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Isotope fractionation studies of molybdenum

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Abstract

Mass spectrometric studies of the isotopic composition of molybdenum have become an active area of research in stable isotope geochemistry, biogeochemistry and cosmochemistry. The redox chemistry of Mo, together with its proclivity for covalent bonding, indicates its importance in isotope fractionation studies such as palaeoceanography. The measurement of the magnitude of isotope fractionation of Mo in natural systems is a challenging task, in that natural fractionation has to be carefully distinguished from chemical and instrumental isotope fractionation. An ion exchange chemical separation procedure has been developed with high efficiency and low blank, to ensure that the isobaric elements Zr and Ru are removed from the samples before mass spectrometric analysis. The isotope fractionation resulting from this procedure is 0.14‰ per u. The isotopic composition of Mo of a Laboratory Standard has been measured by positive and negative thermal ionization mass spectrometry (P-TIMS and N-TIMS, respectively), to give an isotope fractionation of 6.4‰ and 0.5‰ per u, respectively, with respect to the absolute isotope abundances of Mo. In both cases the lighter isotopes are enhanced with respect to the heavier isotopes. An ascorbic acid activator has enabled the sensitivity of P-TIMS to be improved as compared to traditional methods. The same experiment was repeated using a multiple collector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) to give an isotope fractionation of approximately 17.0‰ per u. In this case the heavier isotopes are enhanced with respect to the lighter isotopes. The strengths and weaknesses of these three mass spectrometric techniques are evaluated. We conclude that MC-ICP-MS is the optimum mass spectrometric method for accurately measuring the isotope fractionation of Mo in natural materials, provided chemical and instrumental isotope fractionation can be resolved from naturally induced isotope fractionation. There is an urgent need for an internationally accepted calibrated reference material to be developed. Our Laboratory Standard has recently been calibrated at Curtin University by measurements of gravimetric mixtures of two enriched isotopes of Mo, to obtain the absolute isotope abundances of Mo. This Laboratory Standard can be made available to those laboratories in which isotopic studies of Mo are executed, to enable meaningful inter-laboratory comparisons to be conducted.

Keywords: Double spiking; Ion exchange; Isotope fractionation; Mass spectrometry; Molybdenum

1. Introduction

Molybdenum has an atomic number of 42 and possesses seven stable isotopes, spanning a mass range from 92 to 100 (see Fig. 1). Isotopes of Mo are synthesized by the p-process (^{92}Mo and ^{94}Mo), the s-only process (^{96}Mo), the r-only process (^{100}Mo) and by a combination of the s- and r- processes (^{95}Mo, ^{97}Mo, and ^{98}Mo) [1]. Molybdenum covers a mass range of approximately 8% and its isotopes are of similar abundance. It is therefore an element which lends itself to mass spectrometric analysis, not only for nucleosynthetic studies, but also for isotope fractionation effects.

Mass spectrometric studies of the isotopic composition of Mo have a long and somewhat checquered history. As early as 1962, significant variations in the isotope fractionation of Mo in some iron meteorites were reported [2], but these findings were refuted by Wetherill [3] who used the double spike technique to distinguish instrumental isotope fractionation from that produced by nature in iron meteorites. There has been an increasing interest in isotope fractionation studies of "non-traditional isotopes," particularly the transition metals (Fe, Ni, Cu, Zn and Mo) because of their potential value in biogeochemical studies. If such fractionation effects are associated with the metabolic use of these elements, they could provide biosignatures preserved in the geological record [4]. Molybdenum isotope fractionation studies have the potential to be an important geochemical tool in ore genesis studies, and in quantifying redox conditions in palaeo-environments, particularly for those experiments that

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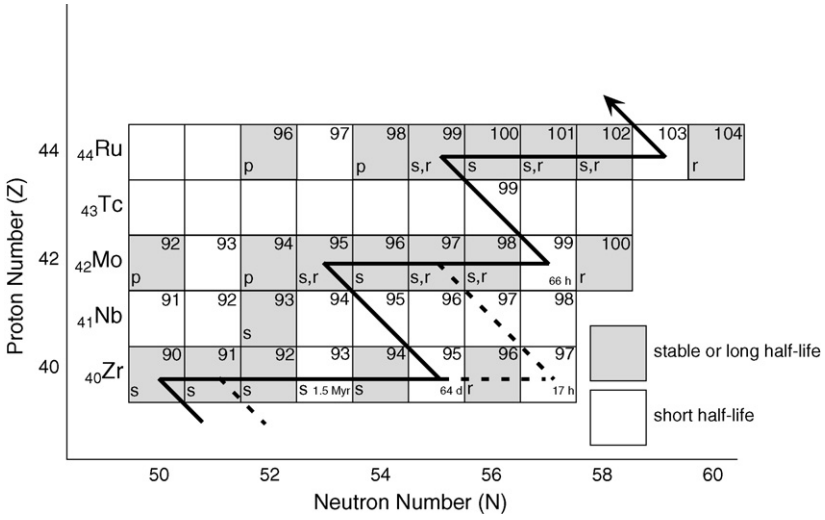

Fig. 1. The chart of the nuclides in the mass region of Mo, showing the isobaric isotopes ^{92,94,96}Zr and ^{96,98,100}Ru. The s-process neutron capture path is the "zig–zag" line which transects most of the stable isotopes, whilst the s-process, p-process and r-process produced isotopes are as indicated.

involve biogeochemical reactions [5]. Mo is an essential enzyme cofactor in most organisms, and hence is important in studies of nitrogen fixation and reduction, and in sulfite oxidation.

