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High-Precision Measurement of Molybdenum Isotopic Compositions of Selected Geochemical Reference Materials

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Here we describe high-precision molybdenum isotopic composition measurements of geological reference materials, performed using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS). Purification of Mo for isotopic measurements was achieved by ion exchange chromatography using Bio-Rad AG® 1-X8 anion exchange resin. Instrumental mass bias was corrected using ^{100}Mo-^{97}Mo double spiking techniques. The precision under intermediate measurement conditions (eighteen measurement sessions over 20 months) in terms of $\delta^{98/95}$Mo was 0.10‰ (2*s*). The measurement output was approximately four times more efficient than previous techniques, with no compromise in precision. The Mo isotopic compositions of seven geochemical reference materials, seawater (IAPSO), manganese nodules (NOD-P-1 and NOD-A-1), copper-molybdenum ore (HV-2), basalt (BCR-2) and shale (SGR-1b and SCo-1), were measured. $\delta^{98/95}$Mo values were obtained for IAPSO (2.25 ± 0.09‰), NOD-P-1 (-0.66 ± 0.05‰), NOD-A-1 (-0.48 ± 0.05‰), HV-2 (-0.23 ± 0.10‰), BCR-2 (0.21 ± 0.07‰), SCo-1 (-0.24 ± 0.06‰) and SGR-1b (0.63 ± 0.02‰) by calculating $\delta^{98/95}$Mo relative to NIST SRM 3134 (0.25‰, 2*s*). The molybdenum isotopic compositions of IAPSO, NOD-A-1 and NOD-P-1 obtained in this study are within error of the compositions reported previously. Molybdenum isotopic compositions for BCR-2, SCo-1 and SGR-1b are reported for the first time.

Keywords: molybdenum isotopes, ion exchange chromatography, geochemical reference materials, multi-collector inductively coupled plasma-mass spectrometry, certified reference materials.

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Nous décrivons ici des mesures de haute précision de la composition isotopique du molybdène dans des matériaux géologiques de référence, effectuées à l'aide de la spectrométrie de masse avec plasma à couplage inductif et à multi-collection (MC-ICP-MS). La purification du Mo pour les mesures isotopiques a été réalisée par chromatographie échangeuse d'ions en utilisant la résine échangeuse d'anions Bio-Rad AG® 1-X8. Le biais de masse instrumental a été corrigé en utilisant des techniques de double spike Mo^{100}-Mo^{97}. La précision dans des conditions de mesure intermédiaires (dix-huit séances de mesure sur 20 mois) en termes de δMo$^{98/95}$ était de 0,10 ‰ (2s). La sortie de mesure était environ quatre fois plus efficace que pour les techniques précédentes, sans compromis sur la précision. Les compositions isotopiques du Mo de sept matériaux de référence géochimiques, eau de mer (IAPSO), nodules de manganèse (NOD-P-1 et NO-A-1), minerai de cuivre-molybdène (HV-2), basalte (BCR-2) et schistes (SGR-1b et SCo-1), ont été mesurées. Les valeurs de δMo$^{98/95}$ ont été obtenus pour IAPSO (2,25 ± 0,09 ‰), NOD-P-1 (-0,66 ± 0,05 ‰), NOD-A-1 (-0,48 ± 0,05 ‰), HV-2 (-0,23 ± 0,10 ‰), BCR-2 (0,21 ± 0,07 ‰), SCo-1 (-0,24 ± 0,06 ‰) et SGR-1b (0,63 ± 0,02 ‰) en calculant δMo$^{98/95}$ par rapport au NIST SRM 3134 (0,25 ‰, 2s). Les compositions isotopiques du molybdène d'IAPSO, NOD-A-1 et NOD-P-1 obtenu dans cette étude sont dans la fourchette d'erreur des compositions déjà rapportées. Les compositions isotopiques du molybdène pour BCR-2, SCO-1 et SGR-1b sont rapportées pour la première fois.

Mots-clés : isotopes du molybdène, chromatographie échangeuse d'ions, matériaux de référence géochimiques, MC-ICP-MS, matériaux de référence certifiés.

