

Absolute isotopic composition of molybdenum and the solar abundances of the *p*-process nuclides $^{92,94}\text{Mo}$

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The isotopic composition of molybdenum has been measured with high precision using a thermal ionization mass spectrometer, the linearity of which has been verified by measuring the isotopically-certified reference material for strontium (NIST 987). The abundance sensitivity of the mass spectrometer in the vicinity of the molybdenum ion beams has been carefully examined to ensure the absence of tailing effects. Particular care was given to ensuring that potential isobaric interferences from zirconium and ruthenium did not affect the measurement of the isotopic composition of molybdenum. Gravimetric mixtures of two isotopically enriched isotopes, ^{92}Mo and ^{98}Mo , were analyzed mass spectrometrically to calibrate the mass spectrometer, in order to establish the isotope fractionation of the spectrometer for the molybdenum isotopes. This enabled the “absolute” isotopic composition of molybdenum to be determined. An accurate determination of the isotopic composition is required in order to calculate the atomic weight of molybdenum, which is one of the least accurately known values of all the elements. The absolute isotope abundances (in atom %) of molybdenum measured in this experiment are as follows: $^{92}\text{Mo} = 14.5246 \pm 0.0015$; $^{94}\text{Mo} = 9.1514 \pm 0.0074$; $^{95}\text{Mo} = 15.8375 \pm 0.0098$; $^{96}\text{Mo} = 16.672 \pm 0.019$; $^{97}\text{Mo} = 9.5991 \pm 0.0073$; $^{98}\text{Mo} = 24.391 \pm 0.018$; and $^{100}\text{Mo} = 9.824 \pm 0.050$, with uncertainties at the 1s level. These values enable an atomic weight $A_r(\text{Mo})$ of 95.9602 ± 0.0023 (1s) to be calculated, which is slightly higher than the current Standard Atomic Weight $A_r(\text{Mo}) = 95.94 \pm 0.02$ and with a much improved uncertainty interval. These “absolute” isotope abundances also enable the Solar System abundances of molybdenum to be calculated for astrophysical purposes. Of particular interest are the Solar System abundances of the two *p*-process nuclides— ^{92}Mo and ^{94}Mo , which are present in far greater abundance than *p*-process theory suggests. The Solar System abundances for ^{92}Mo and ^{94}Mo of 0.364 ± 0.012 and 0.230 ± 0.008 respectively, (with respect to silicon = 10^6 atoms), are the most accurate values measured to date, and should therefore be adopted in future *p*-process calculations, rather than the existing values of 0.378 ± 0.021 and 0.236 ± 0.013 , respectively.

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I. INTRODUCTION

Molybdenum was discovered by the Swedish chemist Carl Wilhelm Scheele in 1778, and was isolated by Peter-Jacob Hjelm three years later. Its name is derived from the Greek word “molybdos” meaning lead, as this term was used for any black mineral that left a mark on paper. Molybdenum has an atomic number of 42 and possesses seven stable isotopes, as shown in Fig. 1. From a nuclear astrophysics perspective, Mo is an interesting element because its isotopes are produced by a variety of nucleosynthetic processes. The two light isotopes— $^{92,94}\text{Mo}$, are synthesised solely by the *p*-process, $^{95,97,98}\text{Mo}$ by a combination of the slow (*s*) and rapid (*r*) neutron capture processes, ^{96}Mo by the *s*-only process, and ^{100}Mo by the *r*-only nucleosynthetic process [1]. Furthermore, ^{96}Mo is produced by the double beta decay of ^{96}Zr [2]. Molybdenum is located near the peak of the lower mass hump in the asymmetric nuclear fission of the actinides, and $^{95,97,98,100}\text{Mo}$ are produced as cumulative fission yields of U fission (e.g. [3]).

The atomic weight of Mo was given a value of 95.94, based on the Harvard chemical methodology, in the 1961 report of the Commission on Atomic Weights and Isotopic Abundances (CAWIA), which is a Commission of the International Union of Pure and Applied Chemistry (IUPAC) [4]. The name of the commission has recently been changed to the Commission on Isotopic Abundances and Atomic Weights (CIAAW), to reflect the increasing importance of isotope abundance measurements. In its 1975 report, CAWIA gave the atomic weight an uncertainty of 0.01 such that $A_r(\text{Mo}) = 95.94 \pm 0.01$ [5], based on five uncalibrated mass spectrometric experiments [6–10]. However, in its 2001 report [11], CAWIA took the unusual step of increasing the uncertainty to $U_r(\text{Mo}) = 0.02$, based on a new mass spectrometric analysis by Wieser and de Laeter [12], using revised statistical guidelines. This value of the atomic weight $A_r(\text{Mo}) = 95.94 \pm 0.02$ is the presently-accepted value, and its magnitude has therefore remained unchanged since 1961.

