncertainty of the Mo isotopic composition reported by Yin et al. (2002), but is in good agreement with data reported by Dauphas et al. (2002) and Burkhardt et al. (2011) for meteorites from the IAB group. Likewise, $\mu^{97}\text{Mo}$ for the two digestions of Skookum are in agreement with data reported for irons of the IVB group (Yin et al., 2002; Dauphas et al., 2002; and Burkhardt et al., 2011). These data demonstrate that the analyses are not affected by variable yield or different chromatographic processing. The data for Allegan are in agreement with H5 chondrite data from Burkhardt et al. (2011). This indicates that the methods described above are applicable to metallic and silicate matrices.

5. Conclusions

The procedures for measuring Mo by N-TIMS using the *Thermo-Fisher Triton Plus* are shown to be accurate and precise. The use of a double filament assembly improved signal stability and duration over those achieved using single filaments. Repeated analyses of the *Alfa*

Aesar Specpure® Mo plasma standard using the oxygen isotope composition measured *in situ* and a *line by line* oxide correction yields a long-term external reproducibility of 5.4 ppm for $\mu^{97}\text{Mo}$. The repeated measurement of $\mu^{97}\text{Mo}$ that is in agreement with the predicted value of the gravimetrically prepared ^{97}Mo spike-standard mixture demonstrates the accuracy of the technique and that differences in $\mu^{97}\text{Mo} \geq 10$ ppm can be resolved. The precision for $^{97}\text{Mo}/^{96}\text{Mo}$ was increased by a factor of ~ 3.9 compared to ICP-MS (Burkhardt et al. 2011), and by a factor of ~ 2.4 compared to other TIMS methods (Nagai and Yokoyama, 2016). The analyses of iron meteorite and chondrite samples show that different dissolutions and chromatographic procedures do not produce analytical artifacts related to variable yields, blanks, or matrices.

Acknowledgements

This work was supported by NASA Cosmochemistry grant NNX13AF83G which is gratefully acknowledged. We thank Igor Puchtel and Richard Ash for assistance in the lab, analytical guidance, and discussion. We also thank Anne Trinquier and Greg Archer for helpful discussion of the oxide correction methods.

References

- Aggarwal S. K., Wang B. -S., You C. -F., and Chung C. -H. 2009. Fractionation correction methodology for precise and accurate isotopic analysis of boron by negative thermal ionization mass spectrometry based on BO_2^- ions and using the $^{18}\text{O}/^{16}\text{O}$ ratio from ReO_4^- for internal normalization. *Anal. Chem.* **81**, 7420-7427.
- Anbar A. D., Knab K. A., and Barling J., 2001. Precise determination of mass-dependent variations in the isotopic composition of molybdenum using MC-ICPMS. *Anal. Chem.* **73**, 1425-1431.
- Baertschi P., 1976. Absolute ^{18}O content of standard mean ocean water. *Earth Planet. Sci. Lett.* **31**, 341-344.
- Bandi W. R., Buyok E. G., Lewis L. L., and Melnick L. M., 1961. Anion exchange separation of zirconium, titanium, niobium, tantalum, tungsten, and molybdenum. *Anal. Chem.* **33**, 1275-1278.
- Barling, J., Arnold, G. L., and Anbar, A. D., 2001. Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet. Sc. Lett.* **193**, 447-457.
- Becker, H. and Walker, R. J., 2003. Efficient mixing of the solar nebula from uniform Mo isotopic composition of meteorites. *Nature* **425**, 152-155.
- Bermingham K. R., Walker R. J., and Worsham E. A., 2016. Refinement of high precision Ru isotope analysis using negative thermal ionization mass spectrometry. *Int. J. Mass Spec.* *in press*.
- Burkhardt C., Kleine, T., Oberli F., Pack A., Bourdon B., and Wieler, R., 2011. Molybdenum isotope anomalies in meteorites: Constraints on solar nebula evolution and origin of the Earth. *Earth Planet. Sc. Lett.* **312**, 390-400.
- Burkhardt C., Hin R. C., Kleine T., and Bourdon B., 2014. Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation. *Earth Planet. Sc. Lett.* **391**, 201-211.
- Chatterjee R. and Lassiter J. C., 2015. High precision Os isotopic measurement using N-TIMS: Quantification of various sources of error in $^{186}\text{Os}/^{188}\text{Os}$ measurements. *Chem. Geol.* **396**, 112-123.
- Chu Z. -Y., Li C. -F., Chen Z., Xu J. -J., Di Y. -K., and Guo J. -H., 2015. High-precision measurement of $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$: Isobaric oxide corrections with in-run measured oxygen isotope ratios. *Anal. Chem.* **87**, 8765-8771.
- Creaser R. A., Papanastassiou D. A., and Wasserburg G. J., 1991. Negative thermal ion mass spectrometry of osmium, rhenium and iridium. *Geochim. Cosmochim. Acta* **55**, 397-401.

