High Accuracy Measurement of Isotope Ratios of Molybdenum in Some Terrestrial Molybdenites

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The isotope ratios of molybdenum in molybdenites were studied. A special triple filament technique was used to obtain stable and lasting signals for Mo^+. There are no differences bigger than ± 0.4 parts per 10^4 among four samples and the standard. (*J Am Soc Mass Spectrom 1992, 3, 10–17*)

Molybdenum is a very interesting element because its seven isotopes can reflect several effects related to nuclear physics. The nuclear phenomena that may affect the isotope ratios in question are (1) the synthesis of seven isotopes of Mo involving three processes (r, s, and p) in the standard model of nucleosynthesis [1]; (2) the nuclear fission of uranium-238, which produces ^{95}Mo, ^{97}Mo, ^{98}Mo, and ^{100}Mo; and (3) the double-beta decays of ^{96}Zr and ^{100}Mo leading to ^{96}Mo and ^{100}Ru. Another intriguing property of this element is that the anomalous abundance of ^{97}Mo could be evidence for extinct ^{97}Tc which decayed through electron capture. Additionally, it was suggested that ^{97}Tc and ^{99}Tc can be engendered in molybdenites by the boron-8 solar neutrino flux, which could provide evidence for the first test of "nonstandard solar models" [2].

The isotope ratios of molybdenum of terrestrial and meteoritic origin were investigated with various approaches [3–11]. However, including measurement with the double-spike technique [9], few measurements of Mo isotope ratios with high reliability have been reported. The main difficulties could be because: (1) the first ionization potential of molybdenum (7.10 eV) is too high to yield high efficiency in ionization by traditional thermal ionization techniques; (2) a Mo sample loaded on a filament is volatilized very easily at the high temperatures usually available for surface ionization, and (3) the interference of molecular and atomic ions with mass range $m/z = 90$–104 can be too great for precise isotopic measurement. For the reasons mentioned above, little progress has been made in the field of measurement of isotope ratios of molyb-

denum thus far, in spite of the potential importance of research in isotopic abundance of molybdenum.

In this study we have established a method for securing stable and lasting current of Mo^+ and examined the mass fractionation of Mo isotopes during measurement. Based on these studies, the isotope ratios of Mo were determined with high precision for some molybdenites from a variety of locations throughout the world. The present study will afford a foundation for further precise studies of molybdenum isotopes involving meteorites and terrestrial rocks.

Experiment

Reagents

The water and hydrofluoric (HF), hydrochloric (HCl), nitric (HNO_3), and perchloric ($HClO_4$) acids used in the analyses were purified by subboiling distillation. The following chemical reagents and materials were used without further purification in the laboratory: ammonium hydroxide (NH_4OH) in which Mo is < 0.005 ppm, *bis*(2-ethylhexyl) hydrogen-phosphate (HDEHP), sulfuric acid (total content of metals < 5 ppb), molybdenum metal (99.99%), molybdenum trioxide (99.999% in metallic purity), and cyclohexane (high performance liquid chromatography grade).

Decomposition of Molybdenite and Chemical Treatment

A laboratory microwave oven, model MDS-81D (CEM Corp., Matthews, NC) was used to dissolve molybdenites. An accurately weighed quantity (0.3–0.5 g) of homogenized molybdenite powder (> 150 mesh) was added to a 120-mL Teflon digestion vessel. Approximately 5 g of distilled water, 5 g of 14 M HNO_3, and 3 g of concentrated H_2SO_4 were subsequently added to

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the vessel. The container cap was then immediately tightened and the container was placed in the microwave oven to be heated. For the sake of safety, the following heating program was arranged for the stages designated below: stages 1, 3, and 5 were 3 min at 20%, 30%, and 40% power, whereas stages 2 and 4 were 5 min at 0% power, respectively; full power for the microwave oven is 730 ± 70 W. Upon cooling in a refrigerator the container was opened and the solution was ready for chemical separation.