The first well-documented study of the isotopic composition of Mo was carried out by bombarding molybdenum hexacarbonyl vapour with 100 eV electrons [13]. Both the singly-charged Mo^+ and doubly-charged Mo^{++} ions were produced using this ionization technique, with good agreement between the two data sets. A value of 95.90 for the atomic

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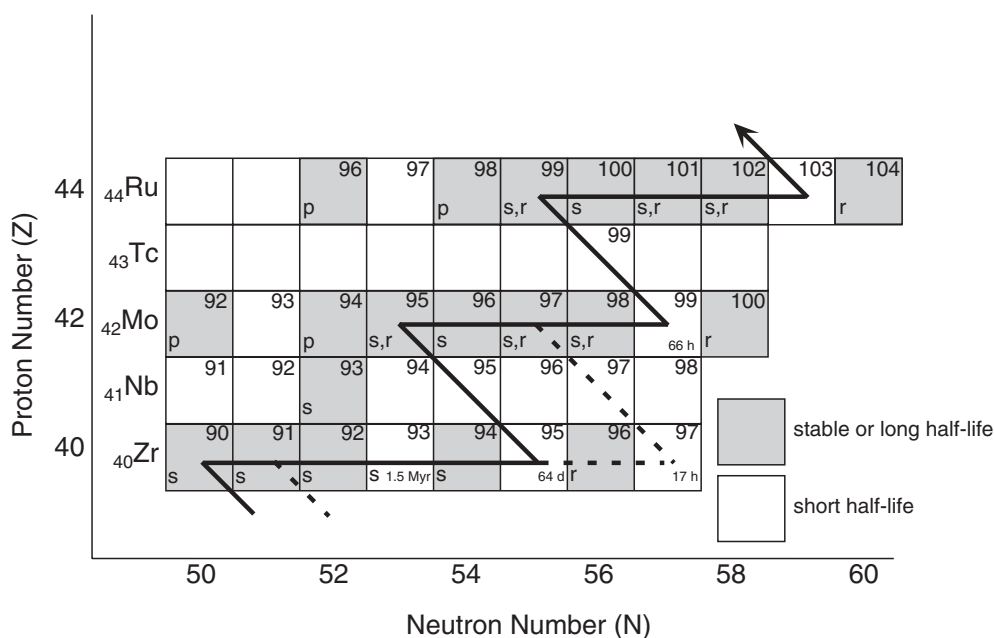


FIG. 1. The chart of the nuclides in the mass region of Mo showing the isobaric nuclides $^{92,94,96}\text{Zr}$ and $^{96,98,100}\text{Ru}$. The “zig-zag” s-process neutron capture path is shown, together with the r- and p-process produced isotopes.

weight of Mo was calculated from this isotopic data [13]. A comprehensive study of the isotopic composition of Mo in three terrestrial samples and eight iron meteorites by thermal ionization mass spectrometry (TIMS) was performed by Murthy [6,14]. Murthy [14] reported that Mo extracted from some of the meteorites was isotopically fractionated by up to 7% in the $^{92}\text{Mo}/^{100}\text{Mo}$ ratio, with respect to his laboratory standard. However, Wetherill [8], using the double spike technique, refuted Murthy’s results, and concluded that the anomalous data were probably the result of variable isotope fractionation in the TIMS used in the experiment. It is important to note that the measured $^{92}\text{Mo}/^{100}\text{Mo}$ isotope ratio of 1.540 of Murthy [14] for the terrestrial samples was adopted by Wetherill [8] to normalise his data for comparison purposes. In 1974, Moore *et al.* [10] also adopted the same ratio to normalise their Mo data, and, until recently, the isotopic composition reported by Moore *et al.* [10] was accepted by IUPAC as the “best measurement” for Mo from a single terrestrial source, in the Table of Isotopic Composition of the Elements [15]. A high-precision study of the Mo isotopes using Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) adopted a normalization procedure based on a $^{94}\text{Mo}/^{98}\text{Mo}$ ratio of 0.38315 [16], derived from the “best” measurement of Moore *et al.* [10]. A similar normalization procedure was also used by Kawashima *et al.* [17] in their experiment to determine the double beta decay half-life of ^{96}Zr . Thus, the original isotope normalization ratio of 1.540 for $^{92}\text{Mo}/^{100}\text{Mo}$ of Murthy [14], was propagated in subsequent determinations of the isotopic composition of Mo, despite the fact that convincing evidence of instrumentally-induced mass fractionation in these measurements was demonstrated by Wetherill [8].