The primary objective of this paper is to identify the magnitude of both chemical and instrumental isotope fractionation for Mo, and examine the isotope fractionation produced by P-TIMS, N-TIMS and MC-ICP-MS in a Laboratory Standard. The strengths and weaknesses of these three mass spectrometric techniques will be evaluated with respect to the measurement of natural isotope fractionation. The importance of a calibrated, internationally accepted, isotopic reference material for Mo is discussed, with respect to normalization and inter-laboratory comparison purposes.

2. Experimental procedures

2.1. Laboratory Standard

Currently, there is no internationally accepted isotopically calibrated reference material (ICRM) for Mo, and thus stringent inter-laboratory comparisons cannot be made. This laboratory has adopted a 99.993% pure metal rod (Johnson–Matthey Chemicals Ltd. JMC 726, Laboratory No. S-8555) as our Laboratory Standard and we are prepared to distribute samples of this specpure material to other laboratories until an ICRM is available. Details of the preparation of the Laboratory Standard working solution are given in [6].

2.2. Chemical isotope fractionation

The success of the mass spectrometric analysis depends, to a significant extent, on the purity of the Mo sample that is to be analysed, irrespective of the mode of mass spectrometric analysis. It is therefore essential that the isobaric elements Zr and Ru, as well as other elements, such as Fe and Mn, are effectively separated from Mo in the chemical separation procedure. The efficiency of the chemical separation process must be kept as high as possible, and terrestrial contamination must be minimized to obtain a low blank. This implies the necessity of a high quality clean-room equipped with HEPA—filtered air, and the availability of high purity water, acids, ion exchange resins and utensils used in the separation process. An ion exchange separation procedure has been developed in which Mo was eluted in 0.5 M HCl from an anion exchange column whilst Zr, Ru and Mn are retained. A second, smaller cation exchange column was used to eliminate other impurities, such as Fe. Molybdenum was eluted in 0.5 M HCl in a form which was suitable for mass spectrometric analysis. The extraction efficiency for the entire separation process was $93 \pm 3\%$ and the procedural blank 5 ± 2 ng Mo, as measured by isotope dilution mass spectrometry (IDMS). This procedure can be used to separate Mo from a variety of natural materials (e.g., [7], in which full details of the extraction procedure are given).

It is often assumed that, provided the efficiency of the extraction procedure is high, isotope fractionation induced by the chemical procedure is negligible. However, each element must be examined on an individual basis, with the specific chemical separation procedure in use. In the case of Mo, it has been shown that the isotopes are isotopically fractionated by eluting various fractions from an anion exchange column [8]. The earliest fraction is enriched in the heavy isotopes by approximately 0.5‰ per u, whereas the final fraction is enriched in the lighter isotopes by approximately 1‰ per u [8]. It has also been shown that isotope fractionation of similar magnitude occurs in eluting Ca from a cation ion exchange column [9]. The underlying mechanism causing this fractionation is complex, but may relate to equilibrium isotope fractionation between dissolved and resin-bound complexes [8]. The chemical separation procedure described above is a two step ion exchange process involving both anion and cation resins. It is therefore essential to measure the isotope fractionation of Mo for the complete separation procedure.

In order to evaluate the magnitude of possible isotope fractionation introduced by the chemical separation procedure, three

Table 1
The isotope abundance ratios of three separate aliquots of the Laboratory Standard subjected to ion exchange chemistry, compared to the isotope abundance ratios of the unprocessed Laboratory Standard expressed as permil deviations

	$\delta^{92}Mo/^{95}Mo$	$\delta^{94}Mo/^{95}Mo$	$\delta^{96}Mo/^{95}Mo$	$\delta^{97}Mo/^{95}Mo$	$\delta^{98}Mo/^{95}Mo$	$\delta^{100}Mo/^{95}Mo$
Aliquot #1	0.6(4)	0.1(3)	−0.2(2)	−0.4(3)	−0.6(4)	−1.2(6)
Aliquot #2	0.7(4)	0.2(3)	−0.2(2)	−0.4(3)	−0.6(4)	−1.4(6)
Aliquot #3	0.1(4)	−0.1(3)	0.0(2)	−0.1(3)	−0.1(4)	−0.5(6)
Mean	0.5(6)	0.1(2)	−0.1(2)	−0.3(4)	−0.4(6)	−1(1)

The uncertainties (in parentheses), for the individual aliquots, are the standard errors at the 95% confidence level ($n = 200$), and the uncertainties for the averages of the three sets of permil deviations are the standard deviations at the 95% confidence level. The mean deviation of the three sets of Mo isotope ratios compared to the unprocessed Laboratory Standard is 0.14‰ per u.

separate aliquots of the Laboratory Standard were subjected to the ion exchange procedure described above. The Mo extracted from the complete ion exchange procedure were collected separately and evaporated to dryness. The three separated Mo samples were then re-dissolved in sufficient quantities of 2 M HNO_3 to make three solutions with a Mo concentration of approximately 200 ppb, which were then analysed by MC-ICP-MS following the methodology described below. The analysis of the three solutions was preceded and followed by analyses of the Laboratory Standard that were not subjected to the ion exchange procedure. The isotope abundance ratios of the column-processed samples are compared to the isotope abundance ratios as measured for the unprocessed samples, and the deviations in permil (‰) are listed in Table 1. The data are plotted in Fig. 2, and show evidence of isotope fractionation induced by the ion exchange chemistry, such that the processed samples are enhanced in the lighter isotopes with respect to the heavier isotopes, presumably due to the less than 100% efficiency of the procedure. The average magnitude of the chemically induced fractionation is approximately 0.14‰ per u, which is smaller than the results reported by [8].