The molybdenum (Mo) isotopic system is a useful geochemical tool to track the palaeoredox conditions of the palaeoceans (e.g., Barling *et al.* 2001, Siebert *et al.* 2003, Pearce *et al.* 2008), the pathways of Mo scavenging from ocean water (e.g., Barling and Anbar 2004, Wen *et al.* 2010, Nägler *et al.* 2011), sources of ore formations

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(e.g., Hannah *et al.* 2007, Mathur *et al.* 2010, Greber *et al.* 2011), as well as being a recorder of modern and ancient biological processes (Zerkle *et al.* 2011).

Two kinds of measurement standard are necessary to ensure the reliability of stable isotopic data: (a) single element standard solutions, which are used for instrumental calibration; and (b) geochemical reference materials, which are used to qualify chromatographic separation, total procedure of measurement and precision under intermediate measurement conditions of mass spectrometry performance, as well as enable inter-laboratory comparisons. The U.S. Geological Survey (USGS) Devonian Ohio Shale reference material SDO-1 has been frequently analysed for Mo isotopic compositions (Barling *et al.* 2001, Poulson Brucker *et al.* 2009, Duan *et al.* 2010, Goldberg *et al.* 2013); however, it is now commercially unavailable. Given the widespread interest in the application of Mo isotopes as mentioned above, a database of Mo isotopic compositions in a suite of geochemical reference materials with a range of chemical compositions/matrices is urgently needed.

In this study, the molybdenum isotopic compositions of seven geochemical reference materials (Appendix A), seawater (IAPSO), manganese nodules (NOD-P-1 and NOD-A-1), shale (SCo-1 and SGR-1b), basalt (BCR-2) and copper-molybdenum ore (HV-2) were measured and are reported herein. These reference materials cover the range in current application areas of Mo isotopes in the geosciences.

Experimental procedure

Apparatus, reagents and samples

The preparation and manipulation of samples were performed inside Class 100 laminar flow hoods in a Class 1000 clean room at the Laboratory of Isotopic Geology, Institute of Geology, Chinese Academy of Geological Sciences, Beijing, China. An in-house Savillex® DST-1000 acid purification system was used to purify the acids used in this study, including HCl, HNO_3 and HF. The Savillex® PFA containers were soaked overnight in 5 mol l^{-1} HNO_3 at ~100 °C, rinsed with water (resistivity 15 MΩ cm), then soaked in 1.5 mol l^{-1} purified HNO_3 overnight and rinsed with pure water (resistivity 18.2 MΩ cm) three times, and finally dried before being used in experiments.

A number of single-element standard solutions, including Fe, Ca, Na, Mn, Mg, Sr, Al, Zr, Ti, Cu, K and Mo (all 1000 μg ml^{-1}) from the Central Iron and Steel Research Institute, China, and the "Alfa" Mo standard solution (Lot 13-15044B, 1000 μg ml^{-1}) from Johnson Matthey were used during this study.

Mass fractionation was corrected using the ^{100}Mo-^{97}Mo double spike. The ^{100}Mo spike and ^{97}Mo spike solutions were provided by Dr. Anthony Cohen from the Open University, UK, and were created by dissolving solid ^{100}Mo and ^{97}Mo, obtained from the Oak Ridge National Laboratory, USA, using a mixture of HCl and HNO_3, then diluted and stored in 50 ml of 10% HNO_3, resulting in two single isotopic solutions of ~100 μg ml^{-1}. Aliquots of each spike solution were mixed at 1:1 and diluted to 500 ml in 2% HNO_3 in our laboratory to create a final double spike solution with a concentration of ~2 μg ml^{-1} of each isotope. A $^{100}Mo_{spike}/^{100}Mo_{sample}$ ratio of ~3, calculated using "The double spike toolbox" (Rudge *et al.* 2009) and suggested by Pearce *et al.* (2009), was targeted during sample analysis.

Sample preparation

Three aliquots of the IAPSO seawater reference material (~90 ml) were acidified using 1 ml of 9 mol l^{-1} HCl, to which appropriate amounts of the ^{100}Mo-^{97}Mo double spike were added. The spiked solution was evaporated to dryness before being re-dissolved in 10 ml of 4 mol l^{-1} HCl. Because the salinity of seawater is high (35‰), as 90% water was evaporated there was some salt precipitation as the fluid became oversaturated. Any insoluble salts were separated by centrifuging for 5 min at 4000 rpm.