This unsatisfactory situation led to a redetermination of the isotopic composition of Mo [12], in which a simple but reliable analytical technique using TIMS was developed. These authors

reported 12 replicate analyses of the isotope abundances of Mo in a Laboratory Standard prepared by dissolving a spectroscopically-pure sample of Mo. These authors also measured the isotopic composition of four “off-the-shelf” Mo reagents together with five molybdenite ores. In each case the data was normalized to a $^{98}\text{Mo}/^{95}\text{Mo}$ ratio of 1.52155 using an exponential law to correct the data [18]. Within experimental uncertainties, the isotopic compositions were identical, so that all 21 analyses were pooled to give a composite set of isotope ratios. This composite data set was subsequently selected by CIAAW in 2001 as the “best measurement” of the isotopic composition of Mo from a single terrestrial source [19]. In the intervening period of time, however, it has been demonstrated that noninstrumental isotope fractionation occurs in molybdenites [20], and therefore that the methodology used by Wieser and de Laeter [12] in pooling the molybdenite data with the Laboratory Standard data and “off the shelf” chemicals was incorrect, because the selected isotopic composition was not from a single source as specified by IUPAC [11], and the two sets of data were not identical, as had previously been assumed.

There have been numerous studies of the isotopic composition of Mo reported in the literature. Many of these studies have searched for isotopic anomalies in meteoritic material, often with conflicting results, using a number of mass spectrometric techniques. In recent years, stable isotope geochemistry has embraced the isotope abundance analysis of a number of “nontraditional” elements, which exhibit isotope fractionation produced by physiochemical and/or biogeochemical mechanisms. Molybdenum is one such element that is of importance in these isotope fractionation studies. These isotope fractionation measurements must be undertaken with rigorous mass spectrometric protocols, since the magnitude of the isotope fractionation is usually less than 1 permil per mass unit [21]. All these isotopic studies have been completed in the absence of the knowledge of the

“absolute” isotopic composition of Mo, and the availability of an internationally-accepted Mo reference material.

Numerous studies of natural isotope fractionation in terrestrial materials (e.g. [20]), and the increasing importance of isotopic anomaly investigations of Mo in meteoritic materials (e.g. [22,23]), coupled with the unsatisfactory status of the “best measurement” of Mo in the Table of the Isotopic Composition of the Elements [19], led to the present experiment. This project was undertaken in order to produce an “absolute” isotopic composition for Mo by calibrating a TIMS by gravimetric mixtures of two enriched isotopes— ^{92}Mo and ^{98}Mo , in order to determine the magnitude of instrumental isotope fractionation for the Mo isotopes. This enabled a new set of “absolute” isotopic abundances to be determined, and a new value for the atomic weight of Mo to be calculated, with an order of magnitude improvement in its uncertainty. The new values for the “absolute” isotope abundances of Mo also enable the Solar System abundances of these isotopes to be determined, in particular the p -process nuclides ^{92}Mo and ^{94}Mo , which are important nuclides in studies of p -process nucleosynthesis.

II. EXPERIMENTAL

A. Laboratory standard

In the absence of an internationally-accepted Mo reference material, a Laboratory Standard solution of Mo was prepared by dissolving a 99.993% spectroscopically pure metal rod (Johnson-Matthey Chemicals Ltd., JMC 726, No. S-8555) in aqua regia. Samples of the Laboratory Standard, of approximate size $2\mu\text{g}$, were loaded on a single zone-refined Re filament assembly and taken carefully to dryness with $2\mu\text{l}$ of 6 M HCl to ensure that the sample was in the chloride form. A solution of freshly prepared ascorbic acid was prepared by dissolving 40 mg of Analar grade ascorbic acid in 3 g of 4 M HCl. Approximately $5\mu\text{l}$ of ascorbic acid solution was placed on the Mo sample, and the filament was then heated carefully to dryness with a filament current of approximately 1.5 A, to dry the mixture to a black deposit. The filament was then heated slowly until the deposit fumed and the filament began to glow red. The filament assembly was then mounted in the ion source of a VG 354 TIMS, equipped with nine moveable Faraday Cup collectors and an axial Daly collector. The filament temperature was slowly increased to 1300°C so that the pressure in the ion source stabilized. The mass range from $89.5 \leq A \leq 101.5$ was monitored using the Daly collector, but the Mo peaks were not well defined at this temperature. The temperature of the filament was progressively raised to 1500°C when Mo ion beams can be focussed, and a high sensitivity examination of the mass spectrum in the mass range can be undertaken. Under these operating conditions ion beams of approximately 10^{-12} A were maintained for several hours. Seven of the Faraday Cups were utilized to collect the ion beams simultaneously, whilst the $A = 90$ and $A = 102$ mass positions were monitored throughout the data collection process.

B. Linearity

In order to measure the isotopic composition of any element with high accuracy, it is essential to establish the linearity of

the mass spectrometer detector system at least over a range commensurate with the magnitude of the ratio of the largest and smallest ion beams. In the case of Mo, this does not present a particular problem since the magnitude of the isotope abundances of Mo are remarkably uniform—the mole fraction of the lowest abundance isotope being $^{94}\text{Mo} = 0.0923$, and the largest, ^{98}Mo , being 0.2419 giving a range of 2.62 [19]. This situation occurs because of the relatively large abundances of the two p -process nuclides ^{92}Mo and ^{94}Mo . The isotopically certified reference material NIST 987 for Sr, which is in the same mass region as Mo, was measured under similar conditions in the same TIMS as used for the measurement of the isotopic composition of Mo. The measured Sr data were in excellent agreement with the certified values.