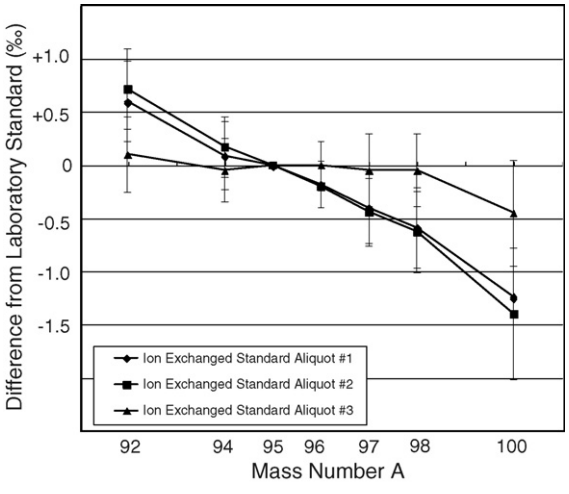

Fig. 2. The deviations of the Mo isotope abundance ratios of three aliquots of the Laboratory Standard subjected to the ion exchange chemistry procedure described in this paper as compared to the Laboratory Standard values. Although the magnitude of this effect is small, chemically induced isotope fractionation is nevertheless of importance in high precision Mo measurements that aim to quantify reliable isotope abundance variations in natural materials.

2.3. Instrumental isotope fractionation

Traditionally, P-TIMS has been the mass spectrometric method of choice for isotopic studies of Mo, despite its relatively high ionization potential (7.1 eV), the possible evaporation of Mo before ionization occurs in the ion source, and the possibility of isobaric interferences from Zr and Ru (see Fig. 1). The latter problem applies to all mass spectrometric techniques, and can be overcome by an efficient chemical extraction procedure. The sensitivity of P-TIMS has been improved by the use of an activator, so that this mass spectrometric technique can be applied to measure the isotopic composition of Mo when only nanogram quantities of Mo are available (e.g., [10]). However, MC-ICP-MS is now an established technique in isotopic analyses of Mo, so it was decided to examine the magnitude and associated uncertainties of isotope fractionation induced by P-TIMS, N-TIMS and MC-ICP-MS in order to evaluate the strengths and weaknesses of each mass spectrometric technique.

2.3.1. Positive-thermal ionization mass spectrometry

A solution of freshly prepared ascorbic acid was produced by dissolving approximately 40 mg of Analar grade L-Ascorbic acid (BDH) in 3 g of 4 M HCl. Approximately 2 μL of ascorbic acid solution was deposited on the centre of a previously outgassed Re filament (99.999% purity, zone-refined). Approximately 1 μg of the Laboratory Standard solution was then carefully placed on top of the ascorbic acid, and the filament was then heated with a 1.5 A current to dry the mixture to a black deposit. The filament was then heated slowly until the deposit fumed. The filament current was turned off as soon as the filament began to glow red. The filament assembly was then loaded into the ion source of a VG 354 TIMS equipped with nine moveable Faraday cup collectors and an axial Daly detector. Once the pressure in the instrument was reduced to 10^{-7} Torr, the filament temperature was slowly increased to 1300 °C. The mass range from 89.5 to 101.5 was monitored using the Daly detector, but the observed peaks were not well-defined at this stage. The filament temperature was then raised to 1450, 1500 and 1550 °C with 5 min intervals after each temperature increase. At 1550 °C the ion beams could be focused on the Faraday cup and measurement of the Mo isotopes commenced. Typically, a 1 μg load of Mo on the centre filament at a temperature of 1550 °C produced an ion current intensity of ^{98}Mo of 10^{-12} A, and the intensity

could be maintained for several hours. On the VG354, seven of the Faraday cup collectors were utilized to collect the Mo ion beams simultaneously. The ^{90}Zr ion current was monitored before and after measurements, and data was utilized only if the ^{90}Zr ion beam was <0.1% of the ^{98}Mo ion beam intensity. Isobaric interferences from Ru were checked by monitoring the ion current at *m*/*q* 99. No Ru isotopes were observed for any of the samples. There was an occasional ion current observed 0.5 u above ^{100}Mo that appeared at low temperatures, but decayed away before the Mo isotope abundance data were collected.

In the absence of the ascorbic acid activator, the ion current was reduced by as much as a factor of 100. It is important to follow the temperature regime outlined above since the stability and duration of the Mo ion beam is poor at elevated temperatures. We have experimented with the use of silica gel both instead of and as well as the ascorbic acid. We have found that silica gel is not necessary to achieve long-lived and stable emission, and the absence of silica gel assists in reducing the loading blank. We have also found that loading Mo in nitric acid essentially destroys any chance of generating stable Mo ion beams. We believe it is imperative to keep Mo in a low oxidation state, and use ascorbic acid as an activator if stable ion beams are to be maintained. The static mode of data collection was used for ion current measurements by P-TIMS. Neither the beam stability or the gain stability of the Faraday cup collectors had a resolvable effect on the precision of the isotope ratio measurements. The in-run fractionation of the relatively light Mo masses and the low ion current had a more significant impact on the precision of the measurements. Gain calibrations were performed at the commencement of each day's mass spectrometric analyses.

Ten Re single filament assemblies, each loaded with approximately 1 μg of the Laboratory Standard, were analysed, and the un-normalized isotope ratios are listed in Table 2, together with their means. Also listed are the Mo isotope ratios currently accepted by the International Union of Pure and Applied Chemistry (IUPAC) as the "best" measurement available [11]. The permil deviations of the measured ratios as compared to the IUPAC values, are also listed in Table 2. An analysis of the deviations of the measured values reveal that they are linearly fractionated by approximately 2.4‰ per u, with the lighter isotopes enhanced with respect to the heavier isotopes. Isotope fractionation in P-TIMS is time-dependent, in that isotope enrichment of the lighter isotopes occurs by a Rayleigh distillation mechanism during the early stages of thermal evaporation. It is therefore important that the operating conditions of the P-TIMS measurements be replicated in an identical manner as possible, including the time-sequencing of data collection. A number of mathematical formulations to describe isotope fractionation effects in TIMS have been investigated (e.g., [12]), but none of these fractionation laws have a sound theoretical basis, and thus each element must be evaluated on its merits.