Three separate dissolutions of NOD-P-1 (~0.01 g), six separate dissolutions of NOD-A-1 (~0.01 g), and three separate dissolutions of HV-2 (~0.01 g) were weighed accurately into 15 ml Savillex® beakers to which the ^{100}Mo-^{97}Mo double spike was added. Samples were digested for 2 days on hot plates at 130 °C using 4 ml of a 3:1 mixture of 17 mol l^{-1} HF and 12 mol l^{-1} HNO_3. All Mo concentrations and Mo isotopic compositions of NOD-A-1 and NOD-P-1 are the result of the total dissolution of the samples. The intention was to obtain the Mo concentration and Mo isotopic composition of Fe-Mn nodules by total dissolution, as they are (USGS) reference materials with only recommended values. However, this may raise some uncertainty in terms of Mo isotopic compositions obtained by only partial dissolution.

Three separate dissolutions of BCR-2 (~0.2 g) were weighed accurately into 15 ml Savillex® beakers to which the ^{100}Mo-^{97}Mo double spike solution was added. The dissolutions were then kept on a hot plate at 130 °C, and digested using 5 ml of a 4:1 mixture of 17 mol l^{-1} HF and 12 mol l^{-1} HNO_3 to ensure complete dissolution.

Five separate dissolutions of SCo-1 (~1 g) and three separate dissolutions of SGR-1b (~0.1 g) were weighed accurately into 50 ml quartz crucibles, to which the ^{100}Mo-^{97}Mo double spike solution was added, and subsequently ashed at 600 °C over 6 hr in a muffle furnace to decompose organic material. After cooling, these samples were carefully transferred to a 15 ml Savillex® beaker and digested using 8 ml of a 3:1 mixture of 17 mol l^{-1} HF and 12 mol l^{-1} HNO_3. The beakers were kept on a hot plate at 130 °C for ~2 days.

Following digestion, IAPSO reference seawater was evaporated to dryness and the residues were then dissolved in 7 ml of 1 mol l^{-1} HF/0.5 mol l^{-1} HCl and centrifuged for 5 min at 4000 rpm to remove any residual solids. NOD-P-1, NOD-A-1, HV-2, BCR-2, SGR-1b and SCo-1 were evaporated to dryness, taken up in 12 mol l^{-1} HNO_3, and evaporated to dryness three times, then taken up in 9 mol l^{-1} HCl and evaporated to dryness three times. The residues were then dissolved in 7 ml of 1 mol l^{-1} HF/0.5 mol l^{-1} HCl and centrifuged for 5 min at 4000 rpm to remove any residual solids. The supernatant liquids were then ready for the chromatographic separation of Mo.

Chromatographic separation of Mo

Purification of Mo is necessary to eliminate potential spectral interferences and minimise matrix effects during MC-ICP-MS measurements. The chromatographic procedure used 2 ml of Bio-Rad AG® 1-X8 anion exchange resin in a 10-ml Poly-Prep® column as reported by Pearce *et al.* (2009). Details of cleaning, conditioning, sample loading, matrix washing and Mo elution for this chromatographic procedure are listed in Table 1.

Table 1.
Elution sequence for ion-exchange chromatography using Bio-Rad AG® 1-X8 anion exchange resin

Eluent	Volume (ml)	Purpose
1 mol l^{-1} HCl	32 ml	Resin cleaning
1 mol l^{-1} HF/0.5 mol l^{-1} HCl	4 ml	Resin conditioning
1 mol l^{-1} HF/0.5 mol l^{-1} HCl	6 ml	Sample load
1 mol l^{-1} HF/0.5 mol l^{-1} HCl	8 ml	Matrix elution
4 mol l^{-1} HCl	8 ml	Matrix elution
3 mol l^{-1} HNO_3	10 ml	Mo elution

