Molybdenum Mass Fractions and Isotopic Compositions of International Geological Reference Materials

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The double-spike method with multi-collector inductively coupled plasma-mass spectrometry was used to measure the Mo mass fractions and isotopic compositions of a set of geological reference materials including the mineral molybdenite, seawater, coral, as well as igneous and sedimentary rocks. The long-term reproducibility of the Mo isotopic measurements, based on two-year analyses of NIST SRM 3134 reference solutions and seawater samples, was $\leq 0.07‰$ (two standard deviations, $2s$, $n = 167$) for $\delta^{98/95}$Mo. Accuracy was evaluated by analyses of Atlantic seawater, which yielded a mean $\delta^{98/95}$Mo of $2.03 \pm 0.06‰$ ($2s$, $n = 30$, relative to NIST SRM 3134 = 0‰) and mass fraction of 0.0104 ± 0.0006 µg g^{-1} ($2s$, $n = 30$), which is indistinguishable from seawater samples taken world-wide and measured in other laboratories. The comprehensive data set presented in this study serves as a reference for quality assurance and interlaboratory comparison of high-precision Mo mass fractions and isotopic compositions.

Keywords: molybdenum, mass fraction, stable isotope, MC-ICP-MS, geological reference materials.

La méthode dite du «double-spike» et la spectrométrie de masse couplée à une source plasma et à multi-collection ont été utilisées pour mesurer les fractions de masse et la composition isotopique du Mo d'un ensemble de matériaux géologiques de référence, y compris la molybdénite, l'eau de mer, des coraux, ainsi que des roches ignées et sédimentaires. La reproductibilité à long terme des mesures isotopiques du Mo, sur la base de deux ans d'analyses de la solution de référence NIST SRM 3134 et d'échantillons d'eau de mer, est $\leq 0,07‰$ (deux écarts-types, $2s$, $n = 167$) pour $\delta^{98/95}$Mo. La précision a été évaluée par des analyses de l'eau de mer de l'Atlantique, ce qui a donné une moyenne pour $\delta^{98/95}$Mo de $2,03 \pm 0,06‰$ ($2s$, $n = 30$, par rapport au NIST SRM 3134 = 0‰) et de $0,0104 \pm 0,0006$ µg g^{-1} ($2s$, $n = 30$) pour la fraction massique, cette eau est de ce fait indiscernable d'échantillons d'eau de mer prélevés dans le monde entier et mesurés dans d'autres laboratoires. La base de données complète présentée dans cette étude sert de référence pour l'assurance qualité et la comparaison inter-laboratoire de haute précision des fractions massique et des compositions isotopiques du Mo.

Mots-clés : molybdène, fraction massique, isotopes stables, MC-ICP-MS, matériaux géologiques de référence.

Molybdenum (Mo) is one of the most abundant transition metals in the oceans and is important for a range of biological and geochemical processes (Manheim and Landergren 1974, Colodner *et al.* 1995, Morford and Emerson 1999, Anbar 2004). It has seven stable isotopes with relative abundances ranging from 9% to 25%, covering a mass range of about 8% (Anbar 2004). Molybdenum isotopes are increasingly being used in Earth sciences. Of particular interest is the highly redox-sensitive behaviour of Mo, which is primarily used to investigate the oxygenation of Earth's ocean and atmosphere (Barling *et al.* 2001, Anbar and Knoll 2002, Siebert *et al.* 2003, Anbar 2004, Arnold *et al.* 2004, Pearce *et al.* 2008, Kendall *et al.* 2009, 2011, Dahl *et al.* 2010, Duan *et al.* 2010, Voegelin *et al.* 2010, Czaja *et al.* 2012). However, applications in other fields are being developed, such as in magmatic and hydrothermal geology, planetary sciences and tracking environmental pollution (Siebert *et al.* 2003, Chappaz *et al.* 2012, Hin *et al.* 2013, Lane *et al.* 2013, Burkhardt *et al.* 2014, Yang *et al.* 2015).