Recently, the absolute isotope abundances of our Laboratory Standard Mo have been determined using gravimetric mixtures of enriched isotopes [13]. These values are also listed in Table 2, together with the permil deviations, of the raw data from these absolute values. As before, the permil deviations show a linear trend, with the lighter isotopes being enhanced with respect to the heavier isotopes. However, the magnitude of the isotope fractionation is now 6.4‰ per u rather than 2.4‰ per u obtained with the IUPAC "best" values. This is comparable to the fractionation estimated for metal ions by the square root of the masses estimate, namely 5.3‰ per u.

2.3.2. Negative-thermal ionization mass spectrometry

Molybdenum isotope abundance ratios were measured as MoO_3^- ions on a Thermo Electron Finnigan Triton multiple collector TIMS. The production and analysis of negative MoO_3^- ions produced on or near the surfaces of the heated metallic filaments resulted in relatively higher and more stable ion currents compared to the analysis of Mo^+ ions by P-TIMS. As with the

Table 2
Mo isotope abundance ratios of 10 analyses of the Laboratory Standard, analyzed by P-TIMS

Laboratory Standard	^{92}Mo/^{95}Mo	^{94}Mo/^{95}Mo	^{96}Mo/^{95}Mo	^{97}Mo/^{95}Mo	^{98}Mo/^{95}Mo	^{100}Mo/^{95}Mo
1	0.93523(94)	0.58076(55)	1.04520(68)	0.59748(53)	1.5096(13)	0.59907(59)
2	0.93583(89)	0.58111(71)	1.0453(11)	0.59772(54)	1.5086(13)	0.59853(69)
3	0.93583(45)	0.58097(36)	1.04456(47)	0.59725(28)	1.50874(76)	0.59780(29)
4	0.93700(25)	0.58136(21)	1.04491(40)	0.59684(20)	1.50734(46)	0.59824(24)
5	0.93530(39)	0.58082(24)	1.04623(37)	0.59824(36)	1.5116(10)	0.59999(43)
6	0.93518(53)	0.58093(32)	1.04618(42)	0.59788(27)	1.51102(52)	0.60019(29)
7	0.93853(43)	0.58111(31)	1.04440(38)	0.59751(25)	1.50516(53)	0.59691(28)
8	0.93583(89)	0.58111(71)	1.0453(11)	0.59772(54)	1.5086(13)	0.59853(69)
9	0.92973(71)	0.58008(37)	1.05028(51)	0.60039(56)	1.5208(14)	0.60537(65)
10	0.93600(55)	0.58111(28)	1.04646(52)	0.59824(44)	1.51015(97)	0.60000(50)
Mean	0.9355(44)	0.58094(70)	1.0459(34)	0.5979(20)	1.5102(82)	0.5995(46)
Data [11]	0.92877(9)	0.58028(9)	1.04865(6)	0.60129(6)	1.52155	0.60791(2)
Δ (‰)	+7.2	+1.1	−2.6	−5.6	−7.5	−13.3
Data [13]	0.9171(9)	0.57783(3)	1.0527(1)	0.6061(3)	1.5401(8)	0.6203(3)
Δ (‰)	+20.1	+5.4	−6.5	−13.5	−19.4	−33.5

The data are not corrected for in-run fractionation. The IUPAC "best" values [11] for the isotope abundance ratios of Mo together with the absolute values [13], are also listed. The uncertainties in parentheses, for the individual runs are the standard errors at the 95% confidence level (n = 200), and the uncertainties for the averages of the isotope abundance ratios are the standard deviations at the 95% confidence level. The deviations (in permil) of the means of the measured isotope ratios as compared to the IUPAC "best" values, together with the deviations Δ, of the isotope ratios compared to the absolute isotope abundances, are also listed.

Table 3
Molecular ions measured to determine Mo isotope abundance ratios using MoO_3^- ions by N-TIMS

m/q	Ion (major species in bold)					
140	$\mathbf{^{92}Mo^{48}O_3}$					
142	$\mathbf{^{94}Mo^{48}O_3}$	$^{92}Mo^{50}O_3$				
143	$\mathbf{^{95}Mo^{48}O_3}$	$^{94}Mo^{49}O_3$	$^{92}Mo^{51}O_3$			
144	$\mathbf{^{96}Mo^{48}O_3}$	$^{95}Mo^{49}O_3$	$^{94}Mo^{50}O_3$	$^{92}Mo^{52}O_3$		
145	$\mathbf{^{97}Mo^{48}O_3}$	$^{96}Mo^{49}O_3$	$^{95}Mo^{50}O_3$	$^{94}Mo^{51}O_3$	$^{92}Mo^{53}O_3$	
146	$\mathbf{^{98}Mo^{48}O_3}$	$^{97}Mo^{49}O_3$	$^{96}Mo^{50}O_3$	$^{95}Mo^{51}O_3$	$^{94}Mo^{52}O_3$	$^{92}Mo^{54}O_3$
148	$\mathbf{^{100}Mo^{48}O_3}$	$^{98}Mo^{50}O_3$	$^{97}Mo^{51}O_3$	$^{96}Mo^{52}O_3$	$^{95}Mo^{53}O_3$	$^{94}Mo^{54}O_3$