Black shales are the most commonly used geological samples in Mo isotopic studies regarding palaeo-redox conditions (e.g., Arnold *et al.* 2004, Pearce *et al.* 2008, Wille *et al.* 2008, Gordon *et al.* 2009, Kendall *et al.* 2009, Dahl *et al.* 2010). Thus, it is important to examine whether the purification method proposed by Pearce *et al.* (2009) is suitable for black shale, given that this was not thoroughly investigated in their study. To investigate this issue, a multi-element solution which simulates the chemical composition of typical black shale was made by mixing the following twelve single-element standard solutions: Fe (13 μg), Ca (13 μg), Na (14 μg), Mn (14 μg), Mg (15 μg), Sr (17 μg), Al (20 μg), Zr (26 μg), Ti (36 μg), Cu (40 μg), K (45 μg), and Mo (25 μg). Some of the included elements (Mg, Ti, K, Na, Ca, Al, Cu and Sr) were not investigated in the original study of Pearce *et al.* (2009). Of these, Sr was used as a dopant for correction of instrumental mass discrimination during Mo isotope measurements in the study of Nakagawa *et al.* (2008), and Mg, Ti, K, Na, Ca and Al are the major elements in black shale. The multi-element standard solution was loaded onto the preconditioned columns in 6 ml of a 1 mol l^{-1} HF/0.5 mol l^{-1} HCl solution. The column was then washed with 8 ml of 1 mol l^{-1} HF/0.5 mol l^{-1} HCl, followed by 8 ml of 4 mol l^{-1} HCl. Finally, 10 ml 3 mol l^{-1} HNO_3 was used to elute the Mo. Eluents were collected in every 1 ml. Elemental concentrations of eluents were determined using IRIS Advantage ICP-AES at the National Research Center for Geoanalysis, Chinese Academy of Geological Sciences, Beijing, China. As illustrated in Figure 1, there is a clear difference between the Mo and matrix fractions, demonstrating the procedure is effective for the separation Mo in black shale as well as other common geological materials from the matrix. Measured Mo recovery for the unspiked solution was 99.3%. The total procedure blank was < 2.5 ng, which is negligible relative to the Mo contents of the samples. The Mo fraction was then evaporated to dryness and re-dissolved in 0.3 mol l^{-1} HNO_3 for determination by MC-ICP-MS.

MC-ICP-MS analysis

All Mo isotopic measurements were made at the Laboratory of Isotopic Geology, Institute of Geology, Chinese Academy of Geological Sciences using a Nu Plasma HR type MC-ICP-MS equipped with a Nu Instruments DSN-100 desolvating nebuliser. Samples were aspirated in 0.3 mol l^{-1} HNO_3 at a rate of ~100 μl min^{-1}, with typical solution concentrations of ~200 ng ml^{-1} for Mo. The Mo isotopic measurements involved the collection of one block of data with twenty cycles in static mode. The integration time for each cycle was 10 s. Background measurements were made before every block by deflection of the ESA. After each

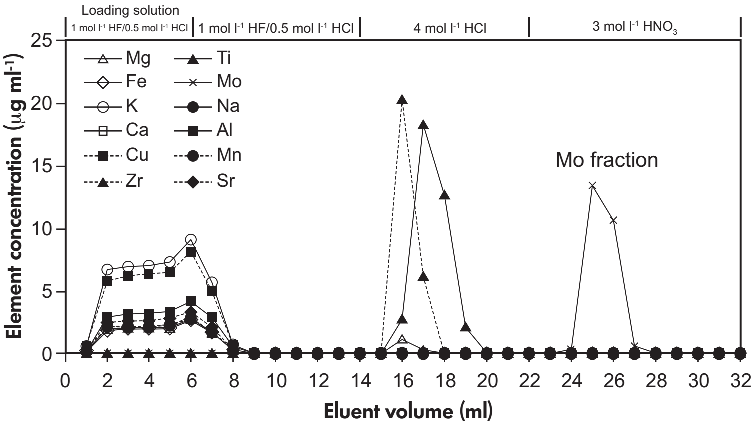

Figure 1. Elution curves of selected elements for the chromatographic separation procedure described in detail in the text.

analysis, the nebuliser and MC-ICP-MS system were rinsed in purified 1.5 mol l^{-1} HNO_3 for 150 s, and in 0.3 mol l^{-1} HNO_3 for 100 s. The Mo isotope data were standardised following Nägler *et al.* (2014), where the $\delta^{98/95}$Mo composition of NIST SRM 3134 (Lot No. 891307) is set to 0.25‰, defined as

$$\delta^{98/95}\mathrm{Mo} = ((^{98}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{sample}}/(^{98}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{NIST\,SRM\,3134}} \times 0.99975 - 1) \times 1000 \qquad (1)$$

where $\delta^{98/95}$Mo is in units of ‰, $\delta^{97/95}\mathrm{Mo} = 0.667 {*} \delta^{98/95}\mathrm{Mo}$ and $\delta^{100/95}\mathrm{Mo} = 1.667 {*} \delta^{98/95}\mathrm{Mo}$.

