

# Variation of Mo isotopes from molybdenite in high-temperature hydrothermal ore deposits

Ryan Mathur · S. Brantley · A. Anbar · F. Munizaga ·  
V. Makshev · R. Newberry · J. Vervoort · G. Hart

Received: 18 February 2009 / Accepted: 31 July 2009 / Published online: 25 August 2009  
© Springer-Verlag 2009

**Abstract** Measurable molybdenum isotope fractionation in molybdenites from different ore deposits through time provides insights into ore genesis and a new technique to identify open-system behavior of Re–Os in molybdenites. Molybdenite samples from six porphyry copper deposits, one epithermal polymetallic vein deposit, four skarns, and three Fe-oxide Cu–Au deposits were analyzed. The  $\delta^{97}\text{Mo}\text{‰}$  (where  $\delta^{97}\text{Mo}\text{‰} = [({}^{97}\text{Mo}/{}^{95}\text{Mo})_{\text{sample}}/({}^{97}\text{Mo}/{}^{95}\text{Mo})_{\text{ICPMS standard}}] - 1 \times 1000$ ) for all samples varied from  $1.34 \pm 0.09\text{‰}$  to  $-0.26 \pm 0.04\text{‰}$ . This is the largest molybdenum isotopic variation in molybdenite from high-temperature ore deposits recorded to date.  $\delta^{97}\text{Mo}\text{‰}$  of molybdenite varies as a function of the deposit type and the rhenium and osmium concentrations

of the samples. Isotope values for Mo also vary within the individual deposits. In general, molybdenites from porphyry copper deposits have the lightest values averaging  $0.07 \pm 0.23\text{‰}$  ( $1\sigma$ ). Molybdenites from the other deposit types average  $0.49 \pm 0.26\text{‰}$  ( $1\sigma$ ). The variations could be related to the fractionation of Mo into different mineral phases during the ore-forming processes. A comparison of the Mo isotope ratios and the Re–Os ages obtained from the same aliquot may possess a geochronological evaluation tool. Samples that yielded robust ages have different Mo isotopic compositions in comparison to samples that yielded geologically unreasonable ages. Another observed relationship between the Re–Os and Mo isotope data reveals a weak correspondence between Re concentration and Mo isotope composition. Molybdenites with higher concentrations of Re correspond to lighter Mo isotope values.

Editorial handling: F. Barra

R. Mathur (✉)  
Department of Geology, Juniata College,  
Huntingdon, PA 16652, USA  
e-mail: Mathur@juniata.edu

S. Brantley  
Pennsylvania State University,  
State College, PA, USA

A. Anbar  
Arizona State University,  
Tempe, AZ, USA

F. Munizaga · V. Makshev  
Universidad de Chile,  
Santiago, Chile

R. Newberry  
University of Alaska,  
Fairbanks, AK, USA

J. Vervoort · G. Hart  
Washington State University,  
Pullman, WA, USA

**Keywords** Molybdenite · Molybdenum isotopes ·  
Re–Os geochronology

## Introduction

The fractionation of transition metal isotopes (Fe, Cu, Zn, and Mo) in high-temperature geologic environments has been documented by several workers (Maréchal et al. 1999; Zhu et al. 2000; Johnson and Beard 2006; Hannah et al. 2007). The variation of Mo isotopes in high-temperature mineralization has only been recently documented by Anbar et al. (2001), Pietruszka et al. (2006), and Hannah et al. (2007). As expected, Mo isotopes have not demonstrated large isotopic fractionation in molybdenite precipitated from high-temperature fluids.

Hannah et al. (2007) presented Mo isotope variations of up to  $0.63\text{‰}$  from different ore deposits of different age.

They examined a total of 20 samples from several skarn, porphyry copper, and metamorphic type deposits. All ore-forming environments were high temperature. In this contribution, we further explore small isotopic fractionations of Mo isotopes during the high-temperature hydrothermal processes associated with formation of molybdenite in different porphyry copper deposits, Fe-oxide Cu–Au deposits, skarn, and epithermal polymetallic vein mineralization. The deposits chosen (Table 1) are located around the world and the molybdenites analyzed have been geochemically and crystallographically characterized in other studies (Tables 2 and 3). The reasons for analyzing Mo isotopes of this diverse suite of samples are the following:

1. To evaluate Mo isotope variation in different high-temperature hydrothermal ore-forming environments
2. To identify causes for the variation of isotopes within and among similar and different ore deposits

3. To assess the viability of using Mo isotopes as a quality control check for Re–Os dating of molybdenite

### Sample descriptions and rationale for the study

Molybdenites from several different ore-forming environments were chosen for analysis. Table 1 shows the deposit type and a description of molybdenite samples analyzed in this study. Although the dataset is relatively small ( $n=28$ ), the variety of deposits analyzed provides the first perspective of possible Mo isotopic variation due to different ore-forming environments.

