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Solvent Extraction, Ion Chromatography, and Mass Spectrometry of Molybdenum Isotopes

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A procedure was developed that allows precise determination of molybdenum isotope abundances in natural samples. Purification of molybdenum was first achieved by solvent extraction using di(2-ethylhexyl) phosphate. Further separation of molybdenum from isobar nuclides was obtained by ion chromatography using AG1-X8 strongly basic anion exchanger. Finally, molybdenum isotopic composition was measured using a multiple collector inductively coupled plasma hexapole mass spectrometer. The abundances of molybdenum isotopes 92, 94, 95, 96, 97, 98, and 100 are 14.8428(510), 9.2498(157), 15.9303(133), 16.6787(37), 9.5534(83), 24.1346(394), and 9.6104(312) respectively, resulting in an atomic mass of 95.9304(45). After internal normalization for mass fractionation, no variation of the molybdenum isotopic composition is observed among terrestrial samples within a relative precision on the order of 0.00001–0.0001. This demonstrates the reliability of the method, which can be applied to searching for possible isotopic anomalies and mass fractionation.

Molybdenum ($Z = 42$) has seven stable ($A = 92, 94, 95, 96, 97$, and 98) and long-lived ($A = 100$) isotopes produced by the p (92 and 94), r ($95, 97, 98$, and 100), and s ($95, 96, 97$, and 98) nucleosynthetic processes.¹ The abundances of molybdenum isotopes corrected for natural and instrumental mass fractionation are known to vary in the solar system as a result of (i) inheritance of nucleosynthetic anomalies,^{2,3} presumably carried by unprocessed presolar dust grains which survived homogenization of the protosolar nebula;^{4,5} (ii) electron capture of the p -process nuclide ^{97}Tc to form ^{97}Mo , with a mean life of 3.7 Ma early in the solar system;^{6,7} (iii) spontaneous fission of uranium;^{8,9} (iv) double β decay of ^{96}Zr to form ^{96}Mo ;⁸ and (v) anomalous isotope effects.¹⁰

During the past decade,^{2–17} great efforts have been made to measure molybdenum isotope abundances accurately and precisely. Such measurements have long been hampered by zirconium ($Z = 40$) and ruthenium ($Z = 44$) isobaric interferences and the high first ionization potential of molybdenum (7.1 eV). We have developed a separation procedure for molybdenum that is based on solvent extraction and ion chromatography which efficiently removes matrix elements and isobar nuclides. Isotopic analyses were performed using a Micromass Isoprobe multiple collector inductively coupled plasma hexapole mass spectrometer (MC-ICP-Hex-MS) equipped with nine Faraday collectors. This instrument allows high ionization yields of molybdenum to be achieved and permits the correction of zirconium and ruthenium isobaric interferences so that the isotopic composition of molybdenum can be measured with high accuracy and precision.

1. EXPERIMENTAL SECTION

Separation Chemistry. The procedure we developed was inspired by the work of Qi-Lu and Masuda,^{11,12,15} who took advantage of the affinity of molybdenum for di(2-ethylhexyl) phosphate ($\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}$, HDEHP)¹⁸ and used a strongly basic anion exchanger (AG1-X8, 100–200 mesh, chloride form)¹⁹ in order to achieve fine separation of molybdenum from potential interfering species. We made several modifications to the Qi-Lu and Masuda separation procedure on the basis of computer simulations. After

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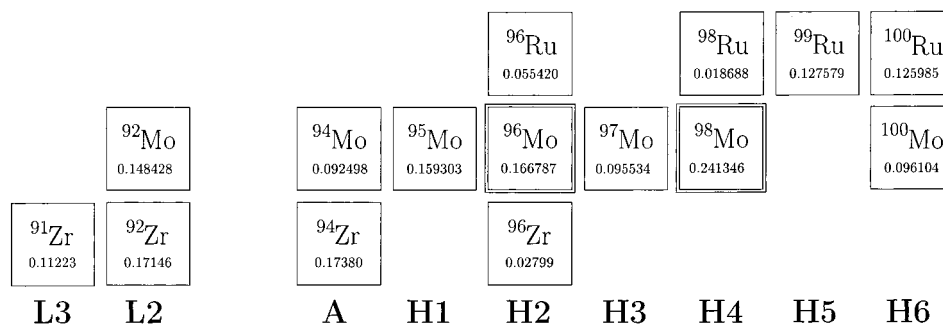