- Dauphas N., Reisberg L., and Marty B., 2001. Solvent extraction, ion chromatography, and mass spectrometry of molybdenum isotopes. *Anal. Chem.* **73**, 2613-2616.
- Dauphas N., Marty B., and Reisberg L., 2002. Molybdenum evidence for inherited planetary scale isotope heterogeneity of the protosolar nebula. *Astrophys. J.* **565**, 640-644.
- Giussani A., Hansen Ch., Nüsslin F., and Werner E., 1995. Application of thermal ionization mass spectrometry to investigations of molybdenum absorption in humans. *Int. J. Mass Spec. Ion Proc.* **148**, 171-178.
- Harper C. L. and Jacobsen S. B., 1996. Evidence for ^{182}Hf in the early Solar System and constraints on the timescale of terrestrial accretion and core formation. *Geochim. Cosmochim. Acta* **60**, 1311-1153.
- Heumann K. G., Eisenhut S., Gallus S., Hebeda E. H., Nusko R., Vengosh A., and Walczyk T., 1995. Recent developments in thermal ionization mass spectrometric techniques for isotope analysis. *Analyst* **120**, 1291-1299.
- Koornneef J. M., Bouman C., Schwieters J. B., and Davies G. R., 2013. Use of $10^{12}\Omega$ current amplifiers in Sr and Nd isotope analyses by TIMS for application to sub-nanogram samples. *J. Anal. At. Spectrom.* **28**, 749-754.
- Koornneef J. M., Bouman C., Schwieters J. B., and Davies G. R., 2014. Measurement of small ion beams by thermal ionization mass spectrometry using new 10^{13} Ohm resistors. *Anal. Chim. Acta* **819**, 49-55.
- Lee D. C. and Halliday A. N., 1995. Precise determinations of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass spectrometry. *Int. J. Mass. Ion Proc.* **31**, 35-46.
- Li W. -J., Jin D., Chang T. -L., 1988. *Kexue Tinboa* **33**, 1610.
- Liu Y., Huang M., Masuda A., and Inoue M., 1998. High-precision determination of osmium and rhenium isotope ratios by in situ oxygen isotope ratio correction using negative thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **173**, 163-175.
- Liu J. and Pearson D., 2014. Rapid, precise and accurate Os isotope ratio measurements of nanogram to sub-nanogram amounts using multiple Faraday collectors and amplifiers equipped with $10^{12}\Omega$ resistors by N-TIMS. *Chem. Geol.* **363**, 301-311.
- Lu Q. and Masuda A., 1992. High accuracy measurement of isotope ratios of molybdenum in some terrestrial molybdenites. *J. Am. Soc. Mass Spectrom.* **3**, 10-17.
- Lu Q. and Masuda A., 1994. The isotopic composition and atomic weight of molybdenum. *Int. J. Mass Spectrom. Ion Proc.* **130**, 65-72.