The development of multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) analytical techniques has allowed Mo isotope ratios to be measured with a precision of $\leq 0.1‰$ (for the $^{98}Mo/^{95}Mo$ ratio), enabling the investigation and application of Mo isotopes in Earth sciences. To express mass-dependent Mo isotope fractionation, Mo isotope ratios have been commonly reported with the delta notation (δ) for two ratios, either $\delta^{98/95}Mo$ or $\delta^{97/95}Mo$. The $\delta^{97/95}Mo$ ratio can be transformed to the $\delta^{98/95}Mo$ ratio by multiplying by 3/2, assuming a linear fractionation law. Recently, the $\delta^{98/95}Mo$ ratio has been adopted by the majority of the Mo isotope research community. The delta notation is calculated as:

$$\delta^{98/95}Mo =[(^{98}Mo/^{95}Mo)_{sample}/$$
$$(^{98}Mo/^{95}Mo)_{reference}-1] \times 1000 \quad (1)$$

The NIST SRM 3134 Mo solution has been proposed as a universal zero-delta reference material for expressing Mo isotope data in delta notation for natural samples (Wen et al. 2010, Greber et al. 2012, Goldberg et al. 2013). As demonstrated by Greber et al. (2012) and Goldberg et al. (2013), interlaboratory comparisons of Mo isotope reference materials yield a lower $\delta^{98/95}Mo$ than NIST SRM 3134 (ranging from -0.16‰ to -0.37‰ relative to NIST SRM 3134); therefore, most data published have been normalised to a narrow range of values slightly below NIST SRM 3134. In addition to the universal zero-delta measurement standard and Mo isotope reference material, there is a critical need for analyses of widely available reference materials to monitor bias induced by Mo purification procedures and matrix materials, and to facilitate comparisons of techniques and $\delta^{98/95}Mo$ values between different laboratories.

Here, we determined the Mo mass fractions and $\delta^{98/95}Mo$ data for twenty-four geological reference materials by an isotope dilution double-spike technique (Dodson 1963). The matrices of these reference materials vary greatly and include igneous rocks ranging from ultramafic to acidic in composition, sedimentary materials, molybdenite, seawater and coral (Table 1). Our work lays the foundation for using these geological reference materials for quality assurance and interlaboratory comparisons of high-precision Mo mass fractions and isotopic data. Although Nägler et al. (2014) suggested setting the $\delta^{98/95}Mo$ of the NIST SRM 3134 to +0.25‰, Mo isotopic ratios of all samples in this study were normalised or renormalised to those of NIST SRM 3134 Mo as the zero-delta measurement standard according to the conversion of Greber et al. (2012).

Experimental procedure

All experiments were performed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS), Guangzhou, China. For details of the procedures for routine sample dissolution, column chemistry and instrumental analysis of Mo isotopes, see Li et al. (2014).

Sample digestion

Test portions of all reference materials were weighed accurately and combined with the ^{97}Mo-^{100}Mo double spike in 15 ml PFA beakers. Each portion contained ~ 150 ng Mo by adjusting sample amount (50–400 mg for solid samples, about 10 g for seawater). Solid silicate samples were dissolved at 120 °C with 6 ml of a 2:1 mixture of HF (22 mol l^{-1}) and HNO_3 (14 mol l^{-1}). To achieve total sample dissolution, the PFA beakers were placed in an ultrasonic bath for 5 min at various intervals during the dissolution period. After digestion and drying at 120 °C, the samples were dissolved in 1 ml of concentrated HCl and then evaporated to dryness. The residue was redissolved in 2–4 ml of a mixture of 0.1 mol l^{-1} HF/1 mol l^{-1} HCl, at which point it was ready for column separation. Coral and carbonatite samples were completely dissolved with 2 mol l^{-1} HCl and the ^{97}Mo-^{100}Mo double spike was then added. The seawater sample was acidified with 1 ml of concentrated HCl, and the ^{97}Mo-^{100}Mo double spike was added. These spiked and acidified solutions were then ready for column separation.