The Mo was separated from sulfuric-nitric solution by solvent extraction. This technique was chosen for this study because of its high efficiency, speed, and simplicity in separation of Mo from Zr, Ru (if present), and most other impure ions. Generally, after dissolution of molybdenites, molybdenum ions in perchloric or nitric solution exist in various complexes of Mo(VI), and these ions and zirconium will be extracted into a HDEHP-cyclohexane phase. For further separation of Zr from Mo, the back-extraction process is performed using 3% H_2O_2 in 10 M HNO_3. Thus, molybdenum ions can be reduced to lower valencies and back-extracted into the aqueous phase from HDEHP-cyclohexane, whereas Zr remains in the organic phase. This method was checked by inductively coupled plasma mass spectrometry for a solution containing Mo, Zr, and Ru. (In this examination, the concentrations of Zr and Ru were 100 times higher than that of Mo, but no interference from Zr and Ru was recognized in the solution finally obtained for isotopic analysis of Mo after chemical removal of Zr and Ru by the solvent extraction.)

The details of the chemical separation of Mo mentioned above are as follows: first, the solution in the 120-mL vessel was transferred into a 50-mL separation funnel, and 5 M $HClO_4$ was added to 20 mL of total aqueous solution. Then ~ 20 mL of 1 M HDEHP in cyclohexane was poured into the separatory funnel. After shaking for 5 min, the aqueous phase was removed to be discarded when separation of the immiscible phases was complete, and the organic phase was washed three times with 20 mL of 5 M $HClO_4$. Secondly, 20 mL of 3% H_2O_2 in 10 M HNO_3 was added to the organic phase, shaken about 5 min, then the HDEHP-cyclohexane was removed. The aqueous phase was transferred to a Teflon beaker and evaporated to dryness at 5% power in the microwave oven. Then the residue was dissolved in 3% NH_4OH and again evaporated to dryness at 5% power in the oven. The salt (ammonium paramolybdate) was taken up in water and diluted to ~ 10 μg/μL. This solution is loaded on the filament and dried for mass spectrometric measurement.

Chemical Treatment of Standard, Mo, and MoO_3

The chemical procedures for dissolution of molybdenum metal and oxide were very similar to that employed by Moore et al. [9], but a further purification of the solutions was carried out by a solvent extraction method as described above for molybdenite.

Mass Spectrometry of Molybdenum

All the isotopic analyses described here were performed on a VG sector 54-30 thermal ionization mass spectrometer (Manchester, UK). A triple filament technique was used for the molybdenum isotopic analyses, where no electric current was applied to the side filament loaded with the sample. No molecular interferences or zirconium and ruthenium ions were detected for the mass range m/z = 90–104 during ~ 5 h by a Daly multiplier detector below 4.5 A of central filament current with a source pressure of 2×10^{-8} torr. To reduce the Mo background emitted from the filament ribbon, the zone-refined Re ribbon (0.001 × 0.03 in) was degassed at 5.5 A for at least 30 min in vacuum. No detectable ($< 10^{-15}$ A) ^{98}Mo was observed at an operating temperature lower than 1750 °C (a dual-wavelength optical pyrometer was used to measure the temperature of the ionizing filament).

The molybdenum (see above) was loaded as ammonium paramolybdate together with 2 μL of a saturated aqueous solution of boric acid and 1 μL of 1 M HNO_3 on an outgassed side filament of zone-refined Re. Normally, 20 μg of molybdenum was sufficient to yield fairly stable ^{96}Mo ion intensity of 2×10^{-12} A at ~ 3.6 A of central filament current (~ 1750 °C) for ~ 5 h.

It was found that intense and stable Mo$^+$ ion current could be obtained in the following way: the central filament current was increased to ~ 2 A within 3–5 min, and to 3.0 A in 3 h, then increased very carefully until the ion intensity of ^{96}Mo was strong enough for measurement, with zero current to the side filament. These current settings effectively suppress the vapor pressure of molybdenum trioxide which is rather volatile and provide adequate intensity of Mo$^+$ ions.

Data acquisition was by peak jumping, using a single Faraday collector with a 10^{11} Ω resistor. Ion intensity for each mass was measured with 5-s integration time and 2-s magnet setting time. About 150 complete spectra were taken per run. Isotopic ratios were normalized to ^{98}Mo, and correction of mass fractionation was performed for each cycle of measurement of isotopic ratios by exponential law, using ^{94}Mo/^{98}Mo = 0.3802 (see below).