Figure 1. Molybdenum data acquisition scheme. Configuration of the nine Faraday collectors L3, L2, A, and H1–H6 made it possible to measure seven molybdenum isotopes at masses 92, 94–98, and 100 and to monitor zirconium and ruthenium isobaric interferences at masses 91 and 99. Precisely determined isotope abundances^{31,32} are reported under nuclide symbols and were used to correct iteratively for interference contributions at masses 92, 94, 96, 98, and 100 and for exponential^{26–28} mass fractionation by normalization to $^{98}\text{Mo}/^{96}\text{Mo} = 1.4470$.

digestion of the samples in a suitable medium,²⁰ the solution was evaporated to dryness and taken up in 5 mL of perchloric acid (HClO_4), 4 M. The solution was poured into a 10-mL polypropylene centrifuge tube where it was equilibrated with 5 mL of HDEHP diluted to 0.72 M with cyclohexane (C_6H_{12}). During this step, the molybdenum was strongly partitioned into the organic phase, while most matrix elements remained in the aqueous phase. The supernatant was hand-pipetted and washed three times with 5 mL HClO_4 , 4 M, and two times with 5 mL nitric acid (HNO_3), 10 M. Next, molybdenum was back-extracted from the organic phase by two equilibrations with 5 mL HNO_3 /hydrogen peroxide (H_2O_2), 10 M/1 M. The back extractant was transferred into a 15-mL Teflon PFA vessel. The solution was doped with 2 mL of H_2O_2 , 9.9 M, and baked overnight at 400 K in order to ensure oxidation and subsequent loss of ruthenium and trace organic phases. The back extractant was evaporated to dryness and taken up in 1 mL of hydrofluoric acid (HF)/hydrochloric acid (HCl), 1 M/0.5 M, which was then loaded onto a Bio-Rad Poly-Prep column filled with 0.6 mL (l , 1.2 cm \times \varnothing 0.8 cm) of AG1-X8, 200–400 mesh, chloride-form resin previously washed and conditioned with 5 mL of H_2O ; 5 mL of HCl, 6 M; 5 mL of H_2O ; 5 mL of HCl, 1 M; 5 mL of H_2O ; and finally, 5 mL of HF/HCl, 1 M/0.5 M. Matrix elements were removed using 6 mL of HF/HCl 1 M/0.5 M. Zirconium was eluted with 4 mL of HCl, 6 M. Finally, molybdenum was stripped from the column using 6 mL of HCl, 1 M. The ion exchange step was repeated twice. Molybdenum was then ready for mass spectrometric analysis. The yields were adequate (0.4–1) and the blanks, negligibly small ($<10^{-10}$ mol).

Mass Spectrometry. Molybdenum isotopic analyses were performed on the MC-ICP-Hex-MS operated at the Centre de Recherches Pétrographiques et Géochimiques, Nancy, France. The dry residue that was obtained after chemical treatment was dissolved in HNO_3 , 0.15 M, to a molybdenum concentration of 10^{-8} mol·g $^{-1}$. The solution was drawn into the source through a Teflon TFE tube (l , 75 cm \times \varnothing 0.018 cm) at an uptake rate of 0.07–0.1 mL·min $^{-1}$, requiring 1 mL of solution per analysis. Aerosols produced in the Meinhard nebulizer (argon flow rate, 1.0 L·min $^{-1}$) were transferred through a Scott spray chamber to the plasma torch (intermediate argon flow rate; 0.8 L·min $^{-1}$, cool gas argon flow rate, 13.5 L·min $^{-1}$; and forward power, 1450 W). Ionized atoms and molecules were extracted into the hexapole

cell through a nickel sample cone (\varnothing 1.1 mm), a nickel skimmer cone (\varnothing 0.8 mm), and a collimator cone (\varnothing 2.0 mm). The hexapole lens²¹ was a gas-filled (argon flow rate, 1.3 mL·min $^{-1}$) radio-frequency collision cell that serves to reduce the energy spread of the incident ions²² and to diminish certain isobaric interferences.^{23,24} After passage through the hexapole cell, the ion beam was transferred through a lens system to the analyzer (–6 kV) where the ions were separated according to their mass-to-charge ratios in a field generated by a fast-scanning laminated magnet ($M/\Delta M = 420$). Ion beam intensities were measured on nine carbon-coated Faraday collectors (two on the low-mass side, one in the axis, and six on the high-mass side). Molybdenum isotope (92, 94–98, and 100) abundances were measured on the L2, A, H1, H2, H3, H4, and H6 detectors, and zirconium (90–92, 94, and 96) and ruthenium (96, 98–102, and 104) isobaric interferences were monitored at masses 91 and 99 on the L3 and H5 collectors, respectively (Figure 1). Each measurement (10–15 min) consisted of one block of 20 cycles. Before each run, the magnetic field was adjusted by centering the monitor peak. The ion beam was automatically focused at the beginning of the analysis. Peak intensities were integrated over 14 s. Background intensity was measured during 14 s (7 + 7) at masses free of potential doubly charged interferences (± 0.3 amu). Before and after each sample measurement, many Alfa Aesar standard solutions were analyzed at concentrations that were adjusted to match that of the sample within 10%. The mass spectrometer sensitivity was approximately 7×10^{-5} ions analyzed/atom injected.