- Luguet A., Nowell G. M., and Pearson G., 2008. $^{184}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ measurements by negative thermal ionization mass spectrometry (N-TIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision. *Chem. Geol.* **248**, 342-362.
- Meija J., Coplen T. B., Berglund M., Brand W. A., De Bièvre P., Gröning M., Holden N. E., Irrgeher J., Loss R. D., Walczyk T., and Prohaska T., 2016. Isotopic compositions of the elements 2013 (IUPAC technical report). *Pure Appl. Chem.* **88**, 293-306.
- Nagai Y. and Yokoyama T., 2014. Chemical separation of Mo and W from terrestrial and extraterrestrial samples via anion exchange chromatography. *Analytical Chem.* **86**, 4856-4863.
- Nagai Y. and Yokoyama T., 2016. Molybdenum isotopic analysis by negative thermal ionization mass spectrometry (N-TIMS): Effects on oxygen isotopic composition. *J. Anal. At. Spectrom.* **29**, 1090-1096.
- Nier A. O., 1950. A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium. *Phys. Rev.* **77**, 789-793.
- Pietruszka A. J., Walker R. J., and Candela P. A., 2006. Determination of mass-dependent molybdenum isotopic variations by MC-ICP-MS: An evaluation of matrix effects. *Chem. Geol.* **225**, 121-136.
- Rizo H., Walker R. J., Carlson R. W., Touboul M., Horan M. F., Puchtel I. S., Boyet M., and Rosing M. T., 2016. Early Earth differentiation investigated through ^{142}Nd , ^{182}W , and highly siderophile element abundances in samples from Isua, Greenland. *Geochim. Cosmochim. Acta* **175**, 319-336.
- Russell W. A., Papanastassiou D. A., Tombrello T. A., 1978. Ca isotope fractionation in the Earth and other solar system materials. *Geochim. Cosmochim. Acta* **42**, 1075-1090.
- Sahoo S. K. and Masuda A., 1997. Precise measurement of zirconium isotopes by thermal ionization mass spectrometry. *Chem. Geol.* **141**, 117-126.
- Scheiderich K., Helz G. R., and Walker R. J., 2010. Century-long record of Mo isotopic composition in sediments of a seasonally anoxic estuary (Chesapeake Bay). *Earth. Planet. Sci. Lett.* **289**, 189-197.
- Siebert, C., Nägler, T. F., von Blanckenburg, F., and Kramers, J. D., 2003. Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth Planet. Sc. Lett.* **211**, 159-171.
- Touboul M. and Walker R. J., 2012. High precision tungsten isotope measurement by thermal ionization mass spectrometry. *Int. J. Mass Spec.* **309**, 109-117.

- Trinquier A., 2016. Fractionation of oxygen isotopes by thermal ionization mass spectrometry inferred from simultaneous measurement of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios and implications for the ^{182}Hf - ^{182}W systematics. *Anal. Chem.* In Press. DOI: 10.1021/acs.analchem.6b01101
- Trinquier A., Touboul M., and Walker R. J., 2016. High-precision tungsten isotopic analysis by multicollection negative thermal ionization mass spectrometry based on simultaneous measurement of W and $^{18}\text{O}/^{16}\text{O}$ isotope ratios for accurate fractionation correction. *Anal. Chem.* **88**, 1542-1546.
- Turnlund J. R., Keyes W. R., and Peiffer G. L., 1993. Isotope ratios of molybdenum determined by thermal ionization mass spectrometry for stable isotope studies of molybdenum metabolism in humans. *Anal. Chem.* **65**, 1717-1722.
- Wieser M. E. and De Laeter J. R., 2000. Thermal ionization mass spectrometry of molybdenum isotopes. *Int. J. Mass Spec.* **197**, 253-261.
- Wieser M. E. and De Laeter J. R., 2009. Molybdenum isotope mass fractionation in iron meteorites. *Int. J. Mass Spec.* **286**, 98-103.
- Wieser M. E., De Laeter J. R., and Varner M. D., 2007. Isotope fractionation studies of molybdenum. *Int. J. Mass Spec.* **265**, 40-48.
- Yin Q. Z., 1995. N-TIMS technique for the Re-Os and Ru isotopic systems and its application to selected geochemical and cosmochemical problems. PhD thesis, University of Mainz and Max Planck Institute for Chemistry.
- Yin, Q. Z., Jacobsen, S. B., and Yamashita, K., 2002. Diverse supernova sources of pre-solar material inferred from molybdenum isotopes in meteorites. *Nature* **415**, 881-883.