Chromatographic separation

Separation and purification of Mo were achieved with an in-house BPHA extraction chromatographic resin (Li et al. 2014). Approximately 0.5 ml of BPHA resin (obtained by impregnating 5 g Amberchrom CG-71 resin with 40 ml of 3% BPHA solution in ethanol) was packed in a Poly-Prep column (8 mm × 40 mm; Bio-Rad Laboratories, Inc., Berkeley, CA, USA). A 2 ml aliquot of the sample solution was loaded onto the column, and the resin was washed with 8 ml of 0.1 mol l^{-1} HF/1 mol l^{-1} HCl. Finally, the adsorbed Mo was eluted with 8 ml of 6 mol l^{-1} HF/1 mol l^{-1} HCl. The Mo was collected in 15 ml PFA vials and evaporated to dryness on a hot plate at 120 °C. Three drops of concentrated HNO_3 and H_2O_2 were added to the evaporated Mo to decompose any organic residue. Following this, 1 ml of 3% v/v HNO_3 was added to the Mo residue, after which the solution was ready for Mo isotopic ratio measurement by MC-ICP-MS. Because molybdenite (MoS_2) has high Mo mass fractions and no other

Table 1.
Molybdenum mass fractions and isotopic compositions of geological reference materials and Atlantic seawater. Relevant literature data are also listed

Reference material	Lithology	Origin	Mo mass fraction ($\mu g\ g^{-1}$)	% RSD	$\delta^{98/95}Mo$ (‰)	2s	N[a]	n[b]
Igneous rocks								
UB-N (ANRT)[c]	Serpentinised peridotite	This work	0.34	12	0.77	0.12	5	5
		Yu et al. (2000)	0.35					
		Wang et al. (2015)	0.30					
GBW07105 (GSR-3) (IGGE)	Olivine basalt	This work	2.92	2.0	-0.51	0.04		
		Xie et al. (1985)	2.6					
BHVO-2 (USGS)	Basalt	This work	3.38	16	-0.05	0.09	5	5
		Pearce et al. (2009)	4.48					
		Burkhardt et al. (2011)	2.28					
		Hin et al. (2013)			-0.06	0.05		
		Li et al. (2014)	3.90		-0.05	0.11		
		Burkhardt et al. (2014)	4.55		-0.06	0.03		
		Wang et al. (2015)	3.30					
		Siebert et al. (2015)	3.70		0.00	0.07		
		Yang et al. (2015)	3.50		0.01	0.06		
JB-2 (GSJ)	Basalt	This work	1.00	11	0.02	0.09	5	5
		Imai et al. (1995)	1.08	44				
W-2a (USGS)	Diabase	This work	0.46	3.6	-0.10	0.08	4	4
		Wieser and DeLaeter (2000)	0.44					
		Gaschnig et al. (2015)	0.46					
		Burkhardt et al. (2014)	0.39		-0.05	0.06		
WGB-1 (CCRMP)	Gabbro	This work	0.67	3.3	0.20	0.11	5	5
		CCRMP 94-3E[d]	1.2					
GBW07104 (GSR-2) (IGGE)	Andesite	This work	0.58	3.0	-0.28	0.07	5	5
		Xie et al. (1985)	0.55					
AGV-2 (USGS)	Andesite	This work	1.95	1.0	-0.14	0.05	5	5
		Gaschnig et al. (2015)	1.93					
JA-2 (GSJ)	Andesite	This work	0.99	19	-0.12	0.14	5	5
		Imai et al. (1995)	0.60	14				
G-2 (USGS)	Granodiorite	This work	0.27	3.7	-0.05	0.11	5	5
		Wieser and DeLaeter (2000)	0.23					
		Gaschnig et al. (2015)	0.37					
JR-2 (GSJ)	Rhyolite	This work	2.66	2.0	-0.01	0.10	5	5
		Imai et al. (1995)	3.35	21				
COQ-1 (USGS)	Carbonatite	This work	7.4	8.1	-0.26	0.10	5	5
Sediments								
SCo-1 (USGS)	Shale	This work	1.20	1.3	-0.41	0.03	5	5
		Hu and Gao (2008)	1.30					
		Wang et al. (2015)	1.12					
SGR-1b (USGS)	Oil shale	This work	35.5	2.3	0.44	0.11	5	5
		Gladney and Roelandts (1988)	35.1	2.6				
GBW07316 (GSMS-3) (NRCG)	Marine sediment	This work	5.11	4.8	-0.65	0.09	5	5
		Li et al. (2014)	5.32		-0.60	0.10		
		Wang et al. (1998)	5.7					
NOD-A-1 (USGS)	Manganese nodule	This work	589	0.45	-0.83	0.05	5	1
		Barling et al. (2001)[e]			-1.20	0.15		
		Asael et al. (2013)			-0.67	0.04		
NOD-P-1 (USGS)	Manganese nodule	This work	637	0.37	-0.88	0.01	5	1
		Barling et al. (2001)[e]			-0.88	0.15		
		Asael et al. (2013)			-0.83	0.10		
GBW07337 (GSMC-1) (NRCG)	Ferromanganese crust	This work	466	2.0	-0.94	0.07	5	1
		Wang et al. (2007)	493					
JCp-1 (GSJ)	Coral *Porites*	This work	0.082	2.4	0.25	0.08	5	5
		Inoue et al. (2004)	0.070	4				