REFERENCE MATERIAL

External normalization was used in order to determine the composition and atomic mass of molybdenum. An Alfa Aesar solution was doped with the strontium standard reference material SRM 987 from the National Institute of Standards and Technology.²⁵ Strontium and molybdenum measurements were performed sequentially. In the first instance, strontium isotopes 86 and 88 were measured on H1 and H3 collectors, while krypton interferences were monitored at mass 83 on the L2 collector. Then molybdenum isotopes 96 and 98 were measured on H2 and H4 collectors while zirconium and ruthenium interferences were

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Table 1. Molybdenum Isotope Abundances and Atomic Masses^a

	92	94	95	96	97	98	100	<i>M</i>
Audi & Wapstra ³⁴	91.906810	93.905087	94.905841	95.904678	96.906021	97.905407	99.907477	
IUPAC ^{29, 30}	14.84(35)	9.25(12)	15.92(13)	16.68(2)	9.55(8)	24.13(31)	9.63(23)	95.94(1)
Turnlund et al. ¹⁴	14.852(6)	9.266(5)	15.921(3)	16.663(4)	9.565(7)	24.115(5)	9.618(5)	95.930(13)
Qi-Lu & Masuda ¹⁵	14.7287(10)	9.2118(6)	15.8935(11)	16.6731(11)	9.5692(7)	24.2289(17)	9.6950(7)	95.9415(1)
Lee & Halliday ¹⁶	14.8389(5)	9.2484(1)	15.9269(3)	16.6770(4)	9.5528(3)	24.1376(4)	9.6184(2)	95.93101(3)
Wieser & De Laeter ¹⁷	14.769(1)	9.228(1)	15.9022(4)	16.676(7)	9.5618(7)	24.1959(6)	9.6671(4)	95.9377(1)
Dauphas et al.	14.8428(510)	9.2498(157)	15.9303(133)	16.6787(37)	9.5534(83)	24.1346(394)	9.6104(312)	95.9304(45)

^a A standard solution was doped with the strontium reference material SRM 987 to correct the ⁹⁸Mo/⁹⁶Mo ratio for exponential mass fractionation by normalizing the ⁸⁸Sr/⁸⁶Sr ratio to 8.37861(325)²⁵ and assuming that $\beta_{\text{Mo}} = 1(0.1)\beta_{\text{Sr}}$. The ⁹⁸Mo/⁹⁶Mo ratio obtained, 1.4470(17), was then used to correct molybdenum analyses for mass discrimination.^{26–28} Uncertainties are 2 σ .

monitored at masses 91 and 99 on L3 and H5 collectors, respectively. The certified ⁸⁸Sr/⁸⁶Sr ratio²⁵ was used in order to correct the observed ⁹⁸Mo/⁹⁶Mo ratio for instrumental mass fractionation.^{26–28} This ratio was then used as a normalization pair in order to correct molybdenum analyses for mass discrimination. Thus, the abundances of molybdenum isotopes 92, 94–98, and 100 are 14.8428(510), 9.2498(157), 15.9303(133), 16.6787(37), 9.5534(83), 24.1346(394), and 9.6104(312) respectively, resulting in an atomic mass of 95.9304(45). Note that error bars include all sources of uncertainties. These estimates are in agreement with those recommended by the International Union of Pure and Applied Chemistry^{29,30} (Table 1).