Aside from large-scale ore deposit process comparisons, the dataset highlights variations within deposits. For instance, molybdenite from six different porphyry copper deposits was chosen for analysis. The genesis of porphyry

**Table 1** Description of samples analyzed in this study

Deposit type	Deposit name/location	Sample name	Sample description	
Porphyry Cu–Mo	El Teniente, Chile	Tt MO-1	Breccia with coarse-grained anh–k-spar–cpy–moly hosted by Sewell stock	
		Tt MO-6	Qtz–moly vein hosted by Teniente dacite, potassic alteration	
		Tt MO-8	Qtz–cpy–moly vein hosted by northern quartz tonalite porphyry, sericite alteration	
	Collahuasi, Chile	Tt 2176	Breccia with coarse-grained anh–bio–cpy–moly hosted by Sewell stock	
		CLL 108B	Qtz–moly vein hosted by Ujina porphyry, Rosario pit, potassic alteration	
		CLL 204	Qtz–moly vein hosted by Ujina porphyry, Rosario pit, potassic alteration	
		CLL 124B	Moly vein hosted by Dacite Ines, Rosario pit, sericite alteration	
		CLL GM	Qtz–moly–cpy–py hosted by Rosario porphyry, Rosario pit, potassic alteration	
	Porphyry Cu–Au	Los Pelambres	Pelambres	Qtz–moly vein
		Grasberg, Irian Jaya	Gras Mo	Qtz–cpy–moly vein hosted by Grasberg qtz monzodiorite, sericite alteration
Andacollo, Chile		Andacollo	Moly vein in biotized andesite near porphyritic dike	
Inca de Oro, Chile		KP 36	Qtz–moly–chl vein hosted by K-spar porphyry	
Skarn	Pine Creek, USA	KP 42	Qtz–py–moly vein hosted by Dinamarquesa porphyry	
		PC 729	Moly–schel vein	
	Alpine, USA	Alp-2	Moly–schel vein	
	Strawberry, USA	Strawberry	Moly–schel vein	
Fe-oxide Cu–Au	Hand Point, USA	Hand Point	Moly–schel vein	
		Serra Verde, Brazil	XB99015	Qtz–cpy–moly in biotized andesite
		XB90018	Qtz–cpy–moly in biotized andesite	
	Garimpo Fernando, Brazil	XB99572	Moly in massive cpy vein with disseminated qtz and hbl	
Metamorphic	Gameleira, Brazil	XB2K001	Moly–cpy in biotized andesite	
		Antietam Reservoir, USA	Ant-1B	Moly flakes in plag–chl dike that crosscuts k-spar–hbl–qtz gneiss
		Ant-Boa	Moly flakes in plag–chl dike that crosscuts k-spar–hbl–qtz gneiss	
Epithermal polymetallic veins	Freiberg district, Germany	Ant-2	Moly flakes in plag–chl dike that crosscuts k-spar–hbl–qtz gneiss	
		Mo altbg	Moly flakes in qtz vein	
		Mo altbg 5000	Moly flakes in qtz vein	

anh anhydrite, bio biotite, chl chlorite, cpy chalcopyrite, hbl hornblende, k-spar K-feldspar, moly molybdenite, plag plagioclase, qtz quartz, schel scheelite

**Table 2** Molybdenum isotope data measured at Washington State University

Deposit type	Deposit	Sample	$\delta^{97}\text{Mo}_{\text{ssb}}$ ‰	$\delta^{97}\text{Mo}_{\text{graphical}}$ ‰	$^{187}\text{Re}$ (ppm)	Crystal type	Re–Os age (Ma)
Porphyry Cu–Mo	El Teniente	Tt MO-1 (4)	0.27±0.04	0.24±0.02	115	2H	5.60±0.02 <sup>a</sup>
		Tt MO-1 <sub>column</sub> (3)	0.19±0.06	0.21±0.03	115	2H	5.60±0.02 <sup>a</sup>
		Tt MO-6 (4)	−0.16±0.04	−0.15±0.03	725	2H	4.87±0.02 <sup>a</sup>
		Tt MO-8 (4)	0.15±0.05	0.10±0.04	160	2H	4.42±0.02 <sup>a</sup>
		Tt 2176 (5)	0.34±0.12	0.30±0.04	46	2H	6.31±0.03 <sup>a</sup>
	Collahuasi	CLL 108B (2)	−0.26±0.04	−0.17±0.04	447	2H	44±0.3 <sup>b</sup>
		CLL 204 (1)	−0.17±n.a.	−0.11±n.a.	633	2H	41±0.3 <sup>b</sup>
		CLL124B (2)	0.04±0.09	0.07±0.10	748	2H	36±0.2 <sup>b</sup>
Porphyry Cu–Au	Grasberg	Gras Mo (3)	−0.07±0.04	−0.03±0.05	1,406	2H	2.88±0.02 <sup>c</sup>
	Andacollo	Andacollo (2)	−0.23±0.02	−0.13±0.06	2,316	2H	109±1 <sup>b</sup>
	Inca de Oro	KP 36 (2)	0.12±0.02	0.08±0.02	574	2H	94±0.5 <sup>b</sup>
		KP 41 (3)	0.53±0.04	0.31±0.04	344	2H	62±0.5 <sup>b</sup>
Fe-oxide Cu–Au	Serra Verde	XB99015 (1)	0.31±n.a.	0.18±n.a.	29	2H	2,609±13 <sup>d</sup>
Epithermal polymetallic veins	Freiberg district	Mo altbg (2)	0.36±0.04	0.30±0.04	0.11	2H	303±3 <sup>b</sup>
		Mo altbg 5000 (2)	0.55±0.04	0.31±0.06	0.53	3R	5,200 <sup>b</sup>