Fig. 1. The $\mu^{97}\text{Mo}$ for repeated analyses of the *Alfa Aesar* Mo plasma standard and the gravimetrically prepared spike-standard mixture. The collection period was 13 months. Data were reduced using *in situ* $^{18}\text{O}/^{16}\text{O}$ measurements and the *line by line* oxide correction. Data were fractionation corrected with $^{98}\text{Mo}/^{96}\text{Mo} = 1.453171$ (Lu and Masuda, 1994) and using the molecular mass instead of the isotope mass as described in text. Dotted lines represent two standard deviations of the analyses (2SD). For standards, $2\text{SD} = \pm 5.4 \text{ ppm}$ and for spike standard mixes, $2\text{SD} = \pm 2.9 \text{ ppm}$. The spike-standard mixture was gravimetrically predicted to have a $\mu^{97}\text{Mo}$ value of + 16.7 ppm. This compares favorably with the measured ratio of $\mu^{97}\text{Mo} = + 15.4 \pm 2.9$. Error bars for the individual analyses are the internal standard error of the mean (2SE).

740

741

742 Fig. 2. In-run $^{18}\text{O}/^{16}\text{O}$ vs. $^{17}\text{O}/^{16}\text{O}$ measured *in situ* for two Mo double spike analyses using the
 743 $^{100}\text{Mo}^{17}\text{O}^{16}\text{O}_2$ and $^{100}\text{Mo}^{18}\text{O}^{16}\text{O}_2$ species and two $10^{12}\Omega$ resistors. The average $^{18}\text{O}/^{16}\text{O}$ and
 744 $^{17}\text{O}/^{16}\text{O}$ measured *in situ* for 14 standards, where $^{17}\text{O}/^{16}\text{O}$ was measured using the $^{92}\text{Mo}^{17}\text{O}^{16}\text{O}_2$
 745 species and a $10^{12}\Omega$ resistor, is shown as the black diamond ($^{18}\text{O}/^{16}\text{O} = 0.002055$ and $^{17}\text{O}/^{16}\text{O} =$
 746 0.0003871 – **Table 5**). Also shown are the oxygen isotopic compositions of Nier (1950), the “best
 747 measured” value reported by IAPC (Meija et al., 2015; citing Baertschi, 1976 and Li et al.,
 748 1988), and the “Mean O” value reported by Nagai and Yokoyama (2016). The black line
 749 represents the terrestrial fractionation line, which is forced through the UMD mean O value and
 750 is calculated using the canonical slope of 0.52.

751

Fig. 3. The $\mu^{97}\text{Mo}$ for the Toluca and Skookum iron meteorites, and the Allegan chondrite, compared to some literature values. For Toluca and Skookum, uncertainties are the 2SD of the separate analyses. For Allegan, the uncertainty is the 2SD external reproducibility of the standards, represented also by the grey bar (± 5.4 ppm). The $\mu^{97}\text{Mo}$ for all three samples are in good agreement with data from meteorites of the same groups (Burkhardt et al., 2011). The datum for Toluca is not within uncertainty of that of Yin et al. (2002).

Tables

Table 1. The anion exchange chromatographic procedures for the separation and purification of Mo.

Acid	Volume per column (ml)	Step
Primary column - 1-8 <i>Biorad</i> columns filled with 1.4 ml AG 1-X8 200-400 mesh		
6M HCl	10	Cleaning
Milli-Q H ₂ O	10	Cleaning
6M HNO ₃ – 3M HF	10	Cleaning
Milli-Q H ₂ O	5	Cleaning
1M HF	3	Equilibration
1M HF	1	Load sample
1M HF	3	Rinse (Fe, matrix)
9M HCl – 0.05M HF	3 + 3	Rinse (Ru, Zr, Ti, Hf)
9M HCl – 1M HF	3 + 3 + 3 + 3	Rinse (W, Re)
Milli-Q H ₂ O	1.5	Remove HCl
6M HNO ₃ – 3M HF	10	Collect Mo
Secondary column - 1 <i>Teflon</i> [®] column filled with ~ 0.3 ml AG 1-X8 200-400 mesh		
0.01 M HCl	4	Cleaning
1M HCl	8	Cleaning
6M HCl	4	Cleaning
6M HCl	0.5	Load sample
6M HCl	4	Rinse remaining matrix
0.01M HCl – 0.1M HF	1	Rinse remaining matrix
0.01M HCl	3	Rinse remaining matrix
1M HCl	12.5	Collect Mo

767

768

769 Table 2. Faraday cup configuration for Mo analyses. The resistors equipped to the amplifiers for
 770 each cup and the trioxide interferences are also shown.