C. Abundance sensitivity

Another important consideration in achieving an accurate isotope ratio measurement is to demonstrate that the mass spectrometer has sufficient mass resolution to ensure that two adjacent ion beams can be measured without “tailing” effects. This is especially important for elements of high mass number A , particularly if an abundant isotope of higher mass is adjacent to an isotope of lower abundance. In the case of Mo, this is not an important issue, because Mo occupies an intermediate mass range $92 \leq A \leq 100$, and all the isotopes have a relatively even spread in abundance. Nevertheless, the mass spectrum in the vicinity of the Mo mass region was carefully examined to ensure the absence of “tailing” effects. Figure 2 is a mass scan in the region $90 \leq A \leq 102$ under the filament current and vacuum conditions at which the Mo^+ ion beams were measured. Typical vacuum conditions in the ion source and mass analyser were approximately 5×10^{-8} torr and $\leq 10^{-9}$ torr respectively during data collection. Before data collection commenced, a high sensitivity examination of the mass spectrum in the Mo mass region was carried out to ensure the absence of “tailing” effects in the Mo mass spectrum.

D. Isobaric isotopes

It is also essential to account for any isobaric isotopes which may be present when the Mo isotopes are being measured. Figure 1 illustrates the situation of the Mo isotopic composition with respect to the isobaric isotopes $^{92,94,96}\text{Zr}$ and $^{96,98,100}\text{Ru}$. The presence of Zr was monitored by examining the ^{90}Zr mass

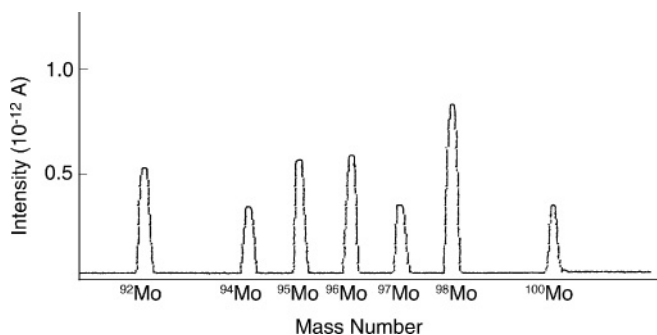


FIG. 2. The mass spectrum of Mo^+ generated by the VG 354 TIMS in the mass region $90 \leq A \leq 102$, under the operating conditions of data collection.

TABLE I. Details of primary solutions PS-A (^{92}Mo) and PS-B (^{98}Mo). All uncertainties are given as 1s.

Sample	PS-A	PS-B
Form	Mo metal	Mo metal
Purity (%)	99.99 ± 0.01	99.99 ± 0.01
Weight (mg)	98.60 ± 0.01	186.40 ± 0.01
Weight of solution (g)	42.28020 ± 0.00001	68.21690 ± 0.00001
Concentration of Mo ($\mu\text{g/g}$)	2331.83 ± 0.14	2732.19 ± 0.17

position, because it is the isotope with the highest abundance of all the Zr isotopes. For the same reason, the presence of Ru was monitored by examining the ^{102}Ru mass position. No evidence of either ^{90}Zr or ^{102}Ru was found in any of the analyses reported in this experiment. Figure 2 does not show any evidence of these two isotopes, but the $A = 90$ and $A = 102$ mass positions were examined at high sensitivity, both before and after data collection, with a null result.

E. Isotope fractionation

Isotope analysis by TIMS invariably introduces time-dependent mass fractionation such that the lighter isotope's ion beam is enhanced with respect to the heavier isotopes, under the normal data collection regime. An accurate assessment of the isotopic composition, and therefore the atomic weight of an element must involve a correction for isotope fractionation, which will decrease the magnitude of the lighter isotopes with respect to the heavier isotopes. This has the effect of increasing the atomic weight. The magnitude of the isotope fractionation correction varies from element to element, but is greater for elements with a lower mass number. It is therefore essential that an accurate assessment of the isotope fractionation of the Mo isotopes be made in order to optimize the accuracy of the atomic weight, as well as to obtain an accurate set of isotope abundances for Mo. The present IUPAC-recommended values for the isotope abundances of Mo from "a single terrestrial source" is given the designation "L", which implies that the linearity of the mass spectrometer from which the recommended data have been measured was demonstrated [19], but that the effect of isotope fractionation for these recommended values was not taken into account. The most definitive method of accurately determining the magnitude of isotope fractionation, is to calibrate the mass spectrometer used in the experiment by obtaining adequate quantities of two isotopically-enriched samples of Mo, of known purity, to prepare gravimetric "spikes". In this experiment, 200 mg of ^{92}Mo and ^{98}Mo were obtained from the Oak Ridge National Laboratory (ORNL) in the metallic form. The metal

TABLE II. The mean of four replicate analyses of the measured isotope ratios of the two enriched isotopes— ^{92}Mo and ^{98}Mo (PS-A and PS-B, respectively). Uncertainties are given as 1s.