DATA PROCESSING

Isobaric interferences and mass fractionation were corrected for in an iterative manner. It has been shown that mass fractionation in SIMS, TIMS, and PIMS follows to first order the exponential law,^{26–28} which relates the measured ratio (*r*) to the true value (*R*) and the relative mass difference ($\Delta M/M$)

$$r = R (1 + \Delta M/M)^\beta$$

The β factor that was required to normalize the measured ⁹⁸Mo/⁹⁶Mo ratio to 1.4470 was calculated. This value was used to compute the corresponding fractionated zirconium and ruthenium isotopic ratios using precisely determined literature isotope abundances^{31,32} for the unfractionated ratios. Then zirconium and ruthenium interferences on molybdenum isotopes were estimated on the basis of the measured intensities at masses 91 and 99 and the calculated fractionated isotopic ratios. After subtraction of isobaric interferences, molybdenum isotope abundances were corrected for mass fractionation. The new β factor was used in order to recalculate the fractionated zirconium and ruthenium isotopic ratios and the resulting interferences. This correction procedure was iterated until convergence of the molybdenum isotopic composition was attained.

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Sample (*x*) and standard (*y*) solutions were measured sequentially (5*y*-*x*...-*y*-*x*-*y*...-*x*-5*y*). For each isotope, *i*, the average (\bar{X}) of the *m* sample ratios (iX) was normalized (ϵ^i) to the average (\bar{Y}) of the *n* surrounding standard ratios (iY). Uncertainties were based on standard replicates and propagated accordingly,

$$\epsilon^i = [^i\bar{X}/^i\bar{Y} - 1] \times 10^4, \\ \sigma(\epsilon^i) = \sqrt{1/m + 1/n} \sigma(^iY)/^i\bar{Y} \times 10^4.$$

2. RESULTS AND DISCUSSION

To test the ability of the data reduction program to correct adequately for isobaric interferences, molybdenum standard solutions (10⁻⁸ mol·g⁻¹) were doped with zirconium and ruthenium at Zr/Mo and Ru/Mo ratios ranging from 0.0001 to 1, approximately. Each interference analysis (*I_i* - *I₀*) was bracketed by standard measurements at interference levels close to that of the mass spectrometer background (*I₀*). The iterative procedure is able to successfully correct for isobaric contributions and mass fractionation up to interference levels as high as 0.01–0.1 (Table 2), which is a major and unexpected result of this work. These levels are much higher than the Zr/Mo and Ru/Mo ratios obtained after chemical treatment. For interference levels higher than 0.01–0.1, the correction procedure breaks down, which may suggest that the exponential law does not adequately correct for mass fractionation or that there are natural isotopic variations of zirconium, molybdenum, or ruthenium.

We measured standard rocks³³ GSD-11 (stream sediment collected from the Shizhuyuan ore field in Binzhou, Hunan province, China), GSD-6 (stream sediment collected from mountainous terrain in Qinghai province, China), GSD-12 (stream sediment sampled from a tributary draining the Yangchun ore field, Guangdong, China), GXR-5 (soil, B zone from Somerset, County, ME), GXR-4 (porphyry copper millhead, Utah), and VS-N (synthetic glass standard, France). If the molybdenum isotopic compositions of terrestrial rocks differ from one another by only mass fractionation, then the isotopic compositions of these samples should be identical when corrected for interference contributions and mass fractionation. This is exactly what is observed (Table 2), which demonstrates that the molybdenum isotopic composition can be measured with high precision in natural samples.

3. CONCLUSIONS

Solvent extraction of molybdenum allows large quantities of sample to be treated. Ion exchange chromatography makes it

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Table 2. Molybdenum Isotope Measurements^a