Number in parenthesis in sample names indicates number of individual measurements. Errors in  $\delta^{97}\text{Mo}$  are at 2 sigma level  
*ssb* stand-sample-standard bracketing, *n.a.* not available, only one measurement

<sup>a</sup> Re–Os ages from Makshev et al. (2004)

<sup>b</sup> Re–Os ages from Masterman et al. (2004)

<sup>c</sup> Re–Os ages from Mathur et al. (2005)

<sup>d</sup> Re–Os ages from Marschik et al. (2005)

**Table 3** Molybdenum isotope data measured at Arizona State University

Deposit type	Deposit	Sample	$\delta^{97}\text{Mo}$ ‰	$^{187}\text{Re}$ (ppm)	Crystal type	Re–Os age (Ma)
Porphyry Cu–Mo	El Teniente	Tt MO-8 (3)	0.15±0.10	254	2H	4.42±0.02 <sup>a</sup>
	Collahuasi	CLL GM (3)	0.26±0.03	367	2H	33.3±0.2 <sup>b</sup>
	Los Pelambres	Pelambres (3)	0.00±0.10	473	2H	10.56±0.05 <sup>c</sup>
Skarn	Pine Creek	PC 729 (2)	0.05±0.01	n.d.	2H	n.d.
	Alpine	Alp-2 (3)	0.44±0.04	n.d.	2H	n.d.
	Strawberry	Strawberry (3)	0.65±0.06	n.d.	2H	n.d.
	Hand Point	Hand Point (3)	0.55±0.10	n.d.	2H	n.d.
	Fe-oxide Cu–Au	Serra Verde	XB90018 (1)	1.34±n.a.	11	2H
	Garimpo Fernando	XB90572 (2)	0.45±0.02	78	2H	2,592±13 <sup>e</sup>
	Gameleira	XB2K001 (2)	0.44±0.10	10	2H	2,614±14 <sup>e</sup>
Metamorphic	Antietam Reservoir	Ant-1B (1)	0.20±n.a.	12.8	2H	983±5 <sup>f</sup>
		Ant-Boa (2)	0.31±0.07	0.35	2H	702 <sup>f</sup>
		Ant-2 (3)	0.31±0.08	0.25	2H	607 <sup>f</sup>

Number in parenthesis in sample names indicates number of individual measurements. Errors in  $\delta^{97}\text{Mo}$  are at 2 sigma level  
*n.a.* not available, only one measurement, *n.d.* not determined

<sup>a</sup> Re–Os ages from Makshev et al. (2004)

<sup>b</sup> Re–Os ages from Masterman et al. (2004)

<sup>c</sup> Re–Os ages from Mathur et al. (2001)

<sup>d</sup> Re–Os ages from This study

<sup>e</sup> Re–Os ages from Marschik et al. (2005)

<sup>f</sup> Re–Os ages from Pierotti et al. (2006)

copper deposits was summarized by Guilbert and Park (1986) and Tittley (1995 and references therein) and mineralization is thought to be related to fluids that exsolved from shallow, intermediate composition, igneous rock. The samples originated from Cu–Mo and Cu–Au types of porphyry deposits: El Teniente, Chile (Cu–Mo); Los Pelambres, Chile (Cu–Mo); Collahuasi, Chile (Cu–Mo); Inca de Oro, Chile (Cu–Au); Andacollo, Chile (Cu–Au), and Grasberg, Irian Jaya (Cu–Au). In a general sense, the Mo isotope data permit comparison of Mo isotope ratios between deposits of the three main mineralization epochs present in the Chilean Cordillera.

A combination of Re–Os geochronological data and Mo isotope data provides two insights: information on deposit-scale processes and identification of open-system behavior of Re–Os in molybdenites. First, we record the variation of Mo isotope ratios for deposits that have experienced multiple mineralization events identified through geochronological data of molybdenite Re–Os ages and zircon U–Pb ages. Samples from Collahuasi (two events as seen in samples CLL GM and CLL 124B; Masterman et al. 2004) and El Teniente (four events as seen in samples Tt-MO-1, Tt-MO-6, Tt-MO-8, Tt-2176; Maksiyev et al. 2004) record distinct mineralization events.

The second contribution of the Mo isotopic data is to evaluate the Re–Os geochronometer. A debate surrounds the possibility of resetting the Re–Os isotopic system. McCandless et al. (1993) first attempted to use crystallographic evidence to demonstrate open-system behavior of Re–Os in molybdenites. This concept was further augmented by Suzuki et al. (2000) with an experimental study of the alteration of molybdenite by saline fluids of moderate temperature (180–200°C). Stein et al. (2001) disputed this claim by producing robust age determinations of molybdenite from high-grade thermally metamorphosed rocks. The debate continues, and in this study, we have examined Mo isotope ratios from molybdenites that yielded geologically unreasonable ages (older than the host rock) in several samples from porphyry copper and other types of deposits. By comparing Mo isotope ratios from molybdenites that yield reasonable ages with molybdenites that do not yield reasonable ages, we attempt to recognize any systematic behavior of the Mo isotopes.