positive ionization technique, the samples were deposited on outgassed zone-refined Re filaments. The filament was coated with 1 μL of a $Ca(NO_3)_2$ solution (1% HNO_3). An aliquot of the sample was then added to the filament and dried for 60 s with a current of 1.3 A. The Ca activator was employed to enhance the production of MoO_3^-. The filament assemblies were loaded in the source of the Finnigan Triton and the vacuum restored to better than 5×10^{-7} Torr. The filament was heated to approximately 1000 °C at 200 mA/min, then to 1150 °C at 25 mA/min. At this temperature, 1 μg of Mo loaded on the filament typically resulted in a $^{98}Mo^{48}O_3^-$ signal intensity of approximately 10^{-11} A for at least 2 h of operation. The ion beam was focused and 10 blocks of 20 ratios each were collected. Seven Faraday cup detectors were positioned to measure *m/q* 140, 142, 143, 144, 145, 146 and 148. The molecular ions found at these locations are given in Table 3. The Mo isotope abundances must be calculated from the measured molecular ions because the resolution of the mass spectrometer was too low to resolve among the isobaric contributions. The oxygen isotopic composition of the MoO_3^- ions was not measured directly by TIMS. Therefore, the IUPAC "best" measurements for the oxygen isotope composition were used for data reduction [11], namely $^{18}O/^{16}O = 0.0020051$ and $^{17}O/^{16}O = 0.0003799$. If one conducts a rigorous propagation of uncertainties in correcting for the oxygen isotopes, the result is an expanded uncertainty interval for the Mo isotope ratios as compared to the raw ratios produced by the instrument. We did not investigate the effect of the use of an oxygen source to improve the production of the MoO_3^- ion beams, but this would be a worthwhile exercise. The role of $Ca(NO_3)_2$ in N-TIMS analyses is not clear-cut. It is possible that electrons are donated by the calcium atoms, or that there is an interaction between the calcium and the rhenium filament which lowers the work function of the filament material, thus enhancing the ionization efficiency.

Seven replicate analyses of the Laboratory Standard are listed in Table 4, together with their means. Uncertainties in the measured MoO_3^- ratios were propagated through the oxygen isotope corrections using a Monte Carlo approach. The permil deviations of the measured isotope ratios, as compared to the IUPAC "best" values [11] and the recent absolute isotope abundance determination [13] are listed in Table 4. Compared to the absolute data, the measurements made by N-TIMS are linearly fractionated by approximately 0.5‰ per u, with the lighter isotopes enhanced with respect to the heavier isotopes, compared to 6.4‰ per u for the same sample of Mo for P-TIMS. This difference can be explained by the fact that the N-TIMS measurements analyse MoO_3^- ions, whereas P-TIMS analyses involve Mo^+ ions. The molecular weight of MoO_3^- is 143.9 as compared to the atomic weight of Mo of 94.9. It should be noted that if the raw N-TIMS data are compared to the IUPAC values, the permil deviations reveal that the measured ratios are fractionated by approximately 3.6‰ per u with the heavier isotopes enhanced with respect to the lighter isotopes. Since the primary fractionating mechanism in TIMS is Rayleigh-type distillation, it is difficult to explain how the heavier isotopes are enhanced. The dilemma disappears when the raw N-TIMS

Table 4
Mo isotope abundance ratios of seven analyses of the Laboratory Standard analyzed by N-TIMS

Laboratory Standard	$^{92}Mo/^{95}Mo$	$^{94}Mo/^{95}Mo$	$^{96}Mo/^{95}Mo$	$^{97}Mo/^{95}Mo$	$^{98}Mo/^{95}Mo$	$^{100}Mo/^{95}Mo$
1	0.91934(26)	0.57822(24)	1.05182(40)	0.60535(43)	1.53611(10)	0.61754(37)
2	0.92193(58)	0.57866(58)	1.05097(10)	0.60418(10)	1.53228(16)	0.61539(10)
3	0.91787(34)	0.57790(31)	1.05232(52)	0.60593(56)	1.53876(10)	0.61966(48)
4	0.91945(60)	0.57819(58)	1.05205(10)	0.60540(11)	1.53704(16)	0.61850(10)
5	0.91501(10)	0.57762(10)	1.05339(15)	0.60744(17)	1.54416(28)	0.62362(13)
6	0.91999(36)	0.57801(33)	1.05110(54)	0.60560(58)	1.53544(10)	0.61725(52)
7	0.91582(15)	0.57774(14)	1.05289(23)	0.60661(25)	1.54149(43)	0.62142(21)
Mean	0.9185(48)	0.57805(70)	1.0521(18)	0.6058(20)	1.5379(80)	0.6191(54)
Δ wrt [11] (‰)	−11.1	−3.8	+3.3	+7.5	+10.7	+18.4
Δ wrt [13] (‰)	+1.5	+0.4	−0.6	−0.5	−1.4	−1.9

The data are corrected for isobaric interferences from oxygen isotopes, but the ratios are not corrected for in-run fractionation. The uncertainties in parentheses, for the individual runs are the standard errors at the 95% confidence level ($n = 200$), and the uncertainties for the averages of the isotope abundance ratios are the standard deviations at the 95% confidence level. The deviations (in permil) of the means of the measured isotope ratios as compared to the IUPAC "best" values, together with the deviations Δ of the isotope ratios compared to the absolute isotope abundances, are also listed.

data are corrected against the absolute Mo values. This example illustrates the importance of correcting raw isotope ratios by absolute isotope abundances if at all possible. The terminology used by IUPAC in describing the isotopic composition of certain elements as the "best" measurement from a single source is somewhat misleading, and that a "best" value is not necessarily a "good" value [14]. It is apparent the IUPAC "best" values for Mo are isotopically fractionated with respect to the absolute isotope abundances.

The double spiking technique is an effective method to eliminate chemical and instrumental isotope fractionation in TIMS [15]. It is a transparent, reliable and robust method, and, like IDMS, is based on conceptually simple premises [16]. An alternative approach to correct for isotope fractionation effects in TIMS is the total evaporation technique, in which the sample is run to extinction, with the ion currents being integrated over the life of the sample [17]. Internal normalization can be used for those elements which possess three or more isotopes, provided at least two of them are stable (e.g., in Rb–Sr geochronology where the $^{86}Sr/^{88}Sr$ ratio is assumed to be invariant).