Table 1 (continued).
Molybdenum mass fractions and isotopic compositions of geological reference materials and Atlantic seawater. Relevant literature data are also listed

Reference material	Lithology	Origin	Mo mass fraction (μg g^{-1})	% RSD	$\delta^{98/95}$Mo (‰)	2s	N[a]	n[b]
Molybdenite								
GBW04436 (JDC) (NRCG)	Molybdenite	This work			-0.14	0.07	5	1
		Malinovsky et al. (2005)			-0.09	0.03		
GBW04435 (HLP) (NRCG)	Molybdenite	This work			-0.59	0.02	5	1
		Siebert et al. (2001)			-0.58	0.07		
		Malinovsky et al. (2005)			-0.55	0.03		
Seawater								
IAPSO (OSIL)	Atlantic seawater	This work[f]	0.0105	2.7	2.02	0.06	20	20
Atlantic water (OSIL)		This work	0.0107	2.1	2.04	0.05	6	6
NASS-6 (CCRMP)		This work	0.0099	1.0	2.03	0.09	4	4
		Mean[g]	0.0104	3.2	2.03	0.06		
		Siebert et al. (2003)			2.03			
		Pearce et al. (2009)	0.0116		2.04	0.07		
		Greber et al. (2012)	0.0100		2.09	0.05		
		Li et al. (2014)	0.0103		2.00	0.03		

[a] Number of analyses of a reference material.

[b] Number of digestions.

[c] Source of the reference material. ANRT, Association Nationale de la Recherche Technique, France; CCRMP, Canadian Certified Reference Materials Project; GSJ, Geological Society of Japan; IGGE, Institute of Geophysical and Geochemical Exploration, China; NRCG, National Research Center of Geoanalysis, China; OSIL, Ocean Scientific International Ltd; USGS, United States Geological Survey.

[d] This is an official certification report.

[e] $\delta^{98/95}$Mo ratio is transformed from $\delta^{97/95}$Mo by multiplying by 3/2.

[f] Three of the twenty analyses are from our previous study (Li et al. 2014).

[g] Mean of the above results obtained for the three seawater reference materials.

$\delta^{98/95}$Mo represents Mo isotopic compositions normalised to NIST SRM 3134 using Equation (1). Relative standard deviations (% RSD) are given for the Mo mass fraction.

major constituents apart from sulfur, molybdenite samples were simply dissolved in aqua regia and reconstituted in 3% v/v HNO$_3$ without separation or purification of Mo from the sample matrix.

MC-ICP-MS analysis

Molybdenum isotopic ratios were determined on a Thermo-Fisher Scientific Neptune Plus MC-ICP-MS at the State Key Laboratory of Isotope Geochemistry, GIG-CAS. Samples and reference solutions were introduced into the plasma through an Aridus II® desolvating sample introduction system (CETAC Technologies, Omaha, USA). This system removes water from the sample solutions by passage through a desolvating membrane at 160 °C, providing a 'dry' sample to the plasma, which increases sensitivity by a factor of 5–10 over wet plasma sample introduction systems. The typical Mo sensitivity achieved was 180–200 V per μg g^{-1}. Prior to starting an analytical session, the spiked reference solution (NIST SRM 3134) was typically analysed five times to check the MC-ICP-MS performance. During an analytical session, the reference solution was measured after

each batch of three samples. Correction for mass fractionation during chemical separation as well as mass spectrometry followed the double-spike deconvolution methods described by Siebert et al. (2001). Total procedural blanks were calculated by isotope dilution and ranged from 0.3 to 1.0 ng Mo with an average of 0.54 ± 0.60 ng (two standard deviations; 2s, n = 6); blank corrections were therefore unnecessary. After chromatographic separation, interfering species such as Zr and Ru were not detected in the analyte solution by ICP-MS.