	L4	L3 ^c	L2	L1	C	H1	H2	H3	H4
Resistor (Ω) ^a	10 ¹¹	10 ¹²	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹¹	10 ¹²
Species	⁹² Mo ¹⁶ O ₃	⁹² Mo ¹⁷ O ¹⁶ O ₂	⁹⁴ Mo ¹⁶ O ₃	⁹⁵ Mo ¹⁶ O ₃	⁹⁶ Mo ¹⁶ O ₃	⁹⁷ Mo ¹⁶ O ₃	⁹⁸ Mo ¹⁶ O ₃	¹⁰⁰ Mo ¹⁶ O ₃	¹⁰⁰ Mo ¹⁸ O ¹⁶ O ₂
Interfering Trioxyde ^b			⁹² Mo ⁵⁰ O ₃	⁹² Mo ⁵¹ O ₃ ⁹⁴ Mo ⁴⁹ O ₃	⁹² Mo ⁵² O ₃ ⁹⁴ Mo ⁵⁰ O ₃ ⁹⁵ Mo ⁴⁹ O ₃	⁹⁴ Mo ⁵¹ O ₃ ⁹⁵ Mo ⁵⁰ O ₃ ⁹⁶ Mo ⁴⁹ O ₃	⁹⁴ Mo ⁵² O ₃ ⁹⁵ Mo ⁵¹ O ₃ ⁹⁶ Mo ⁵⁰ O ₃ ⁹⁷ Mo ⁴⁹ O ₃	⁹⁶ Mo ⁵² O ₃ ⁹⁷ Mo ⁵¹ O ₃ ⁹⁸ Mo ⁵⁰ O ₃	⁹⁸ Mo ⁵² O ₃

771 ^aOnly amplifiers equipped with 10¹¹ Ω resistors were rotated during analyses to remove amplifier
 772 bias.

773 ^bTrioxyde masses are the total mass of the O₃. For instance, ⁹²Mo⁵⁰O₃ is composed of both
 774 ⁹²Mo¹⁸O¹⁶O₂ and ⁹²Mo¹⁷O¹⁶O.

775 ^cL3 was used to measure ⁹²Mo¹⁷O¹⁶O₂ from standard 35 onward, but was not used to calculate
 776 ¹⁷O/¹⁶O due to the lower internal precision, relative to the ¹⁸O/¹⁶O measurement.

777

Table 3. Molybdenum isotopic compositions of repeated analyses of the *Alfa Aesar Specpure®* Mo plasma standard using the *in situ line by line* oxide correction and fractionation correction using the molecular trioxide mass and $^{98}\text{Mo}/^{96}\text{Mo}$. Measured, not fractionation corrected $^{18}\text{O}/^{16}\text{O}$ ratios, averaged over the course of each analysis, are also shown. The 2SE is given in ppm.

