Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 225 (2003) 177–183

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

A preliminary study of isotope fractionation in molybdenites

Michael E. Wieser[a,b,*], John R. de Laeter[b]

[a] Department of Physics and Astronomy, The University of Calgary, 2500 University Drive NW, Calgary, Alta., Canada T2N IN4
[b] Department of Applied Physics, Curtin University of Technology, G.P.O. Box U1987, Perth 6845, Australia

Received 24 May 2002; accepted 30 November 2002

Abstract

Molybdenum isotope fractionation has the potential to be an important geochemical tool in ore genesis studies, and in quantifying redox conditions in various paleo-environments, particularly in biological reactions, provided high precision mass spectrometric techniques are available to measure the magnitude of the isotope fractionation at the 0.1 per mil per mass unit level. Thermal ionisation mass spectrometry has been used to measure the isotope fractionation of molybdenum in a number of molybdenite samples. The isotope measurements were made using a multicollector ion collector system to achieve high precision measurements. The fractionation was determined by the double spiking method using a ^{94}Mo–^{100}Mo Double Spike. The samples revealed a range of fractionation values from 0 to approximately -0.5 per mil per mass unit, where the fractionated molybdenites are isotopically lighter than the reference sample. It is known that molybdenites are formed from hydrothermal solutions in the temperature range 350–600 °C, and also at higher magmatic temperatures. Further fractionation studies on selected molybdenite samples spanning this temperature range, may provide information on the mechanism of ore genesis of molybdenites.

Keywords: Double spiking; Isotope fractionation; Mass spectrometry; Molybdenites; Molybdenum

1. Introduction

The isotopic composition of some elements may be fractionated by physical, chemical or biological processes, the rates or equilibrium states of which are mass-dependent. These changes are commonly larger and more readily detected in the "light" elements H, Li, B, C, N, O, S and Cl, and these mass-dependent variations have been used in a range of studies in the Earth Sciences [1]. The magnitude of equilibrium isotope fractionation depends in part on state variables, temperature being the most important, whereas the magnitude of kinetic fractionation commonly varies with the overall reaction rate and mechanism involved. Equilibrium isotope fractionation usually results in the heavier isotopes of an element being concentrated in more oxidised compounds and in more condensed phases, whereas kinetic isotope fractionation generally results in the lighter isotopes being concentrated in the products of the reaction and the heavier isotopes concentrated in the residuals.

Stable isotope fractionation effects may also occur in the heavy elements and in some cases may affect the magnitude of the atomic weight [2]. The IUPAC Commission on Atomic Weights and Isotopic Abundances has investigated the range of variation in the

---

[*] Corresponding author. Tel.: +1-403-220-3641; fax: +1-403-289-3331.
E-mail address: mwieser@ucalgary.ca (M.E. Wieser).

1387-3806/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(02)01115-6

isotopic compositions of naturally occurring materials for some elements, and ascertained the effect of these variations on the atomic weight of the element concerned [3].

There has also been an increasing interest in possible isotope fractionation in the transition metals because of their potential value in biogeochemical cycling. If such fractionation effects are associated with metabolic use of these elements they could provide "biosignatures" for studying life in the geological records of Earth or Mars [4].

Iron is of particular interest because it is incorporated in a wide range of biochemical pathways. Beard et al. [5] reported the isotopic composition of sedimentary iron and bacterially-mediated iron products. Modern sediments (Fe–Mn nodules) show 2–3 per mil ^{56}Fe/^{54}Fe isotope abundance variations that can be explained by bacterially-produced fractionation effects [5]. Natural Fe isotope variations in human blood have the potential to identify long-term deficiencies in dietary Fe absorption. In this study, the ^{56}Fe:^{54}Fe isotope abundance ratio of human blood was depleted by 3.1 per mil relative to an iron standard of non-biological origin [6]. Another recent study of isotope fractionation effects in Cr in natural waters show that the lighter isotopes react preferentially during Cr(VI) reduction by magnetite and sediments [7].

Results of this nature are of great potential importance, because they provide the possibility of a new experimental window on the biological use of transition metals in modern environments. However, it must be recognised the non-biological processes can introduce isotope fractionations of the same order of magnitude and these effects may limit the interpretation of isotope abundance variations resulting from biological activity. Interest in isotope fractionation of the "heavy" elements has come not only from the atomic weight and biogeochemical communities, but also from the cosmochemical community (e.g., from isotopic studies of lunar soils [8]). In part, technological advances in mass spectrometry have stimulated the resurgence of interest in isotope fractionation studies. In addition to thermal ionisation mass spectrometry (TIMS), inductively coupled plasma mass spectrometers, especially those with magnetic sector, multi-collector facilities (MC ICP MS), are now demonstrating their capacity to contribute to such studies.