Results and discussion

Procedure validation

In this study, repeat analyses of NIST SRM 3134 reference solutions and well-studied IAPSO seawater reference material allowed evaluation of the whole-procedural long-term reproducibility and accuracy. The $\delta^{98/95}$Mo reproducibility was determined by the spiked NIST SRM 3134 reference solution analyses, which provided a precise and accurate representation of instrument behaviour during
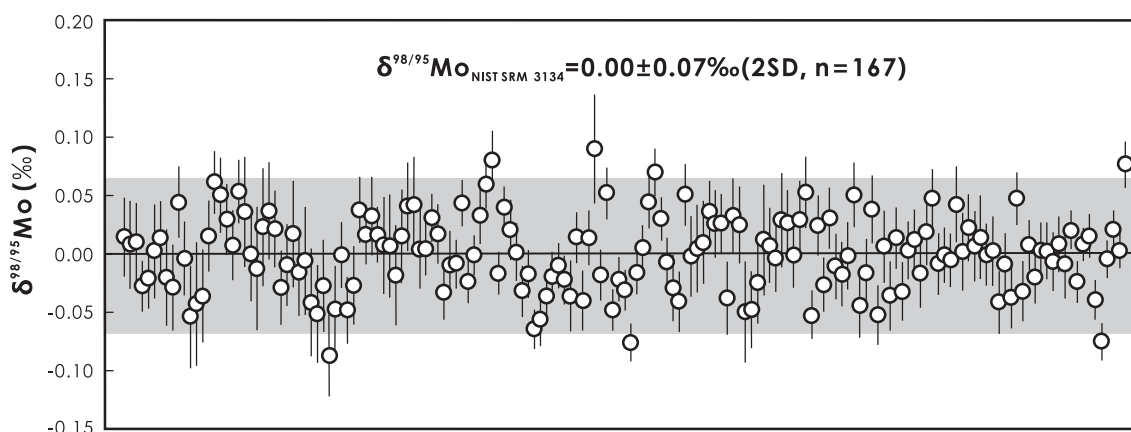
Figure 1. Long-term reproducibility of the spiked Mo reference solution, NIST SRM 3134, over a period of 2 years. Error bars represent 2 standard error of each measurement, whereas the grey band represents the long-term measurement reproducibility ('external precision') (2s) of all analyses. The horizontal line represents the mean $\delta^{98/95}$Mo value.

sample analysis. Analyses of the spiked Mo standard solution yielded a mean $\delta^{98/95}$Mo of $0.00 \pm 0.07‰$ (2s; Figure 1) over a period of 2 years (Figure 1). This precision of ~ 0.07‰ indicates our measurements are precise and accurate at the quoted precision. The accuracy and long-term reproducibility were further evaluated by analysing seawater samples from the Atlantic Ocean over a period of 2 years (Table 1, Figure 2). Previous studies showed that the $\delta^{98/95}$Mo of modern open-ocean water accounts for some of the variation, and reflect a small inherent heterogeneity within $\pm$ 0.10‰ (2s) (Siebert *et al.* 2003, Greber *et al.* 2012, Nakagawa *et al.* 2012, Goldberg *et al.* 2013). Greber *et al.* (2012) renormalised their Mo isotope data for seawater to NIST SRM 3134 = 0‰ and obtained a value of $2.09 \pm 0.07‰$ (2s, n = 5). Goldberg *et al.* (2013) recently compiled $\delta^{98/95}$Mo data for seawater from various sites, obtaining values ranging from 2.00‰ to 2.23‰, with a mean value of $2.09 \pm 0.10‰$ (2s, n = 26), whereas the value for the Atlantic Ocean sample was $2.06 \pm 0.07‰$ (2s, n = 5). In this study, analyses of Atlantic seawater yielded a mean $\delta^{98/95}$Mo of $2.03 \pm 0.06‰$ (2s, n = 30; Figure 2) and mass fraction of 0.0104 ± 0.0006 µg g^{-1} (2s, n = 30). Hence, our results are identical within uncertainty of the Mo isotopic composition of seawater samples world-wide, measured in our laboratory and in other laboratories (Siebert *et al.* 2003, Pearce *et al.* 2010, Greber *et al.* 2012, Goldberg *et al.* 2013, Li *et al.* 2014 and references therein).