Data and Discussion

Admittedly, the choice of a pair of "reference" isotopes whose abundance can be considered fixed presents a problem. Also relevant is the problem of which isotope to take as a denominator of the ratio. From the viewpoint of nuclear physics, ^{92}Mo and ^{94}Mo can be the best choice as a "criterion" pair, because they are considered to be free from any nu-

clear and/or radiogenic effects. However, this pair has a drawback in that the small empirical error in measurement can be multiplied when the result of measurement is extrapolated to such high mass numbers as 98 and 100. Another possible drawback of the pair in question is that $^{92}Zr^+$ and $^{94}Zr^+$ can interfere with $^{92}Mo^+$ and $^{94}Mo^+$ ($^{94}Mo^+$ is more subject to the interference from Zr ions than is $^{92}Mo^+$).

After careful examination and various trials based on many measurements mainly on molybdenite samples, we have been led to a provisional conclusion that, as far as our measurements are concerned, of the pair of ^{94}Mo and ^{98}Mo, employing the latter as a denominator can be used for the corrections for mass fractionation because this choice yields the smallest variations in relative abundance ratios of the seven stable isotopes of molybdenum. (For the aforementioned reason, a very pure Re filament free from Zr should be chosen; we employed the zone-refined Re filament.)

It was necessary to examine several problems in parallel. Figure 1 illustrates the frequency distribution of ratio $^{94}Mo/^{98}Mo$ and the variation of $^{100}Mo/^{98}Mo$ against $^{94}Mo/^{98}Mo$ upon mass fractionation in two different situations. This diagram was prepared by combination of two series of measurements corresponding to two kinds of loading of Mo on the Re filament. It should be noted that in one series of measurements Mo metal was welded onto the Re central filament, whereas in another one the *same* Mo metal was chemically dissolved, treated with solvent extraction, and dried on the Re side filament. Each of two different loadings has its own characteristic distribution of isotopic ratios as shown in Figure 1, and the observed ratio of $^{94}Mo/^{98}Mo$ for compound molybdenum oxide is definitely lower than that for metal, in spite of the fact that the compound loaded on the filament was prepared by dissolution of the metallic

Mo which adhered to the filament. This systematic difference is difficult to explain, but no doubt the difference in chemical state affects the measured ratio. Besides, it is worthwhile to note that, for each of two loading series, as commonly observed, the values for heavier isotopes increase systematically and steadily with the time of measurement. Because it is practically easy to load molybdenum from solution, the solution loading is preferable to the metal loading in the metallic state.

Accordingly, we have chosen the $^{94}Mo/^{98}Mo$ ratio of 0.3802 as a normalizing value, based on the ratio distribution obtained for the "compound" loading. Many previous investigators usually used a value of 1.54, obtained by Murthy [5] from terrestrial materials, for the $^{92}Mo/^{100}Mo$ ratio to normalize the fractionation effect in the measurement of the isotopic abundance of molybdenum. In view of our data, the value of 1.54 for the $^{92}Mo/^{100}Mo$ ratio is too high to be used as a constant value for calculation of the fractionation factor. The corresponding value of $^{92}Mo/^{100}Mo$ obtained in our study is 1.519325, ~ 1% lower than Murthy's value. The uncertainties of measurement of the isotope ratios of molybdenum (~ 0.6%), and the atomic interference by ^{92}Zr emitted from the filament material are considered to be responsible for the analytical error in Murthy's work.