The excitement that surrounds the potential of these isotope fractionation studies for both biological and non-biological systems must be tempered with adequate experimental controls to ensure that the isotopic results are meaningful. Isotope fractionation effects in TIMS are complex and often difficult to interpret, whilst fractionation effects in MC ICP MS require further study in order to understand the nature of the processes involved. The double spike technique was first used by Dietz et al. [9] for measuring natural isotopic fractionation and has been used in TIMS over a period of many years to enable a rigorous correction of instrumentally-produced mass fractionation to be made. This study reports the result of applying double spiking to TIMS measurements for Mo in a number of molybdenite samples.

2. Experimental

2.1. Samples

A Laboratory Standard was prepared from a 99.993% pure molybdenum metal rod obtained from Johnson Matthey Chemicals Ltd. (JMC 726 Laboratory No. S-8555). The molybdenum metal was cleaned in HNO_3, washed, weighed and dried. The sample was then dissolved in a mixture of ultra-high purity 3:1 HCl:HNO_3 in acid-cleaned PFA Savillex vials. The solution was evaporated to dryness. The residue was taken up in 4 M HCl to give a molybdenum concentration of 1 μg/mg of solution. This was the same Laboratory Standard as used by Wieser and de Laeter [10] and details of its isotopic composition measurement are given in that paper.

Five molybdenite samples from Bencubbin, the Edna May mine, India, Kingsgate and Spencer's Brook were selected for analysis. Table 1 gives details of the location and a brief description of these samples. These five molybdenite samples were analysed by Wieser and de Laeter [10], and the mass

Table 1
Details of the molybdenite samples analysed

Sample name[a]	Locality	Description
Bencubbin 9646-50	Waddouring Dam, South West of Western Australia	Found associated with pyrite in small schlieren in granitic rocks
Edna May S1743 B	Westonia gold deposit, Western Australia	Found in quartz veins; the mineralisation is considered to be due to primary magmatism
India WAM 92	Unknown	Unknown
Kingsgate G1343	New England Fold Belt, New South Wales South East of Glen Innes	Post-Orogenic magmatism Molybdenite found in pipes and veins in leucogranites
Spencer's Brook S4516	South West of Western Australia, 3 km south of the Spencer's Brook Railway Station	Found in quartz veins associated with gneissic granite

[a] The numbers with each sample are Western Australian Museum Catalogue numbers.

spectrometrically-determined isotopic composition of these samples are listed in that paper. No molybdenum isotope abundance anomalies were observed in the uncorrected isotopic data with respect to the Laboratory Standard; neither were any obvious effects due to mass-dependent isotope fractionation observed.

2.2. Chemical separation

Approximately 0.4 mg of each of the molybdenite samples was dissolved in a 3:1 mixture of high purity $HCl:HNO_3$ in acid-cleaned PFA vials (Savillex). The dissolved solutions were evaporated to dryness, redissolved in 11 M HCl, evaporated to dryness and redissolved in 4 M HCl to obtain molybdenum concentrations of approximately 1 μg/mg of solution. An aliquot of the ^{94}Mo–^{100}Mo Double Spike was added to the samples. Molybdenum from these molybdenite + Double Spike solutions was isolated by ion-exchange chemistry, details of which are given by Wieser and de Laeter [10].

2.3. Mass spectrometry

Molybdenum samples were mixed with 4 μL of an ascorbic acid solution (20 mg ascorbic acid/g of 4 M HCl). The resulting mixture was deposited on outgassed rhenium filaments and dried with a 1.4 A filament current. The filament was heated to 2 A at which point the deposit fumed and became black. Three microliters of a silica-gel suspension were deposited on the filament and dried. Finally, the filament was heated to a dull red colour for 5 s. Molybdenum isotopic ion currents were measured on a VG 354 thermal ionisation mass spectrometer equipped with nine moveable Faraday cup detectors and an axial Daly detector. Seven of the Faraday cup collectors were arranged to collect the molybdenum isotopes simultaneously. A strict heating and analytical procedure was followed to ensure that all samples were analysed under identical conditions, all of which behaved in a consistent and predictable manner. The ^{90}Zr ion current was monitored before and after the measurements, as was the possible presence of ^{99}Ru. No corrections to the data were required for either isobaric element. Further details of the mass spectrometry of molybdenum are given by [10].