Overall, results from these tests on both NIST SRM 3134 Mo reference solutions and seawater samples demonstrate that Mo isotopes can be measured accurately with a precision of $\pm$ 0.07‰ (2s) for $\delta^{98/95}$Mo.
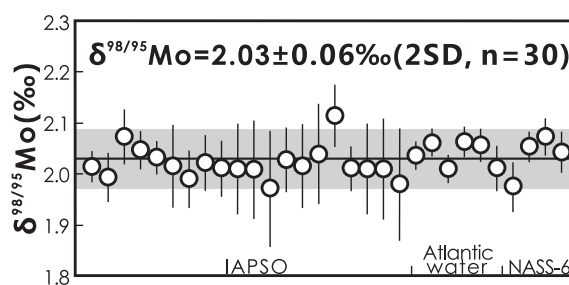

Figure 2. Molybdenum isotopic compositions of Atlantic seawater analysed over a period of 2 years. Error bars represent 2 standard error of each measurement, whereas the grey band represents the long-term measurement reproducibility ('external precision') (2s) of all analyses. The horizontal line represents the mean $\delta^{98/95}$Mo value.

Mo mass fractions and isotopic compositions of geological reference materials

The Mo mass fractions and isotopic compositions of twenty-one geological reference materials analysed in this study are presented in Table 1 and Figure 3, together with literature data for comparison. These analyses include independent digestions of a given rock powder, duplicate column chemistry using aliquots of the same bulk raw solution (Table 1). Regardless of sample composition and digestion method, replicates of Mo mass fractions in most analysed reference materials reproduced within 5% RSD (relative standard deviation, Table 1). The variations were larger for serpentinised peridotite (UB-N), basalt (BHVO-2),

basalt (JB-2) and andesite (JA-2) samples (RSD = 10–19%). Mean values of Mo mass fractions in reference materials generally match literature data (Table 1), except for BHVO-2, gabbro (WGB-1) and JA-2 samples. For instance, our measured Mo mass fractions for UB-N (mean of 0.34 ± 0.08 μg g^{-1}, 2s, n = 5) agree with the value of 0.3 μg g^{-1} reported by Yu et al. (2000) and Wang et al. (2015). For BHVO-2, the measured Mo mass fractions range from 3 to 4 μg g^{-1}, with a mean mass fraction of 3.4 ± 1.2 μg g^{-1} (2s, n = 5) obtained from five independent digestions. This value overlaps with numbers reported recently by Burkhardt et al. (2014), but higher than their previously reported value (2.28 μg g^{-1}; Burkhardt et al. 2011), indicating substantial sample heterogeneity in the BHVO-2 powder when small test portions are used. The average Mo mass fraction of BHVO-2 determined by isotope dilution MC-ICP-MS in this study is identical within uncertainty to the values determined by Yang et al. (2015) and Wang et al. (2015), and also to our previously isotope dilution MC-ICP-MS values (Li et al. 2014). Data for WGB-1 are slightly lower than the reference value (about 0.67 versus 1.2 μg g^{-1}, respectively), whereas data for JA-2 are higher than the reference value (about 0.99 versus 0.6 μg g^{-1}, respectively). These discrepancies may indicate that the batch of these reference materials has different or heterogeneous Mo mass fractions compared with our samples.