Our purpose was to determine precisely the relative isotopic abundances of all seven stable isotopes of molybdenum with mass numbers of 92, 94, 95, 96, 97, 98, and 100. As a matter of course, isotopic fractionation as shown in Figure 1 took place among these seven stable isotopes of molybdenum during the measurement. To get highly dependable values concerning the relative abundance ratios, an adequate correction must be applied to the observed data. Therefore, we have to find the mathematical formula that fits best the isotopic fractionation during the measure-
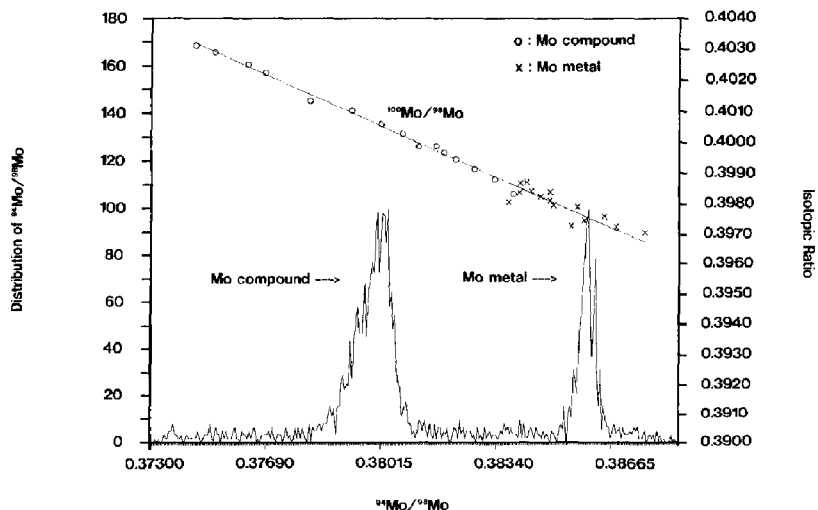
Figure 1. Frequency distribution of $^{94}Mo/^{98}Mo$ in 10 mass spectrometric analyses and the relative changes of $^{100}Mo/^{98}Mo$ upon mass fractionation through one of the measurements (solid line was calculated by exponential law) obtained by two different sample-loading techniques. The ratio distribution was normalized.

Table 1. Constants in all four fractionation laws[a]

	a	b	c
Exponential law	$\dfrac{\ln(M_2/M_3)}{\ln(M_1/M_3)}$	1	0
Power law	$\dfrac{(M_2 - M_3)}{(M_1 - M_3)}$	1	0
Linear law	1	$\dfrac{(M_2 - M_3)}{(M_1 - M_3)}$	1 − b
Rayleigh law	$\dfrac{1 - (M_3/M_2)^{(1/2)}}{1 - (M_3/M_1)^{(1/2)}}$	$\dfrac{(M_3/M_2)^{(1/2)}}{(M_3/M_1)^{(1/2)}}$	0

[a] The values of a, b, and c in all four fractionation laws are calculated by masses, not mass numbers, of nuclides concerned.

ment of isotope ratios. High precision isotopic analyses of strontium and neodymium have been studied through the use of a power law [12]. Hart and Zindler [13] tested various isotope fractionation laws using a mixture of equal amounts of four isotopes of calcium. To describe the isotopic fractionation effect, four laws, i.e., exponential law, power law, linear law, and Rayleigh law, have been proposed thus far. Considering that there is no sound theoretical basis for any of the fractionation laws, and there is no way to decide which law is the best in accounting for the isotopic fractionation of molybdenum isotopes, the four laws were investigated on the basis of data obtained that exhibit very wide ranges of fractionation. All four laws can be written in a general formula as follows:

$$Y_M / Y_T = b\{ X_M / X_T\}^a + c \qquad (1)$$

where X and Y denote the isotope ratios of masses M_1/M_3 and M_2/M_3, and suffixes T and M indicate an assumed "standard" ratio and a measured value, respectively. Mathematical definitions of a, b, and c are presented in Table 1.

To compare the relative degree of fit to the four laws in detail, we prepared Figure 2, where the lines are calculated by linear least squares on the deviations (ϵ units) of the observed $^{92}Mo/^{98}Mo$ ratios (15 blocks: one block involves 10 cycles) relative to that calculated from the normalizing $^{92}Mo/^{98}Mo$ ratio evaluated according to the exponential law (even if the calculation is made based on the normalizing ratio evaluated by other laws, it does not change the slope). It is evident that the Rayleigh model curve is not suitable here, and the data deviate significantly from the theoretical curve. In comparison with Rayleigh law, a better fit to the observed data was achieved by the power law and the linear law, but the best fit was obtained by the exponential law (the smallest slope). Figures 3 and 4 give the data for the same analysis, along with the curves for the exponential model, that are well fitted by the exponential law despite a 3% range of variation of $^{94}Mo/^{98}Mo$ over the time of measurement (4.5 h).