2.4. Double spiking

By adding to each sample a molybdenum spike enriched in two isotopes, it is possible to correct for isotope fractionation that occurred during sample analysis, as the Double Spike provides an internal monitor of the instrumental mass fractionation. Russell [11] showed that a geometrical interpretation of double spiking systematics could provide the discrimination per mass unit and the concentration of the element concerned in the sample, provided the element had at least four isotopes. In the case of Mo, three isotopic ratios are available for the calculations, and any one of these four isotopes may be used as the reference isotope. In Russell's methodology, the three isotope ratios are combined to form a series of vectors, and linear algebra is used to calculate the fractionation results [11]. This double spike technique has been adopted in this study and a computer program was written to calculate the magnitude of the fractionation of the sample with respect to the Laboratory Standard, together with the associated uncertainty determination, which is estimated using a Monte Carlo methodology, according to the procedures of Russell [11].

The input data required are the measured isotope ratios for the Laboratory Standard, the Double Spike, the mixture of the Laboratory Standard with the Double Spike, together with the mixture of each sample with the Double Spike. In the case of molybdenum, two isotopically-enriched samples were obtained from the Oak Ridge National Laboratory, one enriched in ^{94}Mo and the second in ^{100}Mo. These two isotopically-enriched samples were taken into solution in the same manner as described above, and then mixed to form the Double Spike solution used in the experiment. ^{95}Mo was chosen as the reference isotope and the three isotope ratios employed were ^{94}Mo/^{95}Mo, ^{98}Mo/^{95}Mo and ^{100}Mo/^{95}Mo.

3. Results and discussion

The isotopic composition of the ^{94}Mo–^{100}Mo Double Spike used in this study is given in Table 2, together with the corresponding isotope ratios of the Laboratory Standard. Only the three isotope ratios required for the fractionation calculations [11] are given in Table 2. Two mixtures of Laboratory Standard + Double Spike were measured, and both sets of isotope ratios are listed in Table 2, designated DS1 and DS2, respectively. Also listed are the molybdenite + Double Spike isotope ratios for each of the five molybdenite samples.

The data listed in Table 2 can be used to calculate the magnitude and uncertainty of the fractionation for each of the five molybdenite samples with respect to the fractionation of the Laboratory Standard which has been arbitrarily set to zero. The data in Table 3 gives the fractionation of each sample as calculated from the two sets of Laboratory Standard–Double Spike mixtures DS1 and DS2 with respect to the Laboratory Standard. There is excellent correlation between the two calculated fractionation values, so that the mean value for each sample is a good estimate of the fractionation. A negative sign implies that the sample is

Table 2
Isotope ratio measurements[a] for the Laboratory Standard, the Double Spike, and two mixtures of the Double Spike with the Laboratory Standard, and of the Double Spike with each molybdenite sample

Sample	^{94}Mo/^{95}Mo	^{98}Mo/^{95}Mo	^{100}Mo/^{95}Mo
Laboratory Standard[b]	0.58028 (9)	1.52155	0.60791 (2)
Double Spike	30.361 (19)	0.5023 (50)	24.240 (16)
Mixtures			
(1) Laboratory Standard			
DS1	3.72446 (51)	1.40200 (18)	3.09186 (53)
DS2	5.76621 (66)	1.33513 (14)	4.72574 (66)
(2) Molybdenites			
Bencubbin	2.96509 (60)	1.44323 (43)	2.55120 (90)
Edna	2.96422 (52)	1.44483 (39)	2.55572 (95)
India	1.82863 (27)	1.48187 (23)	1.62381 (34)
Kingsgate	1.1341 (12)	1.50333 (19)	1.05614 (20)
Spencer's Brook	2.31919 (78)	1.46521 (41)	2.02000 (62)

[a] Errors shown are at the 95% confidence intervals for the means.

[b] These values are from Wieser and de Laeter [10]. The ratios have been normalised to ^{98}Mo/^{95}Mo $= 1.52155$.

Table 3
Measurements of isotope fractionation of molybdenum in five molybdenite samples

Sample[a]	Mixture[b]	Fractionation of molybdenite with respect to the Laboratory Standard (per mil per mass unit)
Bencubbin	DS1	−0.52 ± 0.15
	DS2	−0.57 ± 0.18
	Mean	−0.54 ± 0.11
Edna May	DS1	−0.48 ± 0.16
	DS2	−0.54 ± 0.20
	Mean	−0.51 ± 0.12
India	DS1	−0.21 ± 0.15
	DS2	−0.27 ± 0.11
	Mean	−0.24 ± 0.09
Kingsgate	DS1	−0.02 ± 0.36
	DS2	−0.07 ± 0.11
	Mean	−0.05 ± 0.27
Spencer's Brook	DS1	+0.07 ± 0.15
	DS2	+0.02 ± 0.16
	Mean	+0.05 ± 0.11

[a] Errors shown are 95% confidence intervals for each analysis.
[b] DS1 and DS2 are two separate mixtures of the Laboratory Standard with the Double Spike.

isotopically lighter than the Laboratory Standard, so that the lighter isotopes are enriched and the heavier isotopes correspondingly depleted with respect to this reference.