	Zr/Mo	Ru/Mo	ϵ^i						
			92	94	95	96	97	98	100
I ₀	1.2×10^{-4}	6.9×10^{-5}	-0.66 ± 0.83	2.67 ± 3.51	0.52 ± 0.87	0	-0.24 ± 0.33	0	1.79 ± 2.28
I ₁	1.0×10^{-3}	6.8×10^{-5}	4.93 ± 6.54	2.32 ± 4.31	0.13 ± 2.97	0	-0.10 ± 0.41	0	1.00 ± 0.48
I ₂	2.7×10^{-4}	1.1×10^{-3}	1.01 ± 3.35	0.34 ± 1.16	-0.19 ± 0.48	0	0.10 ± 0.39	0	-0.95 ± 1.85
I ₃	8.3×10^{-3}	6.3×10^{-5}	3.34 ± 5.11	2.09 ± 1.08	0.12 ± 0.45	0	-0.06 ± 0.27	0	-0.03 ± 0.60
I ₄	1.8×10^{-4}	1.2×10^{-2}	1.63 ± 3.29	1.65 ± 0.84	0.91 ± 0.50	0	0.32 ± 0.45	0	0.38 ± 1.66
I ₅	9.0×10^{-2}	5.6×10^{-5}	-4	8	-1	0	0	0	2
I ₆	1.5×10^{-4}	1.2×10^{-1}	9	7	6	0	2	0	1
I ₇	8.7×10^{-1}	5.7×10^{-5}	-13	106	-23	0	-7	0	16
I ₈	1.6×10^{-4}	1.5×10^0	97	64	49	0	18	0	11
	C, mol·g ⁻¹	yield							
GSD-11	6.1×10^{-8}	1	0.34 ± 2.73	-1.40 ± 2.45	0.55 ± 0.54	0	0.47 ± 0.54	0	0.85 ± 0.74
GSD-11	6.1×10^{-8}	0.6	-1.87 ± 3.43	-1.28 ± 1.40	0.14 ± 0.51	0	0.12 ± 0.30	0	0.97 ± 0.85
GSD-6	8.0×10^{-8}	0.8	2.33 ± 5.33	1.00 ± 2.59	0.04 ± 0.66	0	0.00 ± 0.48	0	0.12 ± 1.83
GSD-6	8.0×10^{-8}	0.6	-0.36 ± 1.39	0.11 ± 1.09	0.18 ± 0.49	0	0.00 ± 0.23	0	-0.19 ± 1.40
GSD-12	8.8×10^{-8}	0.6	-1.83 ± 1.35	1.22 ± 2.04	0.13 ± 0.33	0	-0.13 ± 0.70	0	0.03 ± 1.22
GSD-12	8.8×10^{-8}	0.4	-1.97 ± 1.30	-1.05 ± 0.60	0.03 ± 0.31	0	0.31 ± 0.28	0	0.46 ± 1.27
GXR-5	3.2×10^{-7}	0.7	-0.64 ± 0.92	0.24 ± 0.50	0.02 ± 0.36	0	0.07 ± 0.10	0	0.69 ± 0.44
GXR-5	3.2×10^{-7}	0.5	-0.79 ± 1.31	-0.48 ± 0.87	-0.16 ± 0.31	0	0.19 ± 0.23	0	-0.10 ± 0.47
GXR-4	3.2×10^{-6}	0.6	-1.20 ± 5.49	0.69 ± 1.38	0.20 ± 0.59	0	-0.03 ± 0.42	0	0.64 ± 1.91
GXR-4	3.2×10^{-6}	0.6	-0.81 ± 0.75	-0.62 ± 0.44	-0.07 ± 0.27	0	-0.07 ± 0.20	0	0.05 ± 0.46
VS-N	7.3×10^{-6}	0.5	-2.12 ± 2.17	0.18 ± 0.44	-0.21 ± 0.33	0	-0.11 ± 0.16	0	0.95 ± 0.93
VS-N	7.3×10^{-6}	0.6	-1.26 ± 2.04	-0.69 ± 0.94	-0.16 ± 0.43	0	0.04 ± 0.19	0	-0.07 ± 0.32

^a ϵ^i is defined as $[(^{i}\text{Mo}/^{96}\text{Mo})_{\text{sample}}/(^{i}\text{Mo}/^{96}\text{Mo})_{\text{standard}} - 1] \times 10^4$. Molybdenum isotope abundances were corrected for zirconium³¹ and ruthenium³² isobaric interferences by monitoring the ion beam signal at masses 91 and 99 and for exponential mass fractionation^{26–28} by normalization to $^{98}\text{Mo}/^{96}\text{Mo} = 1.4470$. I₀–I₈ correspond to interference analyses. GSD-11, GSD-6, and GSD-12 are stream sediments, GXR-5 is a soil, GXR-4 is a porphyry copper millhead, and VS-N is a synthetic glass standard.³³ Uncertainties are 2σ .

possible to separate molybdenum completely from interfering species. The recent advent of MC-ICP-Hex-MS offers high sensitivity and efficient correction of isobaric interferences. These advances permit natural molybdenum isotope variations to be investigated with unprecedented precision. Important subjects such as inheritance of molybdenum nucleosynthetic anomalies in the solar system, isotope mass fractionation by use of the multiple spike technique, electron capture of the possible extinct radionuclide ^{97}Tc to form ^{97}Mo , production of molybdenum isotopes from fission, anomalous isotope effects, double β decay of ^{96}Zr to form ^{96}Mo , and molybdenum isotope variations resulting from cosmic ray exposure in space can be addressed confidently with this method.

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