The Mo isotope data from repeated analyses of
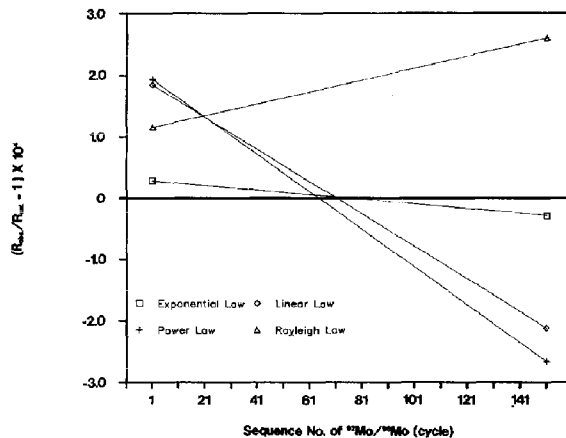
Figure 2. Comparison of exponential law, power law, linear law, and Rayleigh law using linear least squares on the data of $^{92}Mo/^{98}Mo$.
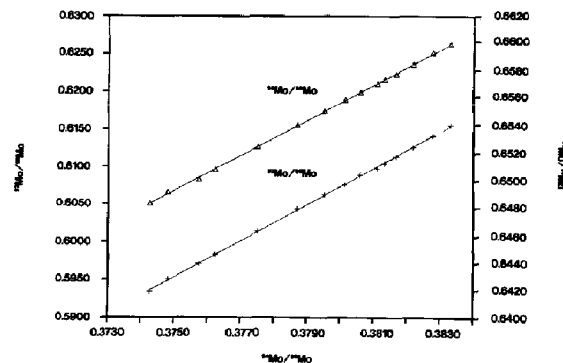
Figure 3. Relative changes of molybdenum isotope ratios upon mass fractionation. The ratios predicted by the exponential law are shown by the solid lines. Upper plot, $^{95}Mo/^{98}Mo$; lower plot, $^{92}Mo/^{98}Mo$.
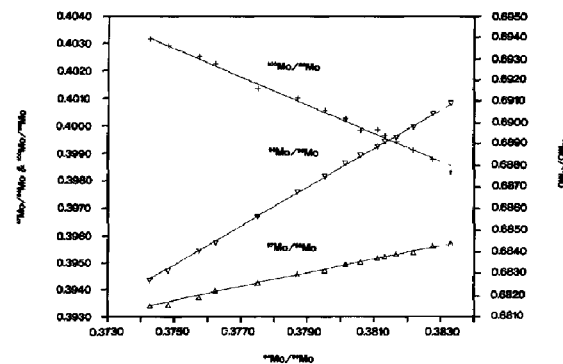
Figure 4. Relative changes of molybdenum isotope ratios upon mass fractionation. The exponential law is shown by the solid lines. Upper plot, $^{100}Mo/^{98}Mo$; middle plot, $^{96}Mo/^{98}Mo$; lower plot, $^{97}Mo/^{98}Mo$.

Aldrich Chemical Co. (St. Louis, MO) Mo standard (MoO_3, 99.999%) are shown in Table 2; the mean values of each of all isotope ratios of Mo are calculated as the weighted mean for seven runs, and errors assigned to the ratios characterize the external reproducibility for 95% confidence limits. It is seen that there are no cases where the isotope abundance ratios for an individual analysis differ from the weighted

mean values by more than two times the error limits. The isotope ratios measured on the four molybdenites of well-defined origin are reported in Table 3, and all ratios are normalized to $^{94}Mo/^{98}Mo = 0.3802$ by exponential law. It is seen that there are no differences bigger than ± 0.4 ϵ among four samples and standard.

