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Molybdenum isotope mass fractionation in iron meteorites

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ABSTRACT

An examination of the isotope fractionation of molybdenum in a range of iron meteorites has been carried out by thermal ionization mass spectrometry incorporating the double spike technique. Ten iron meteorites were dissolved in hydrochloric acid and double spiked with a ^{92}Mo–^{98}Mo mixture of enriched isotopes. An ion exchange-based chemical separation process was then used to remove any vestiges of zirconium and ruthenium from the samples, so as to eliminate any possibility of isobaric interferences, and to provide a final molybdenum extract suitable for mass spectrometric analysis. The molybdenum from each extracted meteorite was analysed under similar mass spectrometric conditions to a Laboratory Standard. The double spike technique enabled the magnitude of the isotope fractionation in the meteorites to be determined with high accuracy relative to the Laboratory Standard, whose absolute isotopic composition is known. The ten iron meteorites gave isotope fractionations in the range −0.5‰ to +1.2‰/mass unit with respect to the terrestrial standard, the isotopic composition of which is identical, within experimental uncertainty, to other terrestrial samples.

1. Introduction

The influential review by Reynolds [1] demonstrated that the isotopic composition of a range of elements in a number of meteorites was found to be identical, within experimental uncertainties, to terrestrial values, once the effects of cosmic ray spallation, radioactive decay and mass-dependent fractionation were eliminated. This led to the hypothesis that the early solar nebula was isotopically homogeneous and that the protoplanetary disk was made of material that condensed from a hot, well-mixed nebula gas [2]. In the early 1970s, this paradigm came under increasing scrutiny after Clayton et al. [3] reported unusual isotope effects on oxygen in refractory calcium–aluminium-rich inclusions (CAIs) in carbonaceous chondrites that were attributed to nucleosynthetic effects. This discovery was followed by numerous cases of isotopic heterogeneity in meteoritic materials in a diversity of elements in which the observed isotopic anomalies were the result of nucleosynthetic effects (e.g., [4]). This research provided evidence that the early solar nebula contained presolar material that had not condensed from a hot nebula gas [5].

Molybdenum has proven to be an interesting element in regard to the question of isotopic heterogeneity in the early solar nebula. The nucleosynthetic processes that produced the isotopes of Mo are discussed by Burbidge et al. [6]. Molybdenum is, in most respects, an ideal element to examine evidence for isotope fractionation, in that it possesses seven isotopes spanning a mass range from 92 to 100 (see Fig. 1). The Mo isotopes cover a mass range of approximately 8% and range in atomic abundance from 9.15% to 24.39% [7]. The relative abundances of the Mo isotopes are of the same order of magnitude, which is an advantage for mass spectrometric analysis. Furthermore, Mo can be analyzed reliably and with good sensitivity, by thermal ionization mass spectrometry (TIMS) [8].

Murthy [9] investigated the isotopic composition of Mo in a number of iron meteorites and reported that some of them displayed a systematic depletion in the light isotopes with respect to the heavy isotopes, as compared to terrestrial samples. In the case of the Aroos meteorite the ^{92}Mo/^{100}Mo ratio was approximately 7% less than the terrestrial value, which was attributed to isotope mass fractionation. A number of isotope studies of iron meteorites have subsequently been reported. Yin et al. [10] measured the isotopic composition of Mo in five iron meteorites, but found no anomalies. Dauphas et al. [11] analysed 14 bulk iron meteorites, two pallasites and one mesosiderite. These authors reported finding small isotopic anomalies in these samples, and concluded that large scale inherited isotope heterogeneity in Mo of the presolar nebular had occurred. They did not report any evidence of isotope fractionation in these iron meteorites.