Isotope abundance ratio	PS-A	PS-B
92/95	170.8 ± 1.7	0.6693 ± 0.0067
94/95	1.264 ± 0.013	0.5083 ± 0.0051
96/95	0.7820 ± 0.0078	1.614 ± 0.016
97/95	0.3650 ± 0.0047	2.619 ± 0.026
98/95	0.8540 ± 0.0085	466.0 ± 4.7
100/95	0.5400 ± 0.0054	1.482 ± 0.015

was preferred to the oxide form to minimise the risk of possible stoichiometric effects. The stated enrichment of the two isotopically enriched samples, as given by ORNL, were 97.31% for ^{92}Mo and 98.15% for ^{98}Mo , respectively. The purity of the ^{92}Mo and ^{98}Mo samples was determined by a spark source mass spectrographic analysis of each sample by ORNL.

III. RESULTS AND DISCUSSION

A. Determination of isotope fractionation

The ^{92}Mo and ^{98}Mo enriched isotopes were accurately weighed, and then dissolved in ultrapure aqua regia in two pre-cleaned Pyrex flasks marked primary solutions A and B respectively. Details of the two primary solutions are given in Table I. Aliquots of the two primary solutions PS-A and PS-B were then measured in the VG 354 TIMS in an identical manner as for the Laboratory Standard. The means of the isotopic composition of replicate analyses of PS-A and PS-B are listed in Table II, the uncertainties of the means are at the 1s level. The isotope abundances of the ^{92}Mo and ^{98}Mo primary solutions and their atomic weights were calculated from these isotope ratios.

Four aliquots of the primary solutions PS-A and PS-B were accurately weighed and thoroughly mixed to produce a number of mixed solutions AB 1 to 4, covering a range in the $^{92}\text{Mo}/^{98}\text{Mo}$ ratio isotope abundance ratio. The $^{92}\text{Mo}/^{98}\text{Mo}$ isotope abundance ratios in each mixture can be written as follows:

$$\left(\frac{92}{98}\right)_{\text{mix}} = \frac{(\#92 \text{ atoms})_{\text{PS-A}} + (\#92 \text{ atoms})_{\text{PS-B}}}{(\#98 \text{ atoms})_{\text{PS-A}} + (\#98 \text{ atoms})_{\text{PS-B}}} \quad (1)$$

where "PS-A" and "PS-B" signify the primary spike solutions A and B, respectively. The number of atoms of ^{92}Mo and ^{98}Mo from each of the primary spike mixtures can be calculated from

$$\#92 \text{ atoms} = \frac{(\text{weight of solution added}) \times (\text{concentration of Mo in solution}) \times (\text{At.\%92}) \times N_A}{(\text{At. weight of Mo in solution})} \quad (2)$$

and

$$\#98 \text{ atoms} = \frac{(\text{weight of solution added}) \times (\text{concentration of Mo in solution}) \times (\text{At.\%98}) \times N_A}{(\text{At. weight of Mo in solution})}, \quad (3)$$

TABLE III. Details of the sample weights of primary solutions PS-A (^{92}Mo) and PS-B (^{98}Mo), for the four mixtures AB 1 to 4, together with their gravimetrically calculated and experimentally measured $^{92}\text{Mo}/^{98}\text{Mo}$ ratios, and the exponential fractionation factors f for each mixture. The tabulated uncertainties are at the 1s level.

Mixture	Amount of PS-A (g)	Amount of PS-B (g)	Calculated $^{92}\text{Mo}/^{98}\text{Mo}$	Measured $^{92}\text{Mo}/^{98}\text{Mo}$	Fractionation factor f
AB1	2.10480 ± 0.00001	0.84840 ± 0.00001	2.2028 ± 0.0011	2.258 ± 0.023	-0.39 ± 0.16
AB2	0.95650 ± 0.00001	1.77130 ± 0.00001	0.48483 ± 0.00023	0.4960 ± 0.0015	-0.36 ± 0.05
AB3	1.05500 ± 0.00001	1.13340 ± 0.00001	0.83323 ± 0.00039	0.8505 ± 0.0069	-0.32 ± 0.13
AB4	1.63260 ± 0.00001	1.01760 ± 0.00001	1.43074 ± 0.00069	1.4613 ± 0.0094	-0.33 ± 0.10
				Mean	-0.35 ± 0.02

where N_A is the Avogadro number. The $^{92}\text{Mo}/^{98}\text{Mo}$ ratios for the four mixtures could be calculated from the weighed amounts and concentrations of the primary solutions and the measured isotopic composition of the enriched isotopes ^{92}Mo and ^{98}Mo . The relevant data for the amounts of solution combined to make the four mixtures are given in Table III.