2.3.3. Multiple collector-inductively coupled plasma-mass spectrometry

Molybdenum isotope abundance ratios were measured using a Thermo Electron Finnigan Neptune MC-ICP-MS. Samples of the Laboratory Standard (Johnson Matthey metal rod), were diluted to a Mo concentration of 200 ppb in 2 M HNO_3. The solutions were aspirated into a wet spray chamber at an uptake rate of 100 μL/min. This resulted in $^{98}Mo^+$ signal intensities of approximately 5×10^{-11} A. Two hundred ratios were collected followed by a 3-min washout with 2 M HNO_3. Typically, a minimum of 1 μg of Mo was consumed for each analysis using the MC-ICP-MS. The Mo ICP standard (Fluka No. 69876) was analyzed at the start of each session to check the stability of the instrument prior to the measurement of Mo samples. The uncorrected $^{98}Mo/^{95}Mo$ isotopic ion current ratio of the ICP standard solution drifted <0.008% over a 12-h measurement session. Seven Faraday cup detectors were positioned to measure *m/q* 92, 94, 95, 96, 97, 98 and 100, which correspond to the seven stable isotopes of Mo. In addition, two cups were aligned to monitor for Ru ($^{99}Ru^+$) and Zr ($^{90}Zr^+$) isobaric interferences. A two-line method was employed because it was not possible to simultaneously measure *m/q* 90 and 92 due to the maximum allowable spacing between the L4 and L3 Faraday cups. Typically, no Zr or Ru interferences were detected. In addition, no polyatomic spectral interferences were identified.

The Laboratory Standard was analysed 10 times by MC-ICP-MS. The un-normalized (raw) ratios are listed in Table 5 together with their mean values. The permil deviations of the measured isotope ratios as compared to the IUPAC "best" values [11] and the recent absolute isotope abundances [13], are also given. Compared to the absolute isotope abundance data the results from the MC-ICP-MS analyses are linearly isotopically fractionated by approximately 17.0‰ per u, with the heavier isotopes enhanced with respect to the lighter isotopes. Isotope fractionation in MC-ICP-MS is caused by several processes, but space charge effects in the skimmer cone region is certainly of significance [18]. The net effect is that the heavier isotopes are transmitted preferentially to the lighter isotopes, as observed in Fig. 3. However, unlike isotope fractionation in TIMS, the effect is time-independent, as the sample is continuously introduced into the plasma. This is an important advantage as compared to TIMS in correcting for isotope fractionation, and various methods have been adopted to correct for the mass discrimination based on the time-independent nature of MC-ICP-MS [19]. Of course, if the raw isotope ratios listed in Tables 2, 4 and 5 are normalized to a selected isotope ratio, the uncertainty in the data sets are thereby reduced. However, there has been no "universal" agreement as to which normalizing ratio should be used for Mo and what its value should be, so that inter-laboratory comparisons are therefore difficult to achieve. In the case of Mo, if the raw isotope ratios are compared to the absolute isotope abundances of [13], the average of the permil deviations is 17.0‰

Table 5
The raw isotope ratios of 10 analyses of the Laboratory Standard analyzed by MC-ICP-MS

Laboratory Standard	$^{92}Mo/^{95}Mo$	$^{94}Mo/^{95}Mo$	$^{96}Mo/^{95}Mo$	$^{97}Mo/^{95}Mo$	$^{98}Mo/^{95}Mo$	$^{100}Mo/^{95}Mo$
1	0.87073(4)	0.56784(3)	1.07056(4)	0.62694(3)	1.61924(6)	0.67384(3)
2	0.87074(5)	0.56787(3)	1.07057(5)	0.62694(4)	1.61926(9)	0.67385(6)
3	0.87084(7)	0.56793(5)	1.07053(8)	0.62690(5)	1.6191(1)	0.67375(6)
4	0.87097(9)	0.56811(7)	1.07055(7)	0.62690(7)	1.6190(2)	0.67374(7)
5	0.8708(1)	0.5680(1)	1.0706(1)	0.6270(1)	1.61942(2)	0.6739(1)
6	0.8712(1)	0.5681(1)	1.0704(2)	0.6268(1)	1.6185(2)	0.6734(2)
7	0.8714(1)	0.56817(9)	1.0704(2)	0.6267(1)	1.6183(2)	0.6732(1)
8	0.87111(7)	0.56798(4)	1.07045(6)	0.62678(5)	1.6186(1)	0.67341(8)
9	0.87101(8)	0.56793(4)	1.0704(6)	0.62682(5)	1.6188(1)	0.67353(8)
10	0.87113(6)	0.56794(3)	1.0704(6)	0.62675(5)	1.6185(1)	0.67334(8)
Mean	0.8710(4)	0.5680(2)	1.0705(1)	0.6269(2)	1.6189(8)	0.6736(7)
Δ wrt [11] (‰)	−62.2	−21.2	+20.8	+42.6	+64.0	+108.1
Δ wrt [13] (‰)	−50.3	−17.0	+16.9	+34.3	+51.2	+85.9

The uncertainties in parentheses, for the individual runs are the standard errors at the 95% confidence level ($n = 200$). The uncertainties for the averages of the isotope abundance ratios are the standard deviations at the 95% confidence level. The deviations (in permil) of the means of the measured isotope ratios as compared to the IUPAC "best" values, together with the deviations Δ of the isotope ratios compared to the absolute isotope abundances, are also listed.