The most important result from this experiment is that there is a range of fractionation values in molybdenites, from 0 to approximately −0.5 per mil per mass unit. Kingsgate and Spencer's Brook do not exhibit any significant fractionation, whereas Bencubbin and Edna May have negative fractionations of approximately 0.5 per mil per mass unit. The molybdenite from India gives an intermediate value of −0.24 per mil per mass unit.

Molybdenum-rich ores may form from hydrothermal solutions in the temperature range 350–600 °C. Molybdenite can also be produced at magmatic temperatures (≥700 °C), in association with crystallising granites and pegmatites, as an accessory mineral. It is possible that molybdenites formed at the lower temperatures may possess measurable fractionation effects, whereas no fractionation is expected at the high temperature end of the hydrothermal range, and for magmatic deposits.

It is interesting to note that Siebert et al. [12] found a fractionation of −0.3 per mil for the ^{98}Mo/^{95}Mo ratio relative to a Laboratory Standard for a hydrothermal molybdenite, determined on a MC ICP MS using the double spike technique. They also measured isotope fractionation of fine-grained sediments between +0.1 and −0.3 per mil on the ^{98}Mo/^{95}Mo ratio using the same methodology [12]. The fractionation is determined on four molybdenum isotope mass ratios, and the external standard reproducibility is 0.06 per mil on the ^{98}Mo/^{95}Mo ratio at the 2s level [12].

Anbar et al. [13] have also reported isotope fractionation in a molybdenite sample from the Climax mine in the United States of America, of approximately 0.3 per mil per mass unit with respect to their reference standard, a JMC-Specpure Mo plasma standard solution. In this case the fractionation is such that the molybdenite sample is isotopically heavier than their reference [13]. Anbar et al. [13] report that differences in ^{95}Mo/^{98}Mo ratios can be determined to a precision of ±0.2 per mil at the 2s level. A MC ICP MS instrument was used for this experiment, but Zr and Ru spikes were employed to correct for instrumental mass bias, rather than the more conventional double spike technique employed by Siebert et al. [12] and in the present study. Anbar et al. [13] also demonstrated that fractionation of Mo isotopes up to 1.5 per mil per mass unit was observed during ion exchange chromatography in which the earliest Mo fraction eluted from anion resin is enriched in the heavier isotopes by approximately 0.5 per mil per mass unit, whereas the last eluted fraction is enriched in the lightest isotopes by approximately 1 per mil per mass unit.

The above experiments indicate that isotope fractionation of Mo in molybdenites does occur, and that this effect can be measured with sufficient precision to enable natural variations to be resolved. The double spike technique is a proven method to determine isotope fractionation, and it has been demonstrated that it can be utilised for Mo either using MC ICP MS [12] or TIMS (present study). The use of a Zr element spike to correct for instrumental mass bias in a

MC ICP MS instruments must be carefully examined in that ^{92,94,96}Zr are isobaric with the corresponding Mo isotopes, and Zr is difficult to separate from Mo by ion-exchange chemistry [14]. In fact Anbar et al. [13] noted that sporadic, unidentified interferences in ^{94}Mo data occur in their measurements. Siebert et al. [12] also state that the relatively higher deviations of some of the Mo isotope data are due to minute Zr contributions that remain, even after chemical separation has been carried out.

To ascertain the usefulness of isotope fractionation studies for our understanding of Mo-ore genesis, it will be necessary to choose a suite of samples that is geologically well documented, particularly regarding their depositional environment, and covering the temperature range of formation discussed above. An analysis of these samples, using the double spike technique, should enable the potential of isotope fractionation to our understanding of the ore genesis of Mo to be evaluated, and serve as the basis to investigate other geological problems.

The question of ion-exchange chemistry-induced isotope fractionation for Mo, as discussed by Anbar et al. [13], needs to be examined with respect to the results of the present experiment. The double spike technique enables instrumental isotope fractionation to be distinguished from natural variations. In the present experiment, the Double Spike was added to the molybdenite sample before chemical separation was undertaken and, in any event, the efficiency of the Mo separation process is greater than 70% [14]. All molybdenite samples were subjected to an identical ion exchange procedure, yet significant variations between −0.5 per mil per mass unit and 0 were measured in the five samples. We are confident that one can eliminate ion-exchange chemistry-induced isotope fractionation as a contributing factor to the data presented in this paper.