Figure 5 displays the discrepancies in nine mea-

Table 2. Mo isotope ratios for Aldrich molybdenum oxide[a]

Running series	92/98	95/98	96/98	97/98	100/98
1	0.607957	0.655927	0.688111	0.394941	0.400101
	± 17	± 20	± 21	± 11	± 12
2	0.607928	0.655950	0.688139	0.394954	0.400133
	± 13	± 13	± 12	± 8	± 9
3	0.607915	0.655965	0.688141	0.394934	0.400132
	± 18	± 18	± 17	± 9	± 13
4	0.607930	0.655978	0.688147	0.394932	0.400112
	± 15	± 15	± 14	± 9	± 11
5	0.607922	0.655948	0.688138	0.394940	0.400125
	± 16	± 15	± 16	± 10	± 11
6	0.607906	0.655962	0.688157	0.394956	0.400146
	± 20	± 22	± 23	± 13	± 15
7	0.607918	0.655955	0.688139	0.394938	0.400133
	± 18	± 19	± 18	± 10	± 12
Weighted mean[b]	0.607926	0.655964	0.688146	0.394947	0.400129
	± 13	± 13	± 11	± 7	± 12

[a] All isotope ratios are normalized to $^{94}Mo/^{98}Mo = 0.3802$ by exponential law. Errors given are one standard error of the mean.
[b] In evaluation of mean values, the weights are given according to the number of measurement for each running series. The uncertainties of the weighted means are the external reproducibility, estimated 95% confidence limits for seven separate analysis.

Table 3. Relative isotope ratios in some molybdenites[a]

	92/98	95/98	96/98	97/98	100/98
Aldrich	0.607926	0.655964	0.688146	0.394947	0.400129
	± 13	± 13	± 11	± 7	± 12
Daehwa mine	0.607929	0.655967	0.688136	0.394951	0.400125
(Korea)	± 15	± 2	± 11	± 4	± 7
Hokuto	0.607907	0.655977	0.688153	0.394951	0.400122
(Japan)	± 15	± 10	± 10	± 6	± 9
Mätäsvaara	0.607950	0.655981	0.688132	0.394943	0.400145
(Finland)	± 14	± 9	± 10	± 6	± 8
Preissac	0.607907	0.655972	0.688149	0.394953	0.400128
(Canada)	± 20	± 12	± 12	± 8	± 11
Köppe and Heumann[b]	0.6039	0.6558	0.6878	0.3945	0.3996
Moore et al.[c]	0.6076	0.6559	0.6870	0.3944	0.3984
Stevens[d]	0.6069	0.6556	0.6801	0.3905	0.3876
Wetherill[e]	0.6080	0.6554	0.6888	0.3945	0.3977

[a] All ratios determined in this study are average of five separate analyses, the means are given as weighted mean, and confidence limits around mean are 95%. All measurements and the prior author's values are normalized to $^{94}Mo/^{98}Mo = 0.3802$.
[b] The experimental precisions were ±0.13-0.38%.
[c] Estimated 95% confidence limits for a single analysis = ±0.1%.
[d] The precision of isotopic ratios was ±0.06-0.10% for a 95% confidence limits.
[e] The experimental mean deviations were ±0.1-0.6%.

surements of isotope abundance of molybdenum published for the last 40 years compared with the result of our study. In the last four rows of Table 3 are listed the relatively recent results of isotopic analyses of molybdenum by some investigators. To make comparison with our data clear, we have normalized their results against our "standard" ratio $^{94}Mo/^{98}Mo = 0.3802$ with corrections for mass fractionation by application of the exponential law to the relevant ratios calculated from the reported data. The deviations resulting from this màthematical treatment relative to the abundance ratios of molybdenum obtained in this work are presented in δ units (parts in 10^3) in Figure