Wetherill [12] was one of the first to report a double spiking experiment, which he undertook to examine the claim by Murthy [9] that Mo showed evidence of isotope fractionation in some iron meteorites. Wetherill [12] refuted the experimental results

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of Murthy [9], arguing that the results were caused by instrumental fractionation and not by natural processes. Wetherill [12] stated that no differences greater than 1% were found between the ^{92}Mo/^{100}Mo ratios of meteoritic and terrestrial Mo, but his conclusion was constrained in that the sum of his experimental uncertainties was approximately ±1%. Wetherill [12] pointed out that a definite improvement in experimental technique would be needed for further investigation of this problem, and that the question of the absolute isotopic composition of Mo remained unanswered.

There is increasing interest in isotope fractionation studies of the "non-traditional elements", particularly the transition elements Fe, Ni, Cu, Zn and Mo, because of their potential value in biogeochemical and ore genesis studies. If such fractionation effects are associated with the metabolic activity of these elements, they can provide biosignatures in the geological record [13]. Isotope fractionation studies of Mo have proven to be of value in the genesis of molybdenites and in quantifying redox conditions in paleoenvironments [13]. It has been shown that mass fractionation of up to 1‰/u caused by redox reactions was found in marine environments that mark variations in the oxidation state of the oceans [14]. It has also been shown that fractionation of Mo isotopes of similar magnitude occurs in molybdenites [15]. Thus, mass-dependent fractionation of Mo isotopes not only occurs in low temperature environments, but also during high temperature magmatic processes. The fractionation of Mo in iron meteorites, originally reported by Murthy [9], therefore requires confirmation at the ‰/u level, commensurate with the magnitude of isotope fractionation found in other high temperature environments. This implies the need to develop chemical and mass spectrometric procedures in conjunction with the double spike technique, to achieve this level of accuracy.

It is the objective of this experiment to repeat the work of Wetherill [12] using modern mass spectrometric techniques and double spiking, so that the experimental uncertainties reported in this paper, are significantly reduced compared to the work of Wetherill [12]. The second objective of this study is to place the isotope fractionation methodology for Mo in these iron meteorites, on an absolute rather than a relative basis, by using a TIMS that was calibrated by gravimetric mixtures of enriched isotopes [16]. A range of iron meteorites has been chosen in order to identify which chemical groups, if any, exhibit isotope fractionation.

2. Experimental procedures

Fig. 1 shows that Mo isotopes have a number of isobaric nuclides in Zr and Ru that could cause a potential interference problem in the analysis of the isotopic composition of Mo. The isotopes ^{92,94,96}Zr are isobaric with the three corresponding Mo isotopes, as are the isobaric nuclides ^{96,98,100}Ru. In order to eliminate any possibility of isotope interferences, it is essential that each iron meteorite sample is subjected to an ion exchange separation procedure which not only removes any vestiges of Zr and Ru, but produces a Mo extract in a form suitable for TIMS analysis such that the sample may be deposited on Re filaments and achieve stable Mo$^+$ ion beams of 10^{-12} A over several hours.

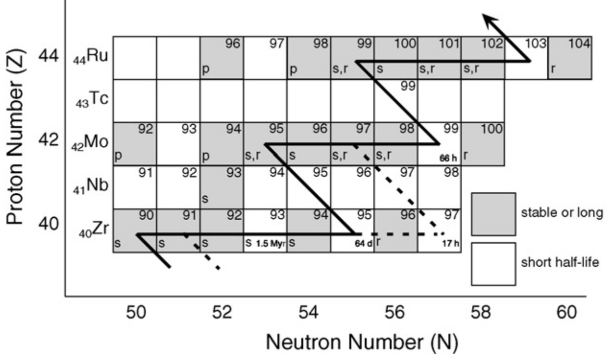

Fig. 1. The chart of the nuclides in the mass region of Mo showing the isobaric nuclides ^{92,94,96}Zr and ^{96,98,100}Ru.