## Materials and methods

All molybdenite samples were hand-picked from veins and powdered. Before powdering, the grain size varied in size from 0.2 to 2 cm.

In order to ensure that the samples were homogenous and mineralogically well characterized, powdered X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) were conducted.

The XRD scans confirmed that the samples are molybdenite and identified the polytype of molybdenite. Molybdenite occurs in two types of structures based on the S–Mo–S layers, where the two layers are stacked in a hexagonal geometry (2H) or three layers are stacked in a rhombohedra geometry (Newberry 1979). An aliquot of approximately 0.2 g was split and powdered for XRD analysis on a Scintag Pad V X-ray powder diffractometer. XRD scans were completed in slow, step-scan mode for precision analysis.

The SEM analysis identified the mineralogical homogeneity or heterogeneity at the micron scale for samples. This is important because Dauphas et al. (2001) and Pietruszka et al. (2006) noted that solution matrices that contain multiple elements may cause matrix effects while measuring the Mo isotopic composition. For analysis of the molybdenite powder in the SEM, strands of double-sided carbon tape were applied to glass slides, the molybdenite thin wafers (approximately 200–400 μm thickness) were pressed onto the tape and carbon-coated. SEM images and EDS analysis were conducted using a JEOL 6460 at 20 Kev with qualitative EDS chemical data calculated using INCA software by Cambridge.

Molybdenite (MoS<sub>2</sub>) has high concentrations of Mo (and sulfur) and no appreciable amount of other metals. Therefore, for Mo isotopic analysis, 0.1 g of molybdenite was dissolved in Teflon beakers by 8 ml of aquaregia. Samples were dried down to a small bead and then diluted for analysis on multicollector inductively coupled plasma mass spectrometer, Neptune<sup>®</sup>, ThermoFinnigan. The measurement of Mo isotopes occurred in two different labs: Arizona State University and Washington State University.

All samples are reported as per mil using the following notation:

$$\delta^{97}\text{Mo} \text{ ‰} = \left( \left[ \frac{\frac{97\text{Mo}}{95\text{Mo}} \text{ sample}}{\frac{97\text{Mo}}{95\text{Mo}} \text{ std}} \right] - 1 \right) \times 1000 \quad (1)$$

In order to generate internally consistent data, the following procedures were kept constant at both locations. We used a Johnson Matthey Specpure Molybdenum Plasma Standard, Mo standard, and a Johnson Matthey Specpure Zirconium Plasma Standard. Isotope ratios were measured in low resolution mode and the cup configurations were as follows: <sup>90</sup>Zr-L4, <sup>91</sup>Zr-L3, <sup>92</sup>Mo-L2, <sup>95</sup>Mo-L1, <sup>96</sup>Mo-Ax, <sup>97</sup>Mo-H1, <sup>98</sup>Mo-H2, and <sup>99</sup>Ru-H3. The reported ratios represent the average of 40 measured ratios for each run. The concentrations of Mo and Zr in the samples and standard were at a constant 2:1 ratio.

Mass bias was corrected by using a Zr dopant. Several methods can be used to correct mass bias using the Zr dopant. In this contribution, we present two methods to

correct for mass bias. For the data collected at Washington State University and Arizona State University (Tables 2 and 3, respectively), the samples were corrected by two methods: the standard-sample-standard bracketing and the graphical method. In the standard-sample-standard method, each sample and standard is corrected using the exponential law equations summarized in Arnold et al. (2004) and then the sample is “bracketed” by the standards. The graphical method summarized by Maréchal et al. (1999) involves calculating the separation between the linear trends of multiple runs of standards and samples on  $\ln \text{Zr}$  versus  $\ln \text{Mo}$  plots to evaluate the power law and determine the method of correction. Figure 1 demonstrates this method.

Reported ratios are averages of multiple runs of the same sample; the small superscript in the sample name in Tables 2 and 3 denotes the number of analyses for each sample. Errors for the analyses are reported at the  $2\sigma$  level. For samples measured at Arizona State University, the stability of the instrument and reproducibility of the measurements was further checked through the analysis of a gravimetric in-house standard and rock standard. Both samples were within the acceptable error of  $\pm 0.06\%$  and  $\pm 0.08\%$ , respectively, of the known values. In order to evaluate possible matrix effects, sample TtMO-1 was processed with ion exchange chromatography (Pietruszka et al. 2006) and the result matched the sample not processed with ion exchange chromatography. One sample from El Teniente (TtMO-8) was run at both Washington State University and Arizona State University and the value was reproduced at both labs within error of the measurement.