Our result for δ$^{98/95}$Mo in BHVO-2 was -0.05 ± 0.07‰ (2s, n = 5; Table 1). Hin et al. (2013), Burkhardt et al. (2014), and Yang et al. (2015) recently reported δ$^{98/95}$Mo values for BHVO-2 of -0.06 ± 0.05‰ (2s, n = 15), -0.06 ± 0.03‰ (2s, n = 23), and 0.01 ± 0.06‰ (2s, n = 10), respectively, relative to NIST SRM 3134. Note that the δ$^{98/95}$Mo value of BHVO-2 is well defined (-0.06‰), indicating that the variable Mo mass fractions observed among powder aliquots do not affect the measured Mo isotope compositions. The δ$^{98/95}$Mo values of W-2a from four different digestions ranged from -0.14‰ to -0.06‰ with an average of -0.10 ± 0.08‰ (2s, n = 4, Table 1), in good agreement with the data (-0.05 ± 0.06‰, 2s, n = 2) reported by Burkhardt et al. (2014).

The five independent digestions of the serpentinised peridotite sample UB-N yielded a mean δ$^{98/95}$Mo of 0.77 ± 0.12‰ (2s, n = 5), which is much heavier than the values for the other igneous rock reference materials determined in this study (Table 1). This shift may provide evidence of fractionation associated with serpentinisation. The eleven igneous rock reference materials, including one carbonatite (except for UB-N), in this study had δ$^{98/95}$Mo

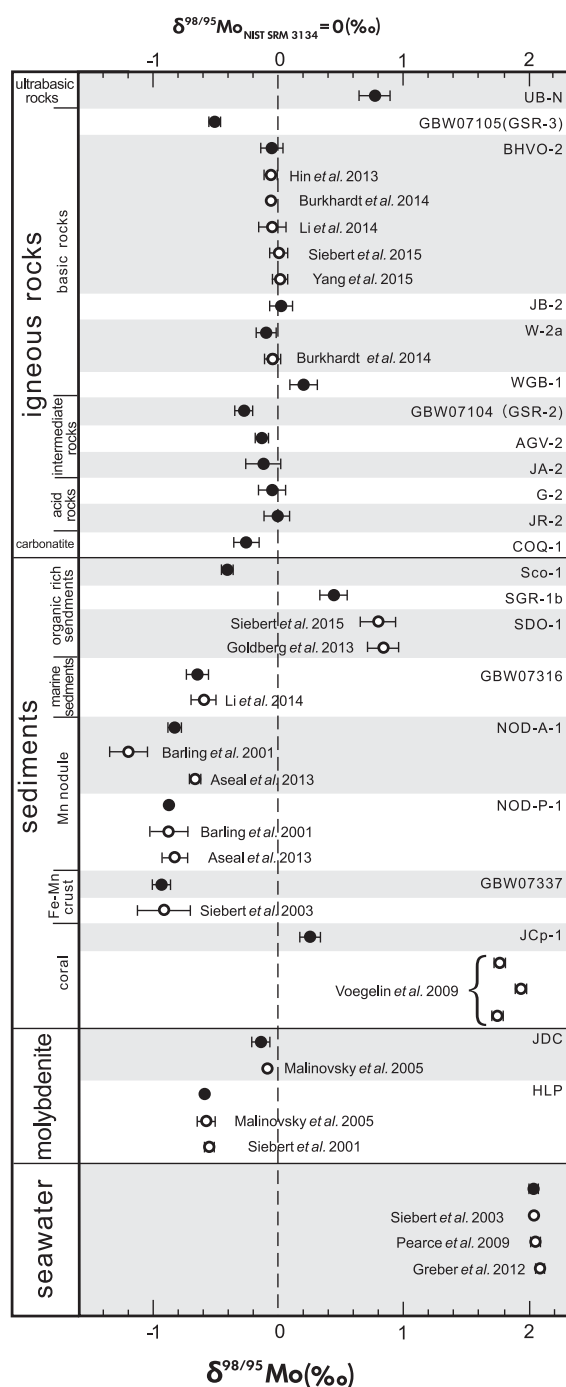**Figure 3.** δ$^{98/95}$**Mo values for geological and seawater reference materials and comparison with literature data, which were normalised to NIST SRM 3134 (= 0‰). The average** δ$^{98/95}$**Mo value obtained from this study is shown as unfilled circles, and literature data are represented by white circles. Error bars are 2s and only shown when larger than the symbol.**

values ranging from -0.51 ± 0.04‰ (2s, n = 5, olivine basalt, GSR-3; Table 1) to +0.20 ± 0.11‰ (2s, n = 5, WGB-1; Table 1), with a mean of -0.12 ± 0.37‰ (2s).