2.1. Laboratory standard

At present there is no internationally accepted isotopic Reference Material for Mo. A Mo metal solution was therefore prepared from a 99.993% pure Mo metal rod (Johnson Matthey Chemicals Ltd., Laboratory Number S-8555). A section of the rod was lightly cleaned in HNO_3, washed in quartz-distilled water, dried and weighed. The sample was then dissolved in a 3:1 mixture of ultra-pure HCl:HNO_3. The solution was evaporated to dryness, redissolved in 10 M HCl, and evaporated to dryness. The residue was taken up in 4 M HCl at a Mo concentration of approximately 1 μg/mg of solution, ready for analysis by TIMS. This Laboratory Standard has been distributed to other laboratories to enable inter-laboratory comparisons to be made, but the need for an internationally accepted Reference Material still remains. The Laboratory Standard used in this project has been adopted in other projects involving the analysis of the isotopic composition of Mo in laboratory reagents [8], zircons [17], and molybdenites [15]. No differences in the analysis of these terrestrial samples from our Laboratory Standard were identified within the experimental uncertainties of the various experiments.

2.2. Sample dissolution

The discovery of isotopically anomalous Ag in iron meteorites only occurred when it was realised that the surface layers of the meteorite needed to be removed in order to eliminate terrestrial surface contamination, which is often encountered in specimens which are "finds" or those which have been stored for long periods of time [18]. Thus great care was taken to remove the outer layer of each iron meteorite sample analysed in this project, by dissolving the outer layer in 6 M HCl. The remaining sample was then washed with quartz-distilled water, before dissolving 0.3–1.5 g of the sample in 6 M HCl. The supernatant was then transferred immediately to the anion exchange column whilst the Fe was still in the Fe^{++} state. The oxidation state of the iron was verified by noting the bright green colour of the solution. No attempt was made to analyse the insoluble residue, which only made up approximately 0.1% by weight of the total sample. Troilite inclusions were also avoided as Mo has an affinity for troilite as shown in the work of Wieser and De Laeter [19]. Thus the data given in this project are for the metal phase of iron meteorites.

2.3. Ion exchange chemistry

Each sample was dissolved in 4 M HCl and loaded on an anion exchange column (AG1-X8, 100–200 mesh) that had been equilibrated with 4 M HCl prior to the addition of the sample. Molybdenum, Ru and Fe^{+++} were retained by the anion resin when washed with 5 column volumes of 4 M HCl, but Zr, Fe^{++}, Ni and Co were eluted at this stage. Molybdenum and Fe^{+++} were eluted from the anion column by washing the resin with two column volumes of 0.5 M HCl [8,20]. The eluate was collected in an acid-cleaned Teflon beaker and the solution slowly taken to dryness under a heat lamp. A second small anion exchange column was used to eliminate any remaining Zr after the primary anion column step, following the same elution procedure as before. The residue was dissolved in 0.3 g of 0.5 M HCl and loaded on a small cation exchange column (AG 50W-X8, 200–400 mesh), that had been equilibrated with this acid concentration. Molybdenum was eluted from the resin with two column volumes of 0.5 M HCl and taken to dryness, ready for TIMS analysis. This ion exchange procedure not only eliminated Zr and Ru, but also produced an extract in a form suitable for mass spectrometric analysis, because the molybdenum salt could be dissolved easily in microlitre quantities of 4 M HCl for deposition on Re filaments, and this chemical form promoted the formation of stable Mo^+ ion beams.

The extraction efficiency for the entire chemical separation was approximately 76% and the procedural blank was 10 ± 2 ng Mo, as measured by the isotope dilution method. Isotope Dilution Mass Spectrometry (IDMS) is a proven, reliable analytical technique for trace element determinations [21,22]. The efficiency of the chemical procedure was obtained by putting a known amount of the Laboratory Standard through the complete extraction process, and then spiking the final extract with a gravimetric amount of an enriched isotope of Mo whose isotopic composition was known. The amount of Mo in the final extract could then be determined, and the efficiency calculated by comparing this value with the original amount of Mo placed on the anion exchange column. One of the advantages of IDMS is that once the spike and sample have been equilibrated, one does not require a high quantitative recovery of the element. The procedural blank was determined by putting a known amount of the enriched isotope through the same chemical extraction procedure, measuring the isotopic composition of the final extract, and calculating the amount of Mo that had been acquired in the extraction process.