Standard #	$^{92}\text{Mo}/^{96}\text{Mo}$	2SE	$^{94}\text{Mo}/^{96}\text{Mo}$	2SE	$^{95}\text{Mo}/^{96}\text{Mo}$	2SE	$^{97}\text{Mo}/^{96}\text{Mo}$	2SE	$^{100}\text{Mo}/^{96}\text{Mo}$	2SE	$^{18}\text{O}/^{16}\text{O}$
1	0.883168	9.5	0.552441	5.9	0.953191	4.5	0.573952	4.2	0.581460	6.6	0.002067
2	0.883225	9.3	0.552453	6.8	0.953205	3.9	0.573950	3.4	0.581472	5.8	0.002072
3	0.883106	6.6	0.552430	4.4	0.953188	2.9	0.573955	2.2	0.581446	3.7	0.002063
4	0.883189	20	0.552443	8.1	0.953197	5.0	0.573953	3.6	0.581465	8.4	0.002074
5	0.883174	8.2	0.552441	4.7	0.953198	3.9	0.573954	3.0	0.581452	4.5	0.002060
6	0.883169	6.3	0.552441	3.9	0.953193	3.0	0.573950	2.3	0.581459	3.5	0.002068
7	0.883211	6.8	0.552450	3.7	0.953206	3.3	0.573951	2.7	0.581468	4.6	0.002066
8	0.883176	11	0.552443	5.0	0.953196	3.3	0.573953	2.6	0.581457	4.8	0.002060
9	0.883189	18	0.552447	8.5	0.953201	5.5	0.573952	3.9	0.581462	8.1	0.002055
10	0.883195	5.6	0.552449	3.3	0.953203	2.8	0.573954	2.2	0.581460	3.4	0.002054
11	0.883135	8.9	0.552437	4.5	0.953195	2.9	0.573953	2.1	0.581450	3.9	0.002058
12	0.883148	8.7	0.552438	5.3	0.953192	3.7	0.573953	2.6	0.581456	4.6	0.002084
13	0.883129	12	0.552434	7.8	0.953185	4.9	0.573953	3.7	0.581455	6.8	0.002089
14	0.883113	7.6	0.552432	5.3	0.953188	3.7	0.573953	2.9	0.581451	4.8	0.002071
15	0.883262	8.9	0.552461	5.4	0.953206	3.9	0.573949	3.5	0.581481	5.0	0.002044
16	0.883197	7.6	0.552448	5.1	0.953198	3.6	0.573952	5.4	0.581473	5.0	0.002062
17	0.883164	10	0.552440	6.5	0.953191	3.9	0.573953	3.8	0.581468	5.8	0.002078
18	0.883180	6.7	0.552443	4.8	0.953190	3.2	0.573952	2.7	0.581469	4.1	0.002064
19	0.883238	9.9	0.552455	5.5	0.953203	4.1	0.573952	2.8	0.581478	5.8	0.002069
20	0.883211	8.7	0.552449	6.4	0.953192	4.7	0.573948	3.3	0.581479	5.9	0.002052
21	0.883186	12	0.552438	7.6	0.953191	6.3	0.573951	5.0	0.581476	7.5	0.002056
22	0.883189	6.9	0.552443	4.8	0.953194	3.6	0.573949	3.1	0.581471	4.3	0.002072
23	0.883194	9.5	0.552441	6.4	0.953191	4.1	0.573950	3.4	0.581476	5.5	0.002053
24	0.883135	7.6	0.552432	5.1	0.953186	3.5	0.573954	3.1	0.581465	5.1	0.002055
25	0.883182	12	0.552444	9.4	0.953186	5.8	0.573952	5.5	0.581479	9.5	0.002058
26	0.883154	5.0	0.552435	3.9	0.953186	2.5	0.573952	2.4	0.581471	3.2	0.002062
27	0.883189	7.5	0.552446	4.1	0.953197	4.1	0.573954	3.7	0.581475	5.2	0.002043
28	0.883138	9.8	0.552434	5.4	0.953188	4.2	0.573952	3.0	0.581465	5.1	0.002056
29	0.883140	6.4	0.552436	3.6	0.953187	3.8	0.573953	2.9	0.581465	4.5	0.002057
30	0.883108	7.0	0.552427	4.1	0.953177	3.1	0.573952	2.4	0.581459	4.2	0.002067
31	0.883093	8.0	0.552424	4.4	0.953175	2.9	0.573954	2.5	0.581460	4.3	0.002064
32	0.883149	8.3	0.552438	5.7	0.953185	4.3	0.573953	3.1	0.581468	5.1	0.002047
33	0.883218	9.9	0.552450	7.4	0.953200	4.5	0.573951	3.9	0.581473	6.4	0.002041
34	0.883100	6.7	0.552428	4.9	0.953176	3.3	0.573954	2.5	0.581461	4.2	0.002059
35	0.883112	5.0	0.552430	3.4	0.953182	2.4	0.573953	1.9	0.581454	3.1	0.002055
36	0.883074	4.7	0.552420	3.3	0.953172	2.4	0.573954	1.8	0.581454	3.1	0.002055
37	0.883200	5.4	0.552444	3.8	0.953189	2.8	0.573951	2.2	0.581475	3.3	0.002056
38	0.883158	5.5	0.552437	3.6	0.953183	2.5	0.573953	2.0	0.581469	3.1	0.002059
39	0.883170	4.9	0.552439	3.8	0.953184	2.5	0.573953	2.0	0.581468	3.4	0.002054
40	0.883155	5.1	0.552437	3.3	0.953184	2.3	0.573952	1.8	0.581465	3.1	0.002053
41	0.883066	5.1	0.552418	3.5	0.953169	2.5	0.573953	2.0	0.581453	3.2	0.002061
42	0.883089	5.8	0.552422	3.8	0.953167	2.5	0.573952	1.8	0.581462	3.3	0.002058
43	0.883090	5.9	0.552424	4.0	0.953170	2.8	0.573951	2.5	0.581452	3.7	0.002056
44	0.883102	5.6	0.552424	4.0	0.953170	2.9	0.573951	2.2	0.581458	3.8	0.002060
45	0.883055	6.6	0.552413	4.6	0.953163	3.5	0.573951	2.9	0.581451	4.4	0.002059
46	0.883172	7.4	0.552437	5.6	0.953181	3.6	0.573950	2.7	0.581475	4.9	0.002049
47	0.883194	5.3	0.552442	3.6	0.953186	2.8	0.573950	2.2	0.581480	3.2	0.002042
48	0.883138	7.1	0.552432	4.6	0.953174	3.2	0.573950	2.3	0.581469	4.0	0.002055
Average	0.883157		0.552438		0.953188		0.573952		0.581465		0.002060
2SD (ppm)	107		37		23		5.4		32		0.96%