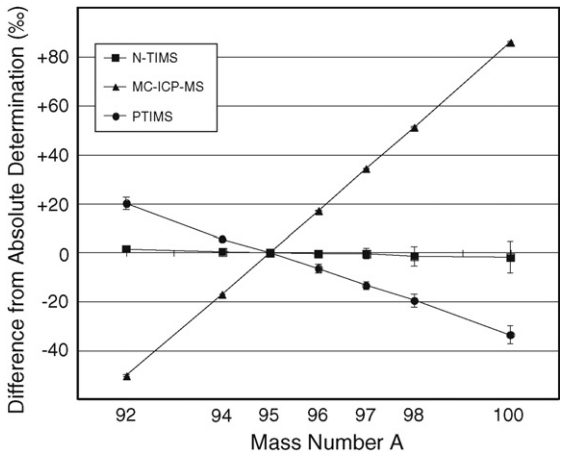

Fig. 3. The deviations of the Mo isotope ratios of the Laboratory Standard as measured by P-TIMS, N-TIMS and MC-ICP-MS, plotted (in permil), against the absolute isotope abundances for Mo obtained by [13]. Error bars are the standard deviations at the 95% confidence level.

per u rather than the average value of 21.1‰ per u determined from the IUPAC "best" values.

3. Discussion

The means of the un-normalized Mo ratios determined by P-TIMS, N-TIMS and MC-ICP-MS are listed in Tables 2, 4 and 5, respectively. The permil deviations of the isotope ratios with reference to the absolute determinations [13], are given in schematic form in Fig. 3. Despite the fact that the identical Mo material was analysed by the same operator, in each case using Faraday cup collection, the three different mass spectrometric techniques produce very different results, predominantly because of instrumental isotope fractionation. Although the outcome of this pattern of isotope fractionation is of no surprise, it demonstrates the fundamental importance of isotope fractionation, particularly for MC-ICP-MS, in part because of the magnitude of the effect. No evidence of any specific isotope anomaly can be observed in any of the isotope ratios from any of the three mass spectrometric techniques used. The magnitude of isotope fractionation for the two TIMS techniques, are relatively small in comparison to the magnitude of isotope fractionation for MC-ICP-MS (Fig. 3). The traditional method of correcting for isotope fractionation, is achieved by normalizing the raw data to a selected Mo isotope ratio. This does not introduce a large uncertainty into the normalized data provided the same normalizing ratio is used throughout. However, the choice of normalizing ratio and its magnitude, is of obvious importance in correcting for isotope fractionation, and more importantly for inter-laboratory comparison purposes.

The results described in this paper clearly show that both chemical and instrumental isotope fractionation exist in the mass spectrometric analysis of Mo. In MC-ICP-MS non-systematic changes in instrument isotope fractionation can occur because of matrix differences between standard and natural samples, which is of more concern for Mo than for major elements such as Fe, because Mo is a trace element in most natural samples other than molybdenites. This implies the necessity of an efficient chemical extraction procedure to ensure that matrix problems are minimized. A double spike can be used as an internal monitor to measure the analytical isotope fractionation arising both from chemical separation and during ionization and ion transmission in the mass spectrometer. Thus, small isotope fractionations that reveal the occurrence of geochemical mass dependent processes, such as are observed in molybdenites, can be precisely determined with MC-ICP-MS using the double spike methodology [20]. The double spike must comprise two enriched isotopes of Mo, which in the study of molybdenite natural fractionation were ^{94}Mo and ^{100}Mo [20].

A minimum of 1 μg of Mo in 5 ml of solution is needed in order to reliably measure isotope abundance ratios with MC-ICP-MS. P-TIMS is better suited to measure Mo isotope ratios when only nanogram amounts of Mo are available (e.g., [10]). Although the sensitivity of N-TIMS is higher than P-TIMS, the final precision of the Mo isotope ratios is similar, in that oxygen isobaric corrections are required in order to obtain the Mo isotope ratios. Our experience in measuring the natural isotope fractionation in molybdenites [7,20], is that MC-ICP-MS is preferred to either P-TIMS or N-TIMS because of the excellent precision which can be routinely achieved, which is essential in order to obtain accurate and reproducible natural isotope fractionation data [20]. Isotope abundance anomalies (such as those produced by nuclear effects), are best analysed by P-TIMS, particularly where the amount of Mo available is limited [10,21].

The key to stable isotope fractionation measurements is the ability to correct for mass fractionation induced by the chemical separation procedure, and more importantly, by the mass spectrometer itself. In contrast to TIMS, there are three approaches to distinguish naturally induced isotope fractionation from these other sources using MC-ICP-MS—namely sample-standard bracketing, element spiking and double spiking. Unfortunately there has not been a single study which has compared the relative merits of these three approaches on the same instrument and on the same samples. Various research groups have shown that consistent isotope fractionation results can be obtained by MC-ICP-MS using these different approaches [22,8,23–26]. The need for rigorous quality control protocols for MC-ICP-MS measurements, has been emphasized [27].

The first attempt to measure the isotope fractionation in Mo produced in natural materials using MC-ICP-MS incorporating the double spike technique was successfully achieved by Siebert et al. [22]. They reported a fractionation of −0.3‰ for the ^{98}Mo/^{95}Mo ratio relative to their Laboratory Standard, for a hydrothermal molybdenite, and between −0.3 and +0.1‰ for the same ^{98}Mo/^{95}Mo ratio in fine-grained sediments. Their fractionation results were determined on four Mo isotope ratios with an external standard reproducibility of 0.06‰ on the same ratio, at the 2S level [22]. Anbar et al. [8] also reported isotope fractionation results for a molybdenite sample of approximately 0.3‰ per u with respect to their Laboratory Standard. They reported that differences in ^{95}Mo/^{98}Mo ratios were determined to a precision of ±0.2‰ at the 2S level. Anbar et al. [8] employed Zr and Ru spikes to correct for instrumental isotope fractionation.