2.4. *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 1 μg of the Laboratory Standard solution was deposited on a single, previously outgassed Re filament. Two millilitres of the ascorbic acid + HCl solution was placed on top of the Mo Laboratory Standard, and the filament was heated with a 1.5 A current to dry the mixture. The filament assembly was loaded into the ion source of a VG 354 TIMS equipped with nine moveable Faraday cup collectors and an axial Daly detector.

Each filament assembly was degassed by heating the filament to 1.8 A. These conditions were maintained for 20 min. The filament temperature was slowly increased to 1550 °C at which point Mo ion beams could be focussed and the measurements commenced. Typically, a 1 μg load of Mo on the filament at a temperature of 1550 °C produced ion current intensities of 10^{-12} A, and this ion beam intensity can be maintained for several hours. 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 with the Daly detector, because the ^{90}Zr ion beams were too small to be detected by Faraday cup collection. Data was only utilized if the ^{90}Zr ion beam was <0.1% of the ^{98}Mo ion beam intensity and no effect from possible ^{90}Zr interference was ever observed over the duration of the analysis period. Isobaric interferences from Ru were checked by monitoring the ion current at m/q 99, but no Ru isotopes were observed for any of the samples. For each sample, 100 ratios were collected in 5 blocks of 20 ratios. The analytical procedure is described in full detail by Wieser and De Laeter [8].

2.5. *Double spiking*

The double spike technique, which is an essential feature of this experiment, provides an internal monitor of chemical and instrumental mass fractionation, provided the element comprises at least four isotopes. A geometrical interpretation of double spike systematics provides both the magnitude of the isotope fractionation and the concentration of Mo in the relevant sample [23]. The magnitude of the isotope fractionation of the sample is determined relative to that of the Laboratory Standard, with the uncertainty of the measurement estimated using a Monte Carlo approach [24]. An inherent characteristic of TIMS is time-dependent mass fractionation, occurring mainly in the ion source by Rayleigh distillation effects. The double spike technique enables the resulting isotopic data to be corrected for mass fractionation introduced by chemical processing of the samples (provided the double spike is introduced at the beginning of the chemical separation procedure) and the subsequent measurement by TIMS.

The input data required by the Russell [23] method are the measured isotope ratios for the Laboratory Standard, the Double Spike, the mixture of the Double Spike with the Laboratory Standard, and the mixture of each sample with the Double Spike. Two isotopically enriched Mo isotopes were obtained from the Oak Ridge National Laboratory, one enriched in ^{92}Mo to 97.31%, and the other enriched in ^{98}Mo to 98.15%, as stated by ORNL. Gravimetric amounts of these two isotopically enriched samples were taken into solution and mixed to form the Double Spike solution used in the experiment. Full details of preparing and characterizing the isotopic composition of the Double Spike are given by Wieser and De Laeter [16]. The reference isotope chosen for this experiment was ^{95}Mo, as this mass does not have any isobars. In the case of Mo, which possesses seven isotopes, it is possible to use more than one set of isotopes to validate the results. Thus, two sets of isotope ratios were used to compute the isotope fractionation of each sample (^{92}Mo/^{95}Mo, ^{97}Mo/^{95}Mo, ^{98}Mo/^{95}Mo and ^{92}Mo/^{95}Mo, ^{98}Mo/^{95}Mo, ^{100}Mo/^{95}Mo). The second set of isotope ratios gave more accurate results, presumably because there are five mass units difference between ^{95}Mo and ^{100}Mo as compared to the two mass unit difference between ^{95}Mo and ^{97}Mo, but the two sets of data are in good agreement. Two different gravimetric mixtures of the Double Spike with the Laboratory Standard were employed in the calculation of the mass fractionation values. In all cases, the results were identical within analytical uncertainty. The isotope amount ratios for the two Double Spike + Laboratory Standard mixtures are provided in Table 2. Note that different amounts of Double Spike and Laboratory Standard were combined to yield mixtures of different isotopic composition.