Re–Os data originate from previous publications (Mathur 2000; Mathur et al. 2001; Makshev et al. 2004; Marschik et al. 2005; Pierotti et al. 2006) and some of the ages are reported here. The concentrations of Re and Os were determined by isotope dilution and measured on a negative thermal ionization mass spectrometer at the University of Arizona. Molybdenite ages are calculated by

assuming no initial  $^{187}\text{Os}$  as described in McCandless and Ruiz (1993) using the decay constant for  $^{187}\text{Re}$  of  $1.666 \times 10^{-11} \text{ year}^{-1} \pm 0.31\%$  (Smoliar et al. 1996). Detailed descriptions of the methods can be found in Mathur (2000).

## Results

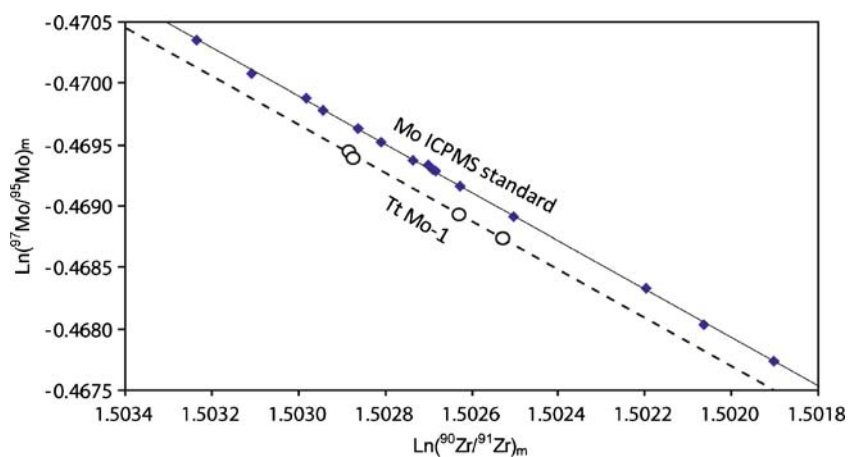
The XRD results indicated that a majority of the molybdenite samples have a 2H structure. Only one sample was identified with an appreciable amount of 3R polytype (sample Mo altbg 5000). The SEM analysis revealed that samples Ant-1B and Ant-Boa from Antietam Reservoir, USA, were the only samples that contained mineral phases such as clay silicates aside from molybdenite. The accessory or contaminating phases appear to be along the borders of the molybdenite grains.

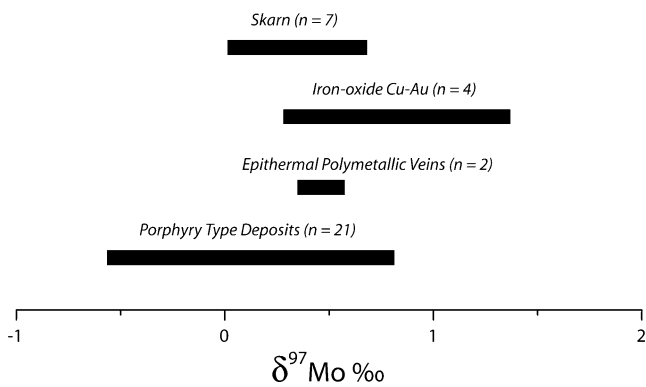
The  $\delta^{97}\text{Mo}$  ratios for all samples vary from  $-0.26\%$  to  $1.34\%$  (Tables 2 and 3). The average error for the Mo standard throughout the sessions was  $0.09\%$  ( $2\sigma$ ). The standard-sample-standard and graphical methods were used to correct for mass bias for the samples analyzed at Washington State University. Both methods yielded the same result within error for every sample except for one sample from Freiberg district, Germany.

Figure 2 compares the Mo isotope composition to the deposit type for data from this contribution and Barling et al. (2001), Anbar et al. (2001), and Pietruszka et al. (2006). Molybdenite from porphyry copper deposits exhibits the greatest range of  $\delta^{97}\text{Mo} = -0.5\%$  to  $0.5\%$  and the lightest values. All other molybdenite samples were equal to or heavier than the standard. The heaviest values are found in molybdenites from skarns and Fe-oxide Cu–Au deposits.

The Re concentrations for the molybdenites vary from as low as 0.2 ppm to as high as 2,316.0 ppm. Figure 3 compares the Re concentration and  $\delta^{97}\text{Mo}$  ratios for all samples. The data best fit a polynomial function that has an

**Fig. 1** Plot of the power law relationship between the measured Zr and Mo isotope ratios; this is the graphical solution developed by Maréchal et al. (1999) for the isotope ratios measured at Washington State University