The isotopic composition of each of the four mixed solutions AB were measured on four separate occasions using the same mass spectrometric procedures as before, and the means of the $^{92}\text{Mo}/^{98}\text{Mo}$ ratios are given in Table III, with uncertainties at the 1s confidence level. The measured $^{92}\text{Mo}/^{98}\text{Mo}$ ratios for each of the four mixed solutions AB were compared with the calculated $^{92}\text{Mo}/^{98}\text{Mo}$ ratios using an exponential mass fractionation law to calculate a fractionation factor f :

$$\left(\frac{^{92}\text{Mo}}{^{98}\text{Mo}}\right)_{\text{measured}} = \left(\frac{^{92}\text{Mo}}{^{98}\text{Mo}}\right)_{\text{calculated}} \left(\frac{\text{Mass } ^{92}\text{Mo}}{\text{Mass } ^{98}\text{Mo}}\right)^f, \quad (4)$$

where f was calculated as -0.34 ± 0.02 . Since the measured isotope compositions of the two primary solutions were also affected by mass fractionation and these data were used to calculate the $^{92}\text{Mo}/^{98}\text{Mo}$ ratios for each of the four mixed solutions, the isotope abundance ratios of the primary spike solutions were corrected using the exponential mass fractionation law and the fractionation factor f given above. The mass fractionation corrected isotope abundances for the two primary solutions are given in Table IV. These data were then used to calculate revised $^{92}\text{Mo}/^{98}\text{Mo}$ isotope abundance ratios and fractionation factors for the four mixtures in Table III. The mean of the four f values was -0.35 ± 0.02 .

B. Laboratory standard

The laboratory standard Mo was measured on a number of occasions on the VG TIMS under as identical mass spectrometric conditions as possible. 11 replicate analyses of the laboratory standard are listed in Table V. Each replicate analysis comprised 150 ratios for each isotope. The grand mean of the 11 Mo isotope analyses was calculated and listed in Table V. The uncertainties of the mean of each isotope ratio are at the 1s level. The isotope fractionation correction factor, $f = -0.35 \pm 0.02$, determined by calibrating the TIMS

with the ^{92}Mo and ^{98}Mo enriched isotopes, was applied to the measured isotope ratios to give a fractionation-corrected set of isotope ratios for Mo, which are listed in Table VI. The 1s uncertainties associated with the fractionation-corrected isotope ratios were derived by applying the uncertainty of f to the mean of the uncorrected values, taking into account the uncertainties of the means of the measured ratios. The corrected isotope abundances were combined to give the ‘‘absolute’’ isotopic composition of Mo, which in turn enabled the atomic weight of Mo to be calculated to be $A_r(\text{Mo}) = 95.9602 \pm 0.0023$ (1s) using the relative atomic masses of Audi *et al.* [24]. These data are given in Table VII.

The p -process nuclides are those stable isotopes with $A \geq 74$ that lie on the proton-rich side of the valley of nuclear stability, and are bypassed by neutron capture chains. As a group, they are the rarest of all the stable isotopes, but the p -process nuclides of Mo have a high abundance in relation to the group as a whole. The stability of ^{92}Mo may, in part, be explained by the fact that it has a closed neutron shell ($N = 50$). A coherent theory of p -process nucleosynthesis has been a controversial topic since Burbidge *et al.* [1] proposed that they were produced in H-rich layers of Type II supernovae where (p, γ) and (γ, n) reactions on s - and r -process seed nuclei occurred. It has since been proposed that p -process nucleosynthesis took place in explosive environments at temperatures of 2 to 3×10^9 K where photodisintegration

TABLE IV. Isotopic composition of samples PS-A and PS-B (in atom %), determined from the isotope ratios given in Table II and an initial calculation of the fractionation factor f . The uncertainties are reported at the 1s level.

Isotope	PS-A (%)	PS-B (%)
92	97.223 ± 0.040	0.1374 ± 0.0030
94	0.7250 ± 0.010	0.1058 ± 0.0022
95	0.5757 ± 0.0098	0.2088 ± 0.0033
96	0.4517 ± 0.0089	0.3382 ± 0.0046
97	0.2116 ± 0.0045	0.5508 ± 0.0077
98	0.4968 ± 0.0098	98.344 ± 0.018
100	0.3163 ± 0.0062	0.3149 ± 0.0044
Atomic weight (u)	92.0223 ± 0.0017	97.88071 ± 0.00029

TABLE V. 11 replicate analyses of the isotope abundance ratios of the Mo Laboratory Standard as measured with the VG 354 TIMS.