6a. Of four sets of measurements, the Köppe-Heumann [11] values, except $^{92}Mo/^{98}Mo$, are the closest to the results of our study within the experimental errors. However, the ratio of $^{92}Mo/^{98}Mo$, is significantly low ($\sim 0.6\%$), for which there is at present no satisfactory explanation. Nevertheless, it is worthwhile to note that the mass number of 92 is the lowest of molybdenum isotopes, and might be related to certain technical problems. The values of Moore et al. [9] as a whole, show a positive trend of biases with the increase of mass number. This positive trend is considered to be an artifact owing to the relatively too low value of ^{98}Mo, which is employed here as one of
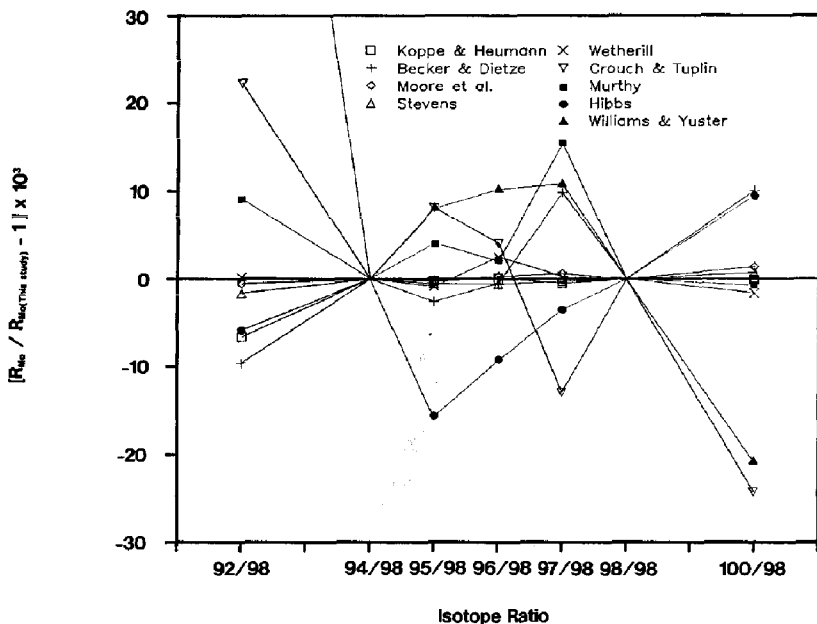

Figure 5. The variations of isotopic abundance of molybdenum published during last 40 years relative to the result of our study.
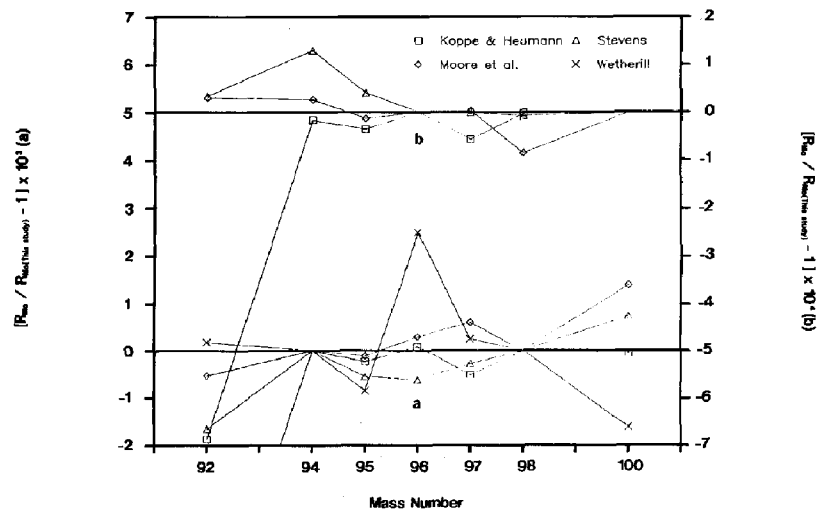

Figure 6. The variations of isotopic abundances of molybdenum measured recently relative to the result of this study. (a) Ratios of molybdenum are normalized to $^{96}Mo/^{100}Mo = 1.7936$. (b) Ratios of molybdenum are normalized to $^{94}Mo/^{98}Mo = 0.3802$.