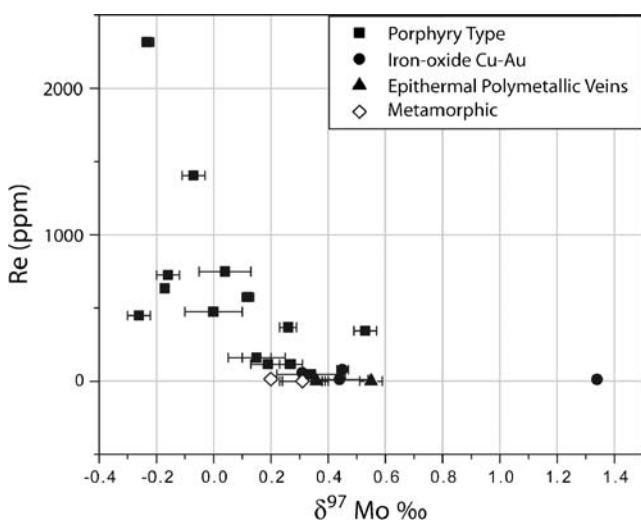




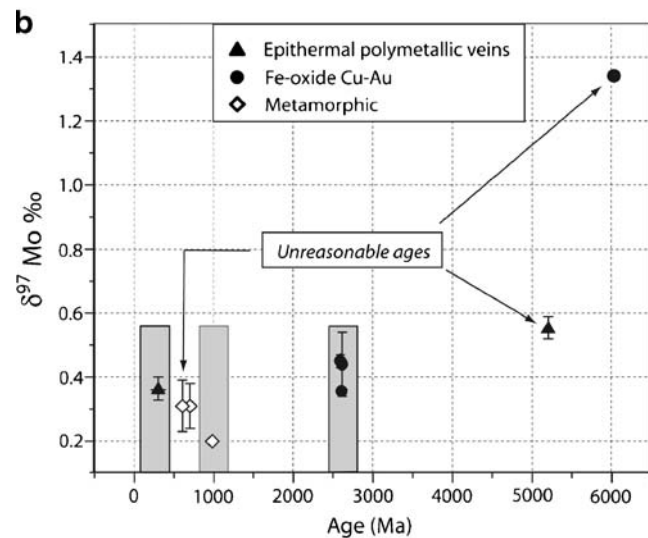
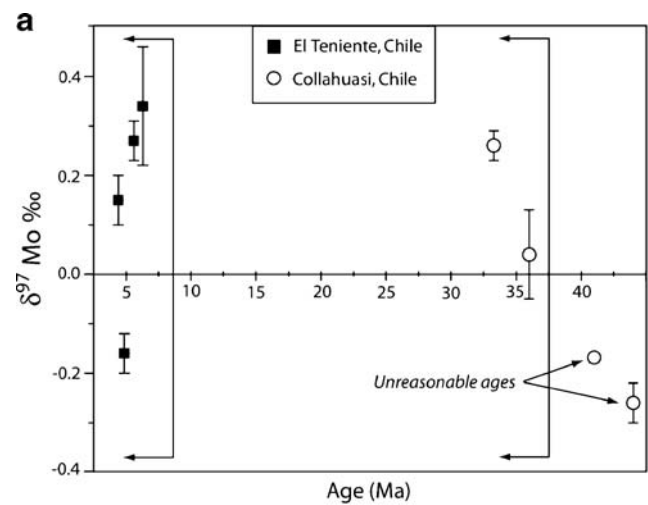
**Fig. 2** Plot of the  $\delta^{97}\text{Mo}$  of molybdenite from different deposits. Data plotted are derived from this contribution along with data from the literature (Pietruszka et al. 2006; Hannah et al. 2007)

$r^2=0.58$ . The weak relationship demonstrates that as Re concentrations decrease, the Mo isotopic composition becomes heavier.

The ages for some samples from the Freiberg district, Germany; Antietam Reservoir, USA; Garimpo Fernando, Brazil; and Collahuasi, Chile are either older than the host rocks that contain the mineralization or geologically unreasonable. Samples with unreasonable ages generally are characterized by Re concentrations that are lower than concentrations in the samples that produced reasonable ages. Figure 4 compares the  $\delta^{97}\text{Mo}$  versus the calculated Re–Os ages for samples that generated reasonable and unreasonable Re–Os ages. Re–Os ages from molybdenite that yielded unreasonable ages have different  $\delta^{97}\text{Mo}$  ratios than samples that produced reasonable ages.



**Fig. 3** Plot of the Re concentration versus  $\delta^{97}\text{Mo}$  of molybdenites. Note that molybdenites with a higher concentration of Re have lighter  $\delta^{97}\text{Mo}$  values



**Fig. 4** Plot of the molybdenite ages versus the  $\delta^{97}\text{Mo}$  values. Lines with arrows and boxed ranges indicate geologically reasonable ages determined from host rock ages and known magmatic activity in the area. **a** Porphyry Cu–Mo deposits and **b** results from Fe-oxide Cu–Au, epithermal polymetallic veins, and metamorphic deposits

## Discussion

### Deposit comparisons

Patterns between the Mo isotope ratio and the deposit type exist in this relatively small dataset. Of the three most sampled deposit types, molybdenite from porphyry copper deposits averaged  $\delta^{97}\text{Mo}=0.07\pm 0.22\text{‰}$ , molybdenite from skarn deposits averaged  $\delta^{97}\text{Mo}=0.42\pm 0.29\text{‰}$ , and molybdenite from Fe-oxide Cu–Au deposits averaged  $\delta^{97}\text{Mo}=0.64\pm 0.32\text{‰}$ . The 20 samples from Hannah et al. (2007) are included in the comparison. The differences in the average isotope ratio also appear in the ranges of Mo isotope ratios illustrated in Fig. 2. More data are needed to statistically define different groups; nonetheless, this dataset

demonstrates the potential to use Mo isotopes to assist in identifying unknown mineral deposits.