Double spiking was employed to correct for instrumental mass bias (Li *et al.* 2011). The ^{100}Mo-^{97}Mo double spike and NIST SRM 3134 composition were calibrated via the Pd-doping method using a ^{104}Pd/^{102}Pd normalisation ratio of 10.922, as described by Siebert *et al.* (2001). The calibration results for the double spike and NIST SRM 3134 are presented in Table 2.

Data reduction was performed offline, with calculated ^{97}Mo/^{95}Mo, ^{98}Mo/^{95}Mo and ^{100}Mo/^{95}Mo ratios input into the same iterative data reduction protocol as that previously described by Pearce *et al.* (2009). Instrumental drift was monitored by analysing both spiked NIST SRM 3134 and spiked Alfa standard solution at the start of each day, and periodically during sample analysis.

Results and discussion

Precision and accuracy

Two hundred analyses of the Alfa standard solution (relative to NIST SRM 3134 = 0.25‰), covering eighteen measurement sessions over a period of 20 months, yielded a result of $\delta^{98/95}$Mo = -0.24 ± 0.10‰ (2*s*) (Figure 2 and Appendix B). This defines precision under intermediate measurement conditions of better than 0.10‰ at the 95% confidence level, which is similar to that reported in the literature (Barling *et al.* 2001, Siebert *et al.* 2001, Malinovsky *et al.* 2005, Pietruszka *et al.* 2006, Pearce *et al.* 2009). The Mo isotopic composition of the IAPSO seawater reference material is presented in Table 3. The $\delta^{98/95}$Mo value obtained in this study is within error of the results of Siebert *et al.* (2003), Pearce *et al.* (2008), Greber *et al.* (2012) and Li *et al.* (2014), further demonstrating the reliability of the measurements.

Results of the analyses of all seven reference materials obtained in this study, together with those from the

Table 2.
Compositions of the ^{100}Mo-^{97}Mo double spike and NIST SRM 3134 standard solution

	^{100}Mo/^{97}Mo	^{98}Mo/^{97}Mo	^{96}Mo/^{97}Mo	^{95}Mo/^{97}Mo	^{94}Mo/^{97}Mo	^{92}Mo/^{97}Mo
NIST SRM 3134	1.00503	2.52566	1.746915	1.669143	0.970418	1.558031
2*s*	0.000179	0.000199	0.000244	0.000252	0.000225	0.00046
Double spike	0.987717	0.061941	0.027204	0.017961	0.009584	0.01687
2*s*	0.000144	0.00004	0.000032	0.00003	0.000016	0.000028

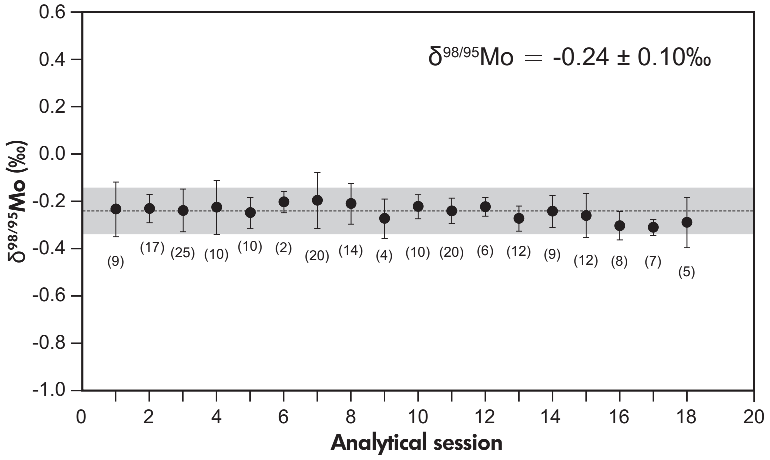

Figure 2. $\delta^{98/95}$Mo of Alfa Mo standard solutions (relative to NIST SRM 3134 = 0.25‰) determined from eighteen measurement sessions. The number of measurements made during each session is shown in brackets. Error bars represent 2*s* during a measurement session, whilst the grey band represents the 2*s* value of all analyses.