The Double Spike technique assumes that the sample is identical in every way to the Laboratory Standard except for mass-dependent variations in isotope fractionation. In the case of this suite of samples, no anomalous isotope abundances were observed from unspiked analyses of these iron meteorites. By adding the Double Spike to the Laboratory Standard, a reference value for the isotope fractionation can be calculated, which enables the isotope fractionation of each sample relative to the Laboratory Standard to be obtained. In this experiment, the absolute isotopic composition of the Laboratory Standard was known, as detailed in Wieser and De Laeter [16]. Thus, the ^{98}Mo/^{95}Mo isotope amount ratio of 1.5401 that is used to normalize the isotopic data is an absolute value. The Double Spike technique relies on the precise determination of the isotopic composition of the Laboratory Standard and Double Spike as well as the relevant mixtures. Therefore, for each of the samples, the Faraday collection system on the VG 354 TIMS was used to measure the ion currents simultaneously to optimise the precision of the isotopic data.

3. Results and discussion

Chemically induced mass fractionation can be produced in Mo unless the efficiency of the extraction procedure is very high [25]. Wieser et al. [26] have shown that the chemical separation

Table 1
The mean isotope ratios of Mo for the 12 analyses of the Laboratory Standard that were measured during this study were normalised to ^{98}Mo/^{95}Mo = 1.5401 [16]. Uncertainties in the isotope amount ratios for each analysis of the standard (standard errors of 100 ratios) are less than 1‰ at the 95% confidence level. Uncertainties of the isotope amount ratios of the mean values are given in parentheses and are the standard errors at the 95% confidence level.

Standard	92/95	94/95	96/95	97/95	98/95	100/95
1	0.9187	0.5783	1.0525	0.6060	1.5401	0.6203
2	0.9184	0.5779	1.0532	0.6064	1.5401	0.6198
3	0.9183	0.5781	1.0533	0.6064	1.5401	0.6193
4	0.9174	0.5777	1.0534	0.6063	1.5401	0.6204
5	0.9173	0.5763	1.0538	0.6070	1.5401	0.6209
6	0.9179	0.5779	1.0532	0.6063	1.5401	0.6197
7	0.9177	0.5773	1.0515	0.6056	1.5401	0.6190
8	0.9154	0.5765	1.0524	0.6071	1.5401	0.6213
9	0.9163	0.5775	1.0518	0.6063	1.5401	0.6210
10	0.9164	0.5766	1.0557	0.6066	1.5401	0.6222
11	0.9164	0.5766	1.0519	0.6073	1.5401	0.6205
12	0.9173	0.5764	1.0520	0.6058	1.5401	0.6215
Mean values	0.9173(6)	0.5773(5)	1.0529(7)	0.6064(3)	1.5401(8)	0.6205(6)

Table 2
The Mo isotope amount ratios of the Laboratory Standard ($n = 12$), Double Spike ($n = 2$), and two different mixtures of the Laboratory Standard with the double spike. The isotope amount ratios are normalised to ^{98}Mo/^{95}Mo = 1.5401 [16]. In the case of the Laboratory Standard, the uncertainties in parentheses are the standard errors for the 12 measurements. In the case of the data of the double spike and mixtures, the uncertainties are the standard errors for 100 isotope amount ratios measured. All uncertainties are at the 95% confidence level.

	92/95	94/95	96/95	97/95	98/95	100/95
Laboratory standard ($n = 12$)	0.9173(6)	0.5773(5)	1.0529(7)	0.6064(3)	1.5401(8)	0.6205(6)
Double spike	104.5(3)	0.9627(30)	1.0651(30)	1.3166(40)	202.2(4)	0.9131(30)
Replicate measurement	104.3(2)	0.9552(30)	1.0645(30)	1.3170(40)	201.6(4)	0.9117(30)
Mixture #1	4.115(2)	0.5939(4)	1.0502(6)	0.6226(6)	7.878(4)	0.6135(6)
Mixture #2	3.664(2)	0.5993(4)	1.0461(8)	0.6182(6)	6.925(4)	0.6082(8)

procedure used in this project introduces an isotope fractionation of approximately 0.14‰/u. Thus, it is essential that the Double Spike is added to the sample at the start of the chemical digestion process, particularly before the ion exchange procedure. This enables one to account for any chemically induced mass fractionation, which could possibly be of the same order of magnitude as natural isotope mass fractionation.