784 Table 4. Comparison of the various data reduction methods. The best external precision (2SD) is
785 obtained for the $^{97}\text{Mo}/^{96}\text{Mo}$ ratio using the *line by line* oxide correction and the molecular mass
786 fractionation correction.

Fractionation correction	Oxygen correction	External Precision (ppm)				
		$^{92}\text{Mo}/^{96}\text{Mo}$	$^{94}\text{Mo}/^{96}\text{Mo}$	$^{95}\text{Mo}/^{96}\text{Mo}$	$^{97}\text{Mo}/^{96}\text{Mo}$	$^{100}\text{Mo}/^{96}\text{Mo}$
Isotope mass	Nier	175	73	45	67	90
	Measured single value	169	50	34	16	42
	Line by line	166	56	30	6.7	45
	Line by line (FC)	158	76	21	20	76
Molecular mass	Nier	117	63	40	66	87
	Measured single value	110	31	28	15	35
	Line by line	107	37	23	5.4	32
	Line by line (FC)	100	54	17	23	55

787

Table 5. Molybdenum isotopic compositions of standards 35-48, where the oxide corrections were done using the measured $^{17}\text{O}/^{16}\text{O}$, as opposed to the $^{17}\text{O}/^{16}\text{O}$ calculated using the TFL. Also shown are the measured $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$, averaged over the course of the analysis and not fractionation corrected.

Standard #	$^{92}\text{Mo}/^{96}\text{Mo}$	2SE	$^{94}\text{Mo}/^{96}\text{Mo}$	2SE	$^{95}\text{Mo}/^{96}\text{Mo}$	2SE	$^{97}\text{Mo}/^{96}\text{Mo}$	2SE	$^{100}\text{Mo}/^{96}\text{Mo}$	2SE	$^{17}\text{O}/^{16}\text{O}$	$^{18}\text{O}/^{16}\text{O}$
Measured $^{17}\text{O}/^{16}\text{O}$												
35	0.883175	5.1	0.552459	3.4	0.953203	2.4	0.573932	1.9	0.581451	3.1	0.0003872	0.002055
36	0.883136	4.7	0.552448	3.3	0.953193	2.4	0.573934	1.8	0.581451	3.1	0.0003871	0.002055
37	0.883262	5.4	0.552472	3.8	0.953210	2.8	0.573930	2.2	0.581472	3.3	0.0003870	0.002056
38	0.883219	5.6	0.552465	3.7	0.953203	2.5	0.573932	2.0	0.581466	3.1	0.0003872	0.002059
39	0.883231	4.9	0.552467	3.8	0.953205	2.5	0.573933	2.0	0.581465	3.4	0.0003869	0.002054
40	0.883218	5.1	0.552466	3.3	0.953205	2.3	0.573932	1.8	0.581462	3.1	0.0003869	0.002053
41	0.883128	5.1	0.552446	3.5	0.953190	2.5	0.573933	2.0	0.581450	3.2	0.0003876	0.002061
42	0.883152	5.9	0.552450	3.8	0.953188	2.5	0.573931	1.8	0.581459	3.3	0.0003875	0.002058
43	0.883151	5.9	0.552452	4.0	0.953191	2.8	0.573930	2.5	0.581449	3.7	0.0003872	0.002056
44	0.883163	5.6	0.552452	4.0	0.953190	2.8	0.573930	2.3	0.581455	3.8	0.0003875	0.002060
45	0.883117	6.6	0.552441	4.6	0.953184	3.4	0.573930	2.8	0.581448	4.4	0.0003875	0.002059
46	0.883233	7.5	0.552465	5.6	0.953201	3.7	0.573930	2.7	0.581471	4.9	0.0003865	0.002049
47	0.883256	5.3	0.552470	3.6	0.953207	2.8	0.573929	2.3	0.581476	3.2	0.0003858	0.002042
48	0.883201	7.2	0.552461	4.6	0.953195	3.2	0.573929	2.3	0.581466	4.0	0.0003874	0.002055
Average	0.883189		0.552458		0.953198		0.573931		0.581460		0.0003871	0.002055
2SD (ppm)	110		36		17		5.2		33		0.25%	0.49%
TFL calculated $^{17}\text{O}/^{16}\text{O}$												
Average	0.883127		0.552430		0.953177		0.573952		0.581463			
2SD (ppm)	111		36		18		5.2		33			