The cause for the isotopic variation, as proposed by Hannah et al. (2007), relates to Rayleigh distillation processes occurring at high temperatures during the precipitation of molybdenite from solution. Given the experimental results of Tossell (2005) that fractionation between  $\text{MoO}_4^{-2}$  and  $\text{MoO}_3 \cdot n\text{H}_2\text{O}$  can occur in high-temperature aqueous systems, distillation processes most likely account for the variations seen in the deposits. Different deposit types experience distinct hydrothermal histories (as evidenced by the alteration assemblages) and may lead to the generation of Mo isotopic signatures that are unique to each deposit type.

### Porphyry copper deposits in Chile

The samples of porphyry copper deposits in Chile studied here are representative of the major episodes of mineralization in the Chilean Andean Cordillera (Sillitoe 1988): Inca del Oro and Andacollo are porphyry deposits of Cretaceous age, Collahuasi is Eocene–Oligocene, and El Teniente and Los Pelambres are Miocene–Pliocene. Overall, the  $\delta^{97}\text{Mo}$  values of the molybdenites in porphyry type deposits (−0.26‰ to 0.55‰) are not observed to vary with the location or age of these deposits, but it does vary in different mineralization events within each deposit. Figure 4a illustrates for El Teniente and Collahuasi that each mineralization event has a different Mo isotopic signature. For the El Teniente molybdenites, the Mo isotopic composition becomes progressive lighter for the younger molybdenites, whereas for Collahuasi, the Mo isotopic composition of the molybdenites becomes progressively heavier for the younger molybdenites. Regardless of the cause for the Mo isotopic variation present, the variability (each event has a different isotopic signature) in the data further augment the concept that multiple mineralization events exist.

### $\delta^{97}\text{Mo}$ used to evaluate Re–Os ages of molybdenite

The open-system behavior of the Re–Os isotope system has been debated in the literature. In this contribution, we present Re–Os ages from molybdenites that are either older than the host rock which hosts the mineralization or older than the formation of the earth. All of these samples contain less rhenium than the samples that yield geologically reasonable ages. We interpret that some process lead to the loss (redistribution) of Re from these samples caused by either high- or low-temperature fluids.

In order to identify molybdenites that could yield unreasonable ages, we tested our samples with the suggested protocol from McCandless et al. (1993). They

suggested that crystallography and associated alteration silicates may provide insight to the open-system behavior of Re–Os isotopes in molybdenite. In that contribution, they concluded that inter-/overgrown alteration silicates (several types of clay) within the molybdenite samples were associated with molybdenites that yielded geologically unreasonable ages. In the samples presented here, we found that the majority of samples possess the 2H structure and only two samples possessed intergrown alteration silicates (Ant-2, Ant-Boa). Thus, the methods proposed by McCandless et al. (1993) did not identify all samples that yielded unreasonable ages.

In an attempt to find other diagnostic features that can be associated with the molybdenites, we compared the measured  $\delta^{97}\text{Mo}$  in molybdenites in samples from the same deposit that yielded reasonable and unreasonable ages. Figure 4 demonstrates that samples that yield reasonable ages have isotopic compositions different than samples that yield geologically unreasonable ages. However, the samples that yield unreasonable ages are either distinctly heavier or distinctly lighter than the samples that yield reasonable ages.

The fractionation of the stable transition metal isotopes has been directly related to the redox conditions associated with fluids responsible for mineralization (Markl et al. 2006). Therefore, different redox conditions of the fluids affecting the molybdenites after the crystallization and closing of the Re–Os isotope system could cause the Mo isotopic variability documented. For instance, the fluids that altered the molybdenite samples from the Fe-oxide Cu–Au deposits in Brazil that leached lighter Mo might have been of a different redox condition than the fluids that leached heavier Mo from the Collahuasi molybdenites.

### Conclusions

This contribution demonstrates the largest variation in the Mo isotopic composition of molybdenites so far observed. The variation can be attributed to a variety of causes, and further laboratory experimental work is needed to clearly identify what the most likely cause may be. Regardless, the variation measured demonstrates the potential to use these isotopes to identify samples that yield unreasonable Re–Os ages along with identifying ore processes within and among ore deposits.

**Acknowledgments** This material is based upon work supported by the National Science Foundation under grant nos. CHE-0431328 and EAR 05-19144. We would like to thank T. Seifert, J. Ruiz, G. Hart, G. Pierotti, J. Dague, and R. Smith for assistance in collecting the samples and helpful discussions about the topic. Finally, we appreciate the thorough review of J. Barling, associate editor F. Barra, and the editor B. Lehmann.