Twelve single Re filaments, each loaded with approximately 1 μg of the Laboratory Standard, were analyzed by TIMS over the course of this experiment. At least one Laboratory Standard sample was loaded with each set of filaments to ensure consistency of the analytical data. A strict heating and measurement procedure, as described above was followed, to ensure that all samples were analyzed under near to identical conditions as possible. This resulted in consistent and predictable isotopic behaviour for the different samples as listed in Table 1. The isotope composition of the Laboratory Standard measured in this experiment is within experimental uncertainty of the absolute isotope amount ratios measured previously (Wieser and De Laeter [16]).

The duplicate isotope measurements of the Double Spike, and the measurement of two different mixtures of the Laboratory Standard and the Double Spike (Mixture # 1 and # 2) are summarized in Table 2. Table 3 lists the measured isotope ratios for the mixtures of the Double Spike with each of the ten iron meteorite samples. In the case of Willow Creek, Mantos Blancos and Warburton Range, duplicate analyses were undertaken, so that the magnitudes of the isotope fractionation could be calculated with greater certainties. Table 4 lists the magnitude of the isotope fractionation of each of the ten iron meteorites as calculated from the data given in Tables 2 and 3. The isotope fractionation values listed in Table 4 are the means of separate calculations of the iron meteorites using Mixtures #1 and # 2 of the Laboratory Standard and Double Spike.

Table 3
The Mo isotope amount ratios measured for the meteorite and Double Spike mixtures for each of the ten meteorites. Full replicates include dissolution of the meteorite sample in HCl, addition of Double Spike, ion exchange, and analysis by TIMS. Uncertainties in parentheses are the standard errors from 100 measurements of the isotope amount ratios and are given at the 95% confidence level.

Standard	Type	92/95	97/95	98/95	100/95
Canyon Diablo	IA	6.1595(17)	0.6385(3)	11.9828(40)	0.6211(3)
Toluca	IA	3.6991(10)	0.6188(3)	7.0312(30)	0.6134(4)
Youndegin	IA	3.2457(13)	0.6163(4)	6.1470(20)	0.6158(4)
Carbo	IID	4.0684(10)	0.6230(3)	7.8363(20)	0.6162(3)
Kumerina	IIE	3.4368(20)	0.6194(5)	6.5567(35)	0.6175(6)
Henbury	IIIA	3.5331(14)	0.6197(3)	6.7501(20)	0.6183(3)
Willow Creek	IIIE	2.9340(12)	0.6110(3)	5.4123(20)	0.6023(3)
Full replicate		2.8531(8)	0.6146(3)	5.3606(12)	0.6124(3)
Mantos Blancos	IVA	2.2148(10)	0.6127(4)	4.1426(20)	0.6169(4)
Full replicate		3.7072(12)	0.6236(4)	7.1189(20)	0.6195(4)
Warburton Range	IVB	1.6203(3)	0.6012(2)	2.8494(7)	0.5982(2)
Full replicate		1.5510(6)	0.6034(3)	2.7290(10)	0.6027(4)
Mount Magnet	Anom	5.1763(15)	0.6322(3)	10.0105(30)	0.6184(4)

Table 4
Isotope fractionation of Mo in iron meteorites measured relative to the Laboratory Standard. Uncertainties in parentheses are the standard deviations at the 95% confidence level and were estimated using a Monte Carlo method (see text).