Siebert et al. [22] point out that double spiking has an advantage as compared to element spiking and sample-standard bracketing with respect to isotope fractionation measurements, in their reliance on a fractionation-free chemical separation procedure and the absence of isobaric interferences in either the analytical element and/or the element used for fractionation correction, which may introduce uncertainties into the measured data. Because of the larger range in the magnitude of the isotope fractionation which occurs in MC-ICP-MS as compared to TIMS, one has to rely on isotope fractionation models being applicable over a wider mass range in the case of element spiking and sample-standard bracketing calibrants, than is the case in the double spiking methodology. Pietruszka et al. [23] have recently shown that isotope fractionation in Mo in molybdenites can be successfully determined using the sample-standard bracketing technique to correct for instrumental mass bias. These authors demonstrated that the precision of this technique is similar to published results using the double spike technique, at least within a factor of two. Malinovsky et al. [26] have shown that instrumental isotope fractionation as measured in freshwater sediments and molybdenites, can be corrected by using Pd spiking and normalizing to an assumed $^{105}Pd/^{104}Pd$ ratio. Mass dependent variations in the isotopic composition of Mo spanning a range of 2.2‰ in terms of the $^{97}Mo/^{95}Mo$ ratio for two sediment columns from different redox environments were successfully resolved, using this element spiking technique.

The inter-laboratory comparisons of the isotopic composition of Mo have been less than optimum because of the lack of an internationally accepted reference material, and the absence of a consistent normalizing isotope ratio in use among the various laboratories involved in Mo isotopic measurements. Some laboratories have chosen a normalizing ratio from the IUPAC "best" measurements [11], but that set of data is not a particularly good set of measurements [28]. Fortunately this deficiency has now been overcome, in that the Laboratory Standard described above has now been calibrated in this laboratory by measurements of gravimetric mixtures of two enriched isotopes—^{92}Mo and ^{98}Mo [13]. Thus, if the Laboratory Standard Mo used in this laboratory is adopted as an acceptable reference material, until such time as an ICRM is available, it is now possible for rigorous inter-laboratory isotopic comparative studies of Mo to be undertaken.

4. Conclusions

The mass spectrometry of Mo is of increasing importance in geochemistry and biogeochemistry. These studies are of particular relevance to isotope fractionation research in natural materials and systems, because of the rich redox chemistry and covalent type bonding of Mo [5]. The diversity of investigations in stable isotope geochemistry and biogeochemistry has been catalysed by the advent of MC-ICP-MS. In many applications the magnitude of isotope fractionation in natural systems is <1‰ per u. It is therefore essential to adopt state-of-the-art mass spectrometric protocols to ensure the accuracy of the magnitude of natural isotope fractionation, including the ability to conduct inter-laboratory comparisons.

This paper has examined the extent of both chemical and instrumental isotope fractionation for Mo. Three mass spectrometric techniques have been used to examine the extent of instrumentally induced fractionation in P-TIMS, N-TIMS and MC-ICP-MS using the same Laboratory Standard, Faraday cup collection and operator in each case. It has been shown that P-TIMS and N-TIMS give isotope fractionations of 6.4‰ and 0.5‰ per u, respectively, both with an enhancement in the lighter isotopes, whereas MC-ICP-MS gives a larger isotope fractionation of 17.0‰ per u, but with an enhancement in the heavier isotopes, when the raw data for each of these techniques is compared to the absolute isotope abundance ratios of Mo [13]. MC-ICP-MS is undoubtedly the superior method for measuring natural isotope fractionation in natural materials, because of its ability to generate highly precise data provided careful attention is paid to distinguish natural fractionation from chemical and more particularly instrumental isotope fractionation. The fundamental advantage of the double spike over an elemental spike such as Pd [26], is that the double spike isotopes follow exactly the same isotope fractionation pathways as the isotopes from the natural samples, provided the double spike is introduced at the commencement of the chemical extraction procedure.

MC-ICP-MS has the advantage as compared to TIMS measurements that the isotope fractionation is time-independent and that three approaches are available to correct for isotope fractionation—namely element spiking, sample-standard bracketing and double spiking, whereas only the latter technique can be used to correct for isotope fractionation in TIMS measurements. Recent improvements in the element spiking and sample-standard bracketing correction techniques for MC-ICP-MS, have enabled instrumental fractionation to be resolved from naturally induced effects. This has enabled natural isotope fractionation in ore genesis studies [23], and in paleooceanography [25] to be successfully determined.

The isotopic composition of Mo is required for a number of scientific applications in which the sample size is often small. This is of particular relevance to cosmochemical experiments in iron and stony meteorites. The ionization efficiency of the traditional P-TIMS methodology has been enhanced by the use of an ascorbic acid activator which enables nanogram sized samples of Mo to be successfully measured, provided strict loading and heating sequences are followed. Details of the operating characteristics of N-TIMS for Mo have been evaluated in which the sample is analysed as MoO_3^-. However, despite the superior ionization efficiency of N-TIMS as compared to P-TIMS, a thorough evaluation of isobaric corrections due to the oxygen isotopes, reduces the precision of the corrected values to approximately the same as for P-TIMS. An ion exchange chemical extraction procedure has been developed for mass spectrometric analysis of Mo which can be applied to a wide range of natural materials, with a high efficiency and a low blank, in which chemical isotope fractionation is kept to a minimum.

Our Laboratory Standard – comprising a spectroscopically pure metal rod – has recently been calibrated using gravimetric mixtures of two enriched Mo isotopes, to obtain the absolute isotope abundances and atomic weight of this element [13]. This calibrated metal reference material can be made available

to other users so that inter-laboratory comparative studies of the isotopic composition of Mo can be made. This calibrated reference material also provides the opportunity of adopting a uniform normalizing ratio when correcting for isotope fractionation.

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