literature, are presented in Table 3. All Mo concentrations obtained during this research were calculated following the use of the double spike method. The Mo concentrations of NOD-A-1, NOD-P-1, SCo-1 and SGR-1b obtained in this study are within error of, or close to the concentrations listed in the certificate of analysis of each reference material. USGS certified Mo concentration for BCR-2 is 248 µg g^{-1}, and the measured result of this study is ~300 µg g^{-1}. The extremely high concentration of Mo confirmed that BCR-2 is contaminated with respect to Mo, because such high values are extremely unlikely for basaltic materials (average crustal Mo concentrations are 1–3 µg g^{-1}). The measurement repeatability of Mo analyses of BCR-2 (329.0 ± 60.5 µg g^{-1}) and HV-2 (715.6 ± 112.1 µg g^{-1}) from separate dissolutions was not good, indicating that the BCR-2 and HV-2 were not homogenous with respect to their Mo concentration.

The $\delta^{98/95}$Mo value of the IAPSO seawater reference material obtained in this study is within error of values reported in the literature. The $\delta^{98/95}$Mo values of manganese nodules obtained in this study are -0.66 ± 0.05‰ and -0.48 ± 0.05‰ for NOD-P-1 and NOD-A-1, respectively. These two reference materials have been measured by Barling *et al.* (2001), Asael *et al.* (2013) and Goto *et al.* (2015). The $\delta^{98/95}$Mo values of NOD-A-1 and NOD-P-1 obtained in this study are within error of the values reported by Asael *et al.* (2013) and Goto *et al.* (2015); however, the study of Barling *et al.* (2001) was made at a very early stage of technical development in Mo isotopic determinations, and it has been argued that those techniques are less reliable than those employed more recently (Goldberg *et al.* 2013). This point is exemplified by the $\delta^{98/95}\text{Mo}_{\text{SDO-1}}$ of Barling *et al.* (2001) having a large positive deviation compared with other studies (Poulson Brucker *et al.* 2009, Duan *et al.* 2010, Scheiderich *et al.* 2010, Goldberg *et al.* 2013), and the $\delta^{98/95}\text{Mo}_{\text{Seawater}}$ of Barling *et al.* (2001) (1.85‰, $\delta^{98/95}$Mo NIST SRM 3134 = 0.25‰) having a large negative deviation (~0.25‰) compared with other studies (Siebert *et al.* 2003, Archer and Vance 2008, Nakagawa *et al.* 2008, Pearce *et al.* 2009, Scheiderich *et al.* 2010, Goldberg *et al.* 2013).

The $\delta^{98/95}$Mo value of the copper-molybdenum ore reference material HV-2 obtained in this study is -0.23 ± 0.10‰. Although this material has been measured for Mo isotopic composition before (Pietruszka *et al.* 2006), these previous results were presented relative to the in-house Mo isotope standard solution (Spex Certiprep, catalog# CLMO9-2Y). However, as differences in Mo isotopic composition between Spex Certiprep and NIST SRM 3134 (or other Mo isotope reference materials related to or compared with NIST SRM 3134) are unknown, it is not possible at this stage to compare our results with those reported by Pietruszka *et al.* (2006). We therefore recommend our result ($\delta^{98/95}$Mo = -0.23 ± 0.10‰) as the Mo isotopic composition of HV-2.