Standard	Type	Fractionation (‰/u)
Canyon Diablo	IA	+0.1 ± 0.4
Toluca	IA	−0.5 ± 0.9
Youndegin	IA	−0.5 ± 0.8
Carbo	IID	−0.2 ± 0.4
Kumerina	IIE	+0.4 ± 0.7
Henbury	IIIA	+0.0 ± 0.7
Willow Creek	IIIE	+1.2 ± 0.4
Mantos Blancos	IVA	+1.2 ± 0.5
Warburton range	IVB	+0.6 ± 0.6
Mount magnet	Anom	+0.4 ± 0.3

The uncertainties listed with the fractionation values are at the 95% confidence level, and include all the uncertainties in the various isotope ratios involved in the calculations of the fractionation and abundance results. A positive value for the mass fractionation implies that the abundances of the heavier isotopes in that sample are greater with respect to those of the Laboratory Standard. An examination of the magnitudes of the isotope fractionation listed in Table 4, shows that Willow Creek and Mantos Blancos samples exhibit mass fractionations of +1.2 ± 0.4‰/u and +1.2 ± 0.5‰/u, respectively. The Mount Magnet sample shows evidence of slight mass fractionation at 0.4 ± 0.3‰/u. The remaining meteorite samples investigated in this study show no mass fractionation relative to the Laboratory Standard within experimental uncertainties. This finding supports the conclusion of Wetherill [12] that mass-dependent isotope fractionation of the Mo isotopes of up to 1% per mass unit is observed in some iron meteorites. The data presented in this paper reflect a significant improvement in the accuracy with which the magnitude of these isotope fractionations were determined as compared to the work of Wetherill [12]. In contrast to earlier research, the mass fractionation data contained in this paper are based on an absolute scale, relative to the calibrated measurement of the Laboratory Standard.

4. Conclusions

It has been shown that Mo can display isotope fractionation effects at the permil per atomic mass unit level in both low temperature (e.g., [14]) and high temperature environments (e.g., [15]). Early work by Murthy [9] had shown evidence of significant isotope fractionation in iron meteorites, although this evidence was refuted by Wetherill [12]. The objective of this experiment was to examine the extent of natural isotope fractionation in a range of iron meteorites, to verify the original work of Wetherill [12], who showed that fractionation of the Mo isotopes existed of up to 1%/u, but with a significant improvement in accuracy as compared to his research. The isotope fractionation data of Wetherill [12] were based on an assumed ^{92}Mo/^{100}Mo ratio for his laboratory standard, as no absolute isotopic composition of Mo existed at that time. The isotope fractionation data reported in this paper, however, are based on the absolute isotopic composition of Mo determined by calibrating the VG 354 TIMS used in this study with a set of gravimetrically prepared mixtures of highly enriched isotopes of Mo [16].

A Double Spike comprising enriched ^{92}Mo and ^{98}Mo was added to each sample at the beginning of the ion exchange chemical extraction. This methodology allowed one to eliminate chemical and instrumental isotope fractionation effects and identify natural isotope fractionation. The ion exchange procedure adopted in this experiment eliminated the possibility of isobaric interferences in ^{92,94,96}Zr and ^{96,98,100}Ru and produced Mo in a form suitable for TIMS analysis. Mass spectrometric procedures were developed which enabled Mo to be accurately analysed by TIMS using an ascorbic acid activator. Accurate TIMS measurements of the isotopic composition of the Laboratory Standard, the Double Spike, the Mixture of the Laboratory Standard and the Double Spike, and mixtures of the Double Spike with each of the ten meteorites, enabled the magnitude of the isotope fractionation of each meteorite to be calculated using the double spike procedure of Russell [23].

Willow Creek and Mantos Blancos samples exhibit mass fractionation at a permil per mass unit level. The sample of Mount Magnet shows resolvable mass fractionation at sub-permil levels. The remaining meteorite samples do not exhibit mass fractionations that are different from the Laboratory Standard. The results support the conclusion of Wetherill [12] that isotope fractionation does occur in iron meteorites but with a significant improvement in accuracy as compared to the original research. This work also places the isotope fractionation data on an absolute scale, relative to the calibrated measurement of the Laboratory Standard. There is strong evidence that the Laboratory Standard used in this experiment is representative of the isotopic composition of Mo in terrestrial material. No conclusions can be drawn on this limited data set as to whether there is any correlation between the magnitude of isotope fractionation and the chemical groupings.

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