Analysis no.	$^{92}\text{Mo}/^{95}\text{Mo}$	$^{94}\text{Mo}/^{95}\text{Mo}$	$^{96}\text{Mo}/^{95}\text{Mo}$	$^{97}\text{Mo}/^{95}\text{Mo}$	$^{98}\text{Mo}/^{95}\text{Mo}$	$^{100}\text{Mo}/^{95}\text{Mo}$
1	0.92528	0.57943	1.05107	0.60302	1.52816	0.61283
2	0.92639	0.57968	1.04825	0.60138	1.52387	0.60925
3	0.93034	0.58024	1.04882	0.60102	1.52006	0.60654
4	0.92798	0.57992	1.04808	0.60103	1.52198	0.60831
5	0.92632	0.57962	1.04862	0.60251	1.52453	0.61012
6	0.92966	0.58072	1.04849	0.60119	1.52152	0.60771
7	0.92352	0.57898	1.05059	0.60359	1.53130	0.61434
8	0.93061	0.58069	1.04908	0.60066	1.51990	0.60677
9	0.92533	0.57926	1.04946	0.60216	1.52595	0.61117
10	0.93466	0.58126	1.04754	0.59869	1.51349	0.60216
11	0.92278	0.58004	1.04715	0.60304	1.52598	0.61232
mean	0.9275	0.57999	1.0488	0.6017	1.5233	0.6092
1s	0.0035	0.00069	0.0012	0.0014	0.0048	0.0035

of heavier nuclei took place in supernovae experiencing C and O “burning” [25].

Hayakawa *et al.* [26] point out that a number of nuclear processes have been proposed for the origin of p -process nuclides. These include Type I X-ray bursts in neutron stars, the rp -process in novae, cosmic-ray spallation reactions, photodisintegration reactions, and neutrino-induced reactions in supernovae explosions. However, the most successful of the theories involve p -process nucleosynthesis in O/Ne layers of Type II supernovae [27], in terms of matching the theoretical abundances with Solar System abundances, although a serious shortcoming is the underproduction of the p -process isotopes of Mo and Ru. Costa *et al.* [28] argue that the problem may be overcome by assuming an increase in the $^{22}\text{Ne}(\alpha, n)^{25}\text{Mg}$ reaction rate, which can possibly be accommodated within the uncertainties of the nuclear parameters of this reaction. Arnould and Coriely [27] also argue that an increase in this reaction rate could, at least, partially explain the underproduction of $^{92,94}\text{Mo}$ and $^{96,98}\text{Ru}$. It is therefore of importance to have an accurate knowledge of the Solar System abundances of the p -process nuclides of Mo.

Anders and Grevesse [29] recommended a Solar System abundance for Mo of 2.55 (based on a scale in which $\text{Si} = 10^6$ atoms). This value was derived from the elemental abundance of Mo in Type C1 carbonaceous chondrites (of $928 \mu\text{g/g}$), and from an analysis of solar photospheric abundances. It has been shown that these primitive meteorites closely approximate the condensable fraction of primordial Solar System material [30]. Previous analyses of Mo in the C1 chondrite Orgueil cover a

range of abundance from $880 \mu\text{g/g}$ to $1.5 \mu\text{g/g}$ using neutron activation analysis, with a selected value of $928 \pm 50 \mu\text{g/g}$ [29]. The Isotope Dilution Mass Spectrometric technique (IDMS) has been used in this Laboratory to measure the elemental abundance of Mo in three separate aliquots of Orgueil and two aliquots of another C1 chondrite, Ivuna to give a mean value of $909 \pm 40 \mu\text{g/g}$ [31]. If we combine the two sets of C1 data, we obtain a revised value of $915 \pm 30 \mu\text{g/g}$ which gives a Solar System abundance value for Mo of 2.51 (with respect to $\text{Si} = 10^6$ atoms). This revised value enables the Solar System abundances of the isotope abundances of Mo to be determined, using the “absolute” isotopic composition of Mo, as listed in Table VII, to be $^{92}\text{Mo} = 0.364 \pm 0.012$, $^{94}\text{Mo} = 0.230 \pm 0.008$, $^{95}\text{Mo} = 0.398 \pm 0.014$, $^{96}\text{Mo} = 0.418 \pm 0.014$, $^{97}\text{Mo} = 0.241 \pm 0.008$, $^{98}\text{Mo} = 0.612 \pm 0.021$, and $^{100}\text{Mo} = 0.247 \pm 0.009$. In particular, the Solar System abundances of the p -process nuclides ^{92}Mo and ^{94}Mo are 0.366, and 0.230, respectively, which should be used in future p -process nucleosynthetic calculations, rather than the existing values of 0.378 ± 0.021 and 0.236 ± 0.013 , respectively [27]. The s-only nuclide ^{96}Mo has a revised Solar System abundance of 0.418 in contrast to the existing value of 0.406 [29]. An alternative evaluation of Solar System abundances has recently been published by Lodders [32] in which the best currently available photospheric abundances have been selected together with meteoritic C1 chondrite data. Lodders [32] recommends a Solar System abundance for Mo of 2.601. The isotopic Solar System abundances detailed by Anders and Grevesse [29], Lodders [32] and this work are listed in Table VIII.