## References

- Anbar AD, Knab KA, Barling J (2001) Precise determination of mass-dependent variations in the isotopic composition of molybdenum using MC-ICPMS. *Anal Chem* 73:1425–1431
- Arnold GL, Anbar AD, Barling J, Lyons TW (2004) Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* 304:87–90
- Barling J, Arnold GL, Anbar AD (2001) Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet Sci Lett* 193:447–457
- Dauphas N, Reisberg L, Marty B (2001) Solvent extraction, ion chromatography, and mass spectrometry of molybdenum isotopes. *Anal Chem* 73:2613–2616
- Guilbert JM, Park CF (1986) *The geology of ore deposits*. Freeman, New York 985 p
- Hannah JL, Stein HJ, Wieser ME, de Laeter JR, Varner MD (2007) Molybdenum isotope variations in molybdenite: vapor transport and Rayleigh fractionation of Mo. *Geology* 35:703–706
- Johnson CM, Beard BL (2006) Fe isotopes; an emerging technique for understanding modern and ancient biogeochemical cycles. *GSA Today* 16:4–10
- Maksaev V, Munizaga F, McWilliams M, Mathur R, Ruiz J, Fanning M (2004) New chronology for El Teniente, Chilean Andes, from U–Pb,  $^{40}\text{Ar}/^{39}\text{Ar}$ , Re–Os, and fission-track dating: implications for the evolution of a supergiant porphyry Cu–Mo deposit. In: Sillitoe RH, Perello J, Vidal CE (eds) *Andean metallogeny: new discoveries, concepts, and updates*. SEG special publication 11. Society of Economic Geologists, Boulder, pp 15–54
- Maréchal C, Telouk P, Albarede F (1999) Precise analysis of copper and zinc isotopic compositions by plasma-source spectrometry. *Chem Geol* 156:251–273
- Markl G, Lahaye Y, Schwinn G (2006) Copper isotopes as monitors of redox processes in hydrothermal mineralization. *Geochim Cosmochim Acta* 70:4215–4228
- Marschik R, Mathur R, Ruiz J, Leville R, de Almeida AJ (2005) Late Archean Cu–Au–Mo mineralization at Gameleira and Serra Verde, Carajás Mineral Province, Brazil: constraints from Re–Os molybdenite ages. *Miner Deposita* 39:983–991
- Masterman GJ, Cook DR, Berry RF, Clark AH, Archibald DA, Mathur R, Walshe JL, Durán M (2004)  $^{40}\text{Ar}$ – $^{39}\text{Ar}$  and Re–Os geochronology of porphyry copper–molybdenum deposits and related copper–silver veins in the Collahuasi district, northern Chile. *Econ Geol* 99:673–690
- Mathur R (2000) Re–Os isotopes of base metal porphyry deposits. Ph. D. dissertation, University of Arizona
- Mathur R, Ruiz J, Munizaga F (2001) Insights into Andean metallogenesis from the perspective of Re–Os analyses of sulfides. Extended Abstract in III SSAGI International Conference 3:34–36
- Mathur R, Titley S, Ruiz J, Gibbins S, Frieauf K (2005) A Re–Os isotope study of sedimentary rocks and copper–gold ores from the Ertzberg District, West Papua, Indonesia. *Ore Geol Rev* 26:207–226
- McCandless TE, Ruiz J (1993) Rhenium–osmium evidence for regionally-timed mineralization events in southwestern North America. *Science* 261:1282–1286
- McCandless TE, Ruiz J, Campbell AR (1993) Rhenium behavior in molybdenite in hypogene and near-surface environments: implications for Re–Os geochronology. *Geochim Cosmochim Acta* 57:889–905
- Newberry RJ (1979) Polytypism in molybdenites (1): a nonequilibrium impurity induced phenomenon. *Amer Min* 64:758–768
- Pierotti G, Mathur R, Smith RC, Barra F (2006) Re–Os molybdenite ages for the Antietam Reservoir, Eastern PA, A story of open-system behavior of Re–Os isotopes in molybdenite. *GSA Abstracts with Programs* 38
- Pietruszka AJ, Walker RJ, Candela PA (2006) Determination of mass-dependent molybdenum isotopic variations by MC-ICP-MS: an evaluation of matrix effects. *Chem Geol* 225:121–136
- Sillitoe RH (1988) Epochs of intrusion-related copper mineralization in the Andes. *J South Am Earth Sci* 1:89–108
- Smoliar MI, Walker RJ, Morgan JW (1996) Re–Os ages of group IIA, IIIA, IVA and IVB iron meteorites. *Science* 271:1099–1102
- Stein H, Morgan J, Scherstén A (2001) The remarkable Re–Os chronometer in molybdenite: how and why it works. *Terra Nova* 13:479–486
- Suzuki K, Kagi H, Nara M, Takano B, Nozaki Y (2000) Experimental alteration of molybdenite: evaluation of the Re–Os system, infrared spectroscopic profile and polytype. *Geochim Cosmochim Acta* 64:223–232
- Titley S (1995) The style and progress of mineralization and alteration in porphyry copper systems. In: Titley S (ed) *Advances in geology of the porphyry copper deposits, southwestern North America*. University of Arizona Press, Tucson, pp 93–115
- Tossell JA (2005) Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochim Cosmochim Acta* 69:2981–2993
- Zhu XK, O’Nions RK, Guo Y, Belshaw NS, Rickard D (2000) Determination of natural Cu-isotope variation by plasma-source mass spectrometry; implications for use as geochemical tracers. *Chem Geol* 163:139–149