Table 6. The magnitude of the oxide interference corrections for each Mo isotope, given as percent relative to the oxide corrected signal intensity. Also shown are the percentages of the most abundant ^{17}O - and ^{18}O -bearing species relative to the total oxide interference signal. Other species incorporating ^{17}O and ^{18}O are minor and not taken into account for these calculations, such that the totals are generally not 100%.

	94	95	96	97	98	100
Total oxide signal (% relative to oxide corrected signal)	0.99	0.066	0.45	1.2	0.47	1.5
Total $^{17}\text{O}^{16}\text{O}_2$ signal (%)	-	99.3	23.9	16.1	9.5	-
Total $^{18}\text{O}^{16}\text{O}_2$ signal (%)	100.0	-	75.9	83.9	90.4	99.8
Total	100.0	99.3	99.7	100.0	99.9	99.8

802

803

804

805 Table 7. $\mu^{97}\text{Mo}$ values for the spike-
806 standard mixes. Mixes 6 and 7 were
807 analyzed with only 400 ng of Mo.

	$\mu^{97}\text{Mo}$	2SE
16.7 ppm mix 1	16.4	2.0
16.7 ppm mix 2	13.8	2.3
16.7 ppm mix 3	16.5	1.9
16.7 ppm mix 4	15.4	1.8
16.7 ppm mix 5	17.5	2.2
16.7 ppm mix 6	13.9	3.1
16.7 ppm mix 7	14.3	2.0
Average	15.4	2.9 (2SD)

808

809

Table 8. Molybdenum isotopic compositions of natural samples (in ppm). Different pieces of the same meteorite are numbered and different analyses of the same solution from the same piece of meteorite are numbered and lettered.

Samples ^a	$\mu^{92}\text{Mo}$	2SD	$\mu^{94}\text{Mo}$	2SD	$\mu^{95}\text{Mo}$	2SD	$\mu^{97}\text{Mo}$	2SD	$\mu^{100}\text{Mo}$	2SD
Toluca 1	-15	111	2.6	36	-9.7	18	2.0	5	3.2	33
Toluca 2	12	90	9.1	29	-5.9	15	1.3	6	0.8	24
Toluca 3	30	92	19	29	-3.9	14	0.02	5	0.4	34
Toluca mean	9	45	10	17	-6.5	6	1.1	2	1.46	3.0
Skookum 1a	302	92	173	29	116	14	51	5	119	34
Skookum 1b	278	92	170	29	114	14	55	5	107	34
Skookum 2a	267	92	164	29	109	14	54	5	109	34
Skookum 2b	146	90	123	29	97	15	57	6	63	24
Skookum mean	248	139	157	46	109	17	54	5	100	50
Allegan	43	111	52	36	22	18	19	5.2	21	33

^aToluca 1 and Allegan were processed using the procedures described here. Toluca 2 and Skookum 2 were digested and processed using the same methods, with the exception that these pieces were loaded onto the primary column using 0.4M HCl-0.5M HF as the loading solution. Toluca 3 was obtained as a byproduct of the chemistry used to separate and purify W (Touboul and Walker, 2012), and was purified using the secondary anion column described here. Skookum 1 was processed using a different primary anion column that was more similar to the secondary column (Pietruszka et al., 2006).