the normalization pair. Stevens' values [8] also appear to show a positive trend for the span of high mass number. This trend can also be regarded as an artifact caused fortuitously by the relatively big deviation for ^{94}Mo, one of the normalization pair. Scrutiny of the deviation patterns of sets for Moore et al. [9] and Stevens [8] in Figure 6a strongly suggests that ^{96}Mo and ^{100}Mo would merit normalization in the cases under consideration. Thus Figure 6b was prepared by the employment of ^{96}Mo and ^{100}Mo as a normalization pair. (Needless to say, the deviations observed in Figure 6b are in strict agreement with those expected mathematically from Figure 6a.) The too high value of ^{94}Mo for Stevens' set [8] can be attributed to interference from ^{94}Zr^{+}. In view of deviations corresponding to mass numbers 92 and 94, ~ 1.1 δ for $m/z = 94$ may be attributed to ^{94}Zr^{+} in the case of Stevens. (Relative to ^{94}Mo, the factors of interference from Zr^{+} are 0.5656 for ^{92}Mo and 0.0891 for ^{95}Mo.) However, a rather big negative deviation (~ −0.87 δ) of ^{98}Mo for the value in Moore et al. cannot be explained in terms of the interfering effects. The scatter of Wetherill's data [7] in Figure 6a (samples were meteorites) is bigger than that of other data, but the depletion of ~ 0.08% at mass 95 and the enrichment of ~ 0.25% at mass 96 may have special meaning because it could be expected that the variations in the ratio ^{95}Mo/^{96}Mo might result from strong neutron irradiation during the early history of the solar system owing to the effect that the isotopes ^{95}Mo and ^{96}Mo have some resonance peaks with high absorption cross sections for neutrons in the 100-eV range [5]. But it is premature to give any conclusive statement about the observed deviations of ^{95}Mo and ^{96}Mo abundance presented by Wetherill [7] in view of the precision of the measurement.

As mentioned above, notable deviations are hardly recognized (Figure 7) between four molybdenites plus the Aldrich standard studied by us. (Note that, in Figure 7, the deviations are shown by ϵ, and those in Figure 6 by δ.) It seems difficult to say definitely at present that special and/or general anomalies are observable in the isotope ratios presented here. However, in future work, we will examine carefully whether the small deviations between these samples have physical meaning.

The results of our measurement of four samples and standard, which are believed to be the most precise compared with those previously, give the following isotopic compositions:

A	
92	14.72926 ± 0.00049
94	9.21179 ± 0.00019
95	15.89342 ± 0.00002
96	16.67290 ± 0.00004
97	9.56915 ± 0.00001
98	24.22879 ± 0.00049
100	9.69467 ± 0.00019

This isotopic composition gives us the atomic weight of 96.03571 ± 0.00002, whereas the value currently accepted by IUPAC [14] is 95.94 (1).

Acknowledgments
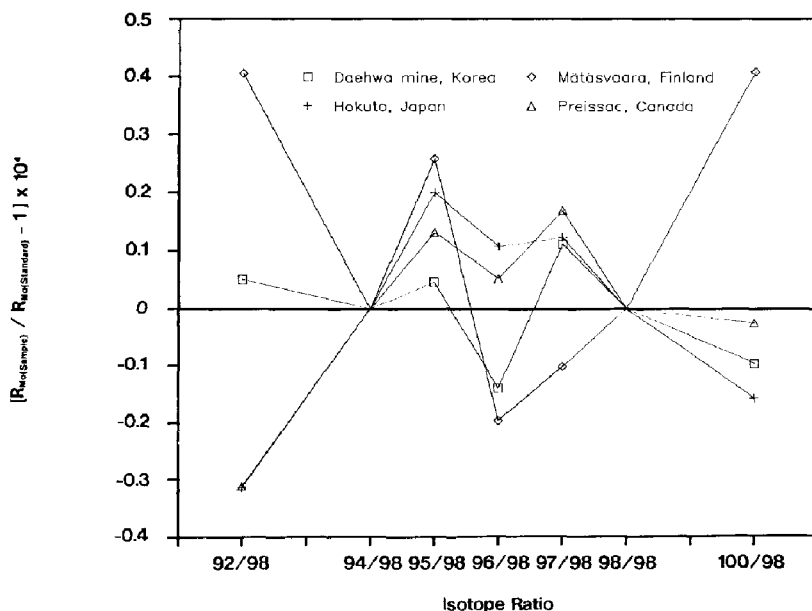
Figure 7. Isotopic composition of molybdenum in four samples in comparison with Aldrich standard.

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