TABLE VI. Means and propagated uncertainties for the fractionation-corrected isotope abundance ratios of the 11 analyses of the laboratory standard. The uncertainties of the means are at the 1s level.

$^{92}\text{Mo}/^{95}\text{Mo}$	$^{94}\text{Mo}/^{95}\text{Mo}$	$^{96}\text{Mo}/^{95}\text{Mo}$	$^{97}\text{Mo}/^{95}\text{Mo}$	$^{98}\text{Mo}/^{95}\text{Mo}$	$^{100}\text{Mo}/^{95}\text{Mo}$
0.9171(9)	0.57783(33)	1.0527(12)	0.6061(3)	1.5401(8)	0.6203(35)

TABLE VII. Absolute isotope compositions and atomic weights of the laboratory standard determined in this work are listed together with the currently accepted values from Böhle *et al.* [19]. The uncertainties from this work are given as 1s, those from [19] are 2s.

Isotope	This work	Ref. [19]
92	14.5246(15)	14.769(1)
94	9.1514(74)	9.228(1)
95	15.8375(98)	15.9022(4)
96	16.672(19)	16.676(7)
97	9.5991(73)	9.5618(7)
98	24.391(18)	24.1959(6)
100	9.824(50)	9.6671(4)
Atomic weight (u)	95.9602(23)	95.94(2)

IV. CONCLUSIONS

The “absolute” isotopic composition of Mo was determined using a VG 354 TIMS whose linearity was demonstrated using Sr isotopically-certified reference material, NIST 987, together with good abundance sensitivity in the mass region $90 \leq A \leq 102$. Special attention was paid to monitor potential isobaric interferences from $^{92,94,96}\text{Zr}$ and $^{96,98,100}\text{Ru}$, but no evidence of isobaric interferences were ever observed. Two highly enriched isotopes ^{92}Mo and ^{98}Mo , were used to calibrate the mass spectrometer used in this experiment, which enabled the isotope fractionation of the Mo isotopes to be determined. This isotope fractionation correction factor was then applied to the other measured isotope ratios to give a final “absolute” isotopic composition in which the isotope abundances are $^{92}\text{Mo} = 14.5246 \pm 0.0015$; $^{94}\text{Mo} = 9.1514 \pm 0.0074$; $^{95}\text{Mo} = 15.8375 \pm 0.0098$; $^{96}\text{Mo} = 16.672 \pm 0.019$; $^{97}\text{Mo} = 9.5991 \pm 0.0073$; $^{98}\text{Mo} = 24.391 \pm 0.018$; and $^{100}\text{Mo} = 9.824 \pm 0.050$. These values should be evaluated by CIAAW to consider their inclusion in a future Table of Isotopic Compositions of the Elements, as the best value from a single terrestrial source. If the Solar System abundance of 2.51 for Mo (with respect to $\text{Si} = 10^6$ atoms) is adopted, the Solar

TABLE VIII. A comparative listing of the Solar System abundances for the Mo isotopes as detailed by [29,32] and from this work, on a scale in which $\text{Si} = 10^6$ atoms. The Uncertainties listed are at the 1s level. No uncertainties were given by [32].

Isotope	Reference [29]	Reference [32]	This work
92	0.378 ± 0.021	0.386	0.364 ± 0.012
94	0.236 ± 0.013	0.241	0.230 ± 0.008
95	0.406 ± 0.022	0.414	0.398 ± 0.014
96	0.425 ± 0.023	0.434	0.418 ± 0.014
97	0.244 ± 0.013	0.249	0.241 ± 0.008
98	0.615 ± 0.034	0.628	0.612 ± 0.021
100	0.246 ± 0.014	0.251	0.247 ± 0.009
Total	2.55	2.60	2.51

System abundances of the seven Mo isotopes are as follows $^{92}\text{Mo} = 0.364 \pm 0.012$, $^{94}\text{Mo} = 0.230 \pm 0.008$, $^{95}\text{Mo} = 0.398 \pm 0.014$, $^{96}\text{Mo} = 0.418 \pm 0.014$, $^{97}\text{Mo} = 0.241 \pm 0.008$, $^{98}\text{Mo} = 0.612 \pm 0.021$, and $^{100}\text{Mo} = 0.247 \pm 0.009$, using the absolute isotopic composition determined in this experiment. The Solar System abundances for the two *p*-process nuclides $^{92,94}\text{Mo}$ and the *s*-only process nuclide ^{96}Mo are of importance in nuclear astrophysics, and these values should therefore be adopted in future nucleosynthetic calculations. If the relative atomic masses of Audi *et al.* [24] are used together with the fractionation-corrected isotope abundances of Mo, an atomic weight of 94.9602 ± 0.0023 (1s) can be calculated. The atomic weight of Mo determined in this experiment, is just beyond the current uncertainty interval of the presently-accepted Standard Atomic Weight $A_r(\text{Mo}) = 95.94 \pm 0.02$.

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