Either $\delta^{98/95}$Mo data (range from -0.56 ± 0.01‰ to +0.53 ± 0.21‰) for a suite of mafic and ultramafic rocks reported by Liang *et al.* (2013), or mean value $\delta^{98/95}$Mo = -0.17 ± 0.22‰ renormalised to NIST SRM 3134 using the conversion of Greber *et al.* (2012) for several igneous rocks from Kamchatka obtained by Siebert *et al.* (2003) are within the range of our Mo isotope data for igneous rock reference materials (Table 1). The Mo isotope compositions for most igneous rocks in the present study (except UB-N, GSR-3, WGB-1; Table 1 and Figure 3) are close to that of estimated chondritic (-0.16 ± 0.02‰, Burkhardt *et al.* 2014) and Bulk Silicate Earth (-0.21 ± 0.06‰, Greber *et al.* 2015).

For the organic rich sediments, SGR-1b is enriched in the heavy Mo isotope ($\delta^{98/95}$Mo = 0.44 ± 0.11‰, 2s; Table 1); however, SCo-1 is enriched in light Mo ($\delta^{98/95}$Mo = -0.41 ± 0.03‰, 2s; Table 1). In previous studies, the organic rich sediments show highly variable $\delta^{98/95}$Mo signatures ranging from -1.79 to 2.08‰ (Kendall *et al.* 2011, Xu *et al.* 2012, Wen *et al.* 2015) and the $\delta^{98/95}$Mo values of SCo-1, SGR-1 and SDO-1 (not measured in this study) are within this range.

The $\delta^{98/95}$Mo values of the marine Fe–Mn precipitates (Nod-P-1, Nod-A-1, and GBW07337) lie in a narrow range of -0.83 ± 0.05‰ to -0.94 ± 0.07‰ (2s, n = 5; Table 1), within the range of Mo isotope values obtained from various other marine ferromanganese crusts and nodules (Barling *et al.* 2001, Siebert *et al.* 2003, Asael *et al.* 2013). The renormalised values of Nod-P-1 and Nod-A-1 from Barling *et al.* (2001) show larger differences in Nod-P-1 compared with our $\delta^{98/95}$Mo data and the data of Asael *et al.* (2013) (-1.3‰ versus -0.8‰ and -0.7‰, respectively; Table 1), but their Nod-A-1 values are in excellent agreement with our $\delta^{98/95}$Mo data and the data reported by Asael *et al.* (2013) (-0.88‰ versus -0.9‰ and 0.83‰, respectively; Table 1). This may indicate that the Nod-P-1 reference materials batches have different or heterogeneous Mo compositions.

The coral sample, JCp-1 (*Porites*) from Ishigaki Island, Japan, has an average $\delta^{98/95}$Mo of 0.25 ± 0.08‰ (2s, n = 5). This value is much lower than values for corals from the Bahamas and Florida (1.7–2.0‰, Voegelin *et al.* 2009). However, the Mo mass fraction of JCp-1 (0.08 μg g^{-1}) is much higher than that for corals from the Bahamas and Florida (0.02–0.03 μg g^{-1}). The differences of mass fractions and Mo isotopic compositions between the Japanese and the Bahamas and Florida corals may indicate different degrees of biologically-induced fractionation in different growing environments (Voegelin *et al.* 2009). The average

$\delta^{98/95}$Mo values for molybdenites from Jinduicheng (JDC) and Hanglongpu (HLP), China, were -0.14 ± 0.07‰ and -0.59 ± 0.02‰ (2s, n = 5; Table 1), respectively. These $\delta^{98/95}$Mo values are within analytical uncertainty of those reported by Siebert *et al.* (2003) and Malinovsky *et al.* (2005), when corrected to the same reference value (NIST SRM 3134).

A comparison of available Mo isotope data with our present results indicates that precise and accurate Mo isotopic data can be routinely obtained in a wide range of natural rocks, minerals and water samples.

Acknowledgements

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