4. Conclusions

This study has demonstrated that naturally-occurring mass-dependent isotope fractionation can be measured in some molybdenites with a precision sufficient to resolve variations at the 0.1 per mil per mass unit level. Isotope fractionation studies in Mo are ideally suited to the double spike technique [11], because this element possesses seven isotopes spanning the mass range from 92 to 100. This enables possible isobaric interferences to be identified and internal consistency to be demonstrated. Thermal ionisation mass spectrometry, incorporating the double spike technique, has been used successfully in this study to give a range in isotope fractionation in molybdenites from 0 to −0.5 per mil per mass unit. Siebert et al. [12] have also demonstrated that a fractionation of −0.3 per mil per mass unit can be observed in the ^{98}Mo/^{95}Mo ratio using MC ICP MS, again using the double spike technique, on a hydrothermal molybdenite. Multiple collector ion detection is essential to enable the degree of precision necessary to detect variations in isotope fractionation of 0.1 per mil per mass unit. High precision mass spectrometric measurements of isotope fractionation of Mo may provide new insights on a range of geological and cosmochemical problems, as well as establishing the methodology to enable biologically-induced fractionation to be examined. Subsequent analyses will focus on molybdenite samples of known age and ore-forming conditions, particularly temperature, to investigate the mechanisms responsible for Mo isotope fractionation.

Isobaric interferences with Zr occur for ^{92,94,96}Mo, but these can be eliminated with careful ion-exchange chemistry [14]. The alternative approach of element doping of the molybdenite samples with Zr, as adopted by Anbar et al. [13], relies on the assumption that instrumental fractionation is identical for the doped element and Mo, and introduces the risk of increased isobaric interferences. We recommend the more general use of the double spike technique in isotope fractionation studies. In addition, there is the need for a Mo isotope reference material that can serve as the standard to which all Mo isotope abundance measurements are compared. Until such material is available, meaningful comparison of data between different laboratories (which may use a variety of analytical procedures) will be difficult to achieve.

Acknowledgements

Dr. A. Bevan from the Western Australian Museum provided the molybdenite samples. The authors thank Dr. H. Stein for discussions regarding high-temperature molybdenite-bearing deposits and her insightful review of this paper. In addition, the authors gratefully acknowledge Professor K.J.R. Rosman and Mr. G. Burton for their advice and assistance, Mr. S. Schediwy for writing a computer program to evaluate the magnitude and uncertainty of the fractionation, and an anonymous reviewer for helpful comments and contributions.

References

[1] E. Roth, Pure Appl. Chem. 69 (1997) 1753.
[2] K.J.R. Rosman, J.R. de Laeter, N. Kempt, Int. J. Mass Spectrom. Ion Process. 93 (1989) 107.
[3] T.B. Coplen, J.A. Hopple, J.K. Böhlke, H.S. Peiser, S.E. Rieder, H.R. Krouse, K.J.R. Rosman, T. Ding, R.D. Vocke, K.M. Révész, A. Lamberty, P.D.P. Taylor, P. De Bièvre, U.S. Geol. Survey Water-Resources Investigations Report 01-4122, 2002.
[4] A.D. Anbar, E.O.S. Transactions, Am. Geophysical Union 82 (2001) 177.
[5] B.L. Beard, C.M. Johnson, L. Cox, H. Sun, K.H. Nealson, C. Aguilar, Science 285 (1999) 1889.
[6] T. Walczyk, F. von Blanckenburg, Science 295 (2002) 2065.
[7] A.S. Ellis, T.M. Johnson, T.D. Bullen, Science 295 (2002) 2060.
[8] D.G. Sands, K.J.R. Rosman, J.R. de Laeter, Earth Planet. Sci. Lett. 186 (2001) 103.
[9] L.A. Dietz, C.F. Pachuchi, G.A. Land, Anal. Chem. 34 (1962) 709.
[10] M.E. Wieser, J.R. de Laeter, Int. J. Mass Spectrom. 197 (2000) 253.
[11] R.D. Russell, J. Geophys. Res. 76 (1971) 4949.
[12] C. Siebert, T.F. Nägler, J.D. Kramers, Geochem. Geophys. Geosystems 2 (2001) 2000GC000124.
[13] A.D. Anbar, K.A. Knab, J. Barling, Anal. Chem. 73 (2001) 1425.
[14] M.E. Wieser, J.R. de Laeter, Phys. Rev. C 64 (2001) 024308-1.