BCR-2 (basalt), SGR-1b (shale) and SCo-1 (shale) are widely used reference materials for various analyses and are commercially available. However, to date, there are no reported Mo isotopic measurements for these materials. We report the Mo isotopic compositions of these reference materials for the first time as follows: $\delta^{98/95}\text{Mo}_{\text{BCR-2}}$ = 0.21 ± 0.07‰ (*n* = 3, 2*s*), $\delta^{98/95}\text{Mo}_{\text{SCo-1}}$ = -0.24 ±

Table 3.
Mo concentrations and Mo isotopic compositions of the analysed reference materials

Geochemical reference materials			[Mo] (µg g^{-1} ± 2*s*)	Reference	$\delta^{100/95}$Mo (‰)	$\delta^{98/95}$Mo (‰)	$\delta^{97/95}$Mo (‰)	Reference
Seawater	IAPSO	IAPSO 1#			3.74	2.26	1.52	This study
		IAPSO 2#			3.79	2.29	1.54	
		IAPSO 3#			3.64	2.20	1.47	
					3.72 ± 0.15	**2.25 ± 0.09**	**1.51 ± 0.07**	
					(*n* = 3, 2*s*)	**(*n* = 3, 2*s*)**	**(*n* = 3, 2*s*)**	
						2.28 ± 0.10		Siebert *et al.* (2003)
						2.16 ± 0.05		Pearce *et al.* (2008)
			0.011	Greber *et al.* (2012)		2.35 ± 0.05		Greber *et al.* (2012)
						2.25 ± 0.03		Li *et al.* (2014)
Manganese nodule	NOD-P-1	NOD-P-1 1#	775.3		-1.03	-0.63	-0.42	This study
		NOD-P-1 2#	782.5		-1.10	-0.67	-0.45	
		NOD-P-1 3#	771.8		-1.09	-0.67	-0.45	
		Average	**776.5 ± 10.9**		**-1.08 ± 0.08**	**-0.66 ± 0.05**	**-0.44 ± 0.03**	
					(*n* = 3, 2*s*)	**(*n* = 3, 2*s*)**	**(*n* = 3, 2*s*)**	
						-0.61 ± 0.10		Goto *et al.* (2015)
						-0.58 ± 0.10		Asael *et al.* (2013)
			760 ± 8	USGS Certificate of Analysis (NOD-P-1)		-0.71^{a}	-0.47 ± 0.10	Barling *et al.* (2001)
Manganese nodule	NOD-A-1	NOD-A-1 1#	481.2		-0.72	-0.44	-0.29	This study
		NOD-A-1 2#	485.0		-0.81	-0.49	-0.33	
		NOD-A-1 3#	484.3		-0.81	-0.5	-0.33	
		NOD-A-1 4#			-0.82	-0.5	-0.34	
		NOD-A-1 5#			-0.73	-0.45	-0.3	
		NOD-A-1 6#			-0.77	-0.47	-0.31	
		Average	**483.5 ± 4.0**		**-0.78 ± 0.09**	**-0.48 ± 0.05**	**-0.32 ± 0.04**	
					(*n* = 6, 2*s*)	**(*n* = 6, 2*s*)**	**(*n* = 6, 2*s*)**	
						-0.41 ± 0.08		Goto *et al.* (2015)
						-0.42 ± 0.04		Asael *et al.* (2013)
			448 ± 18	USGS Certificate of Analysis (NOD-A-1)		-1.04^{a}	-0.69 ± 0.10	Barling *et al.* (2001)
Copper-molybdenum ore	HV-2	HV-2 1#	777.1		-0.46	-0.28	-0.19	This study
		HV-2 2#	702.5		-0.35	-0.22	-0.14	
		HV-2 3#	667.3		-0.30	-0.19	-0.12	
		Average	**715.6 ± 112.1**		**-0.37 ± 0.16**	**-0.23 ± 0.10**	**-0.15 ± 0.06**	
					(*n* = 3, 2*s*)	**(*n* = 3, 2*s*)**	**(*n* = 3, 2*s*)**	
			480 ± 4	Certificate of Analysis HV-2				

Table 3 (continued).
Mo concentrations and Mo isotopic compositions of the analysed reference materials

Geochemical reference materials			**[Mo] ($\mu g\ g^{-1} \pm 2s$)**	**Reference**	**$\delta^{100/95}$Mo (‰)**	**$\delta^{98/95}$Mo (‰)**	**$\delta^{97/95}$Mo (‰)**	**Reference**
Basalt	BCR-2	BCR-2 1#	348.8		0.29	0.17	0.12	This study
		BCR-2 2#	344.1		0.40	0.24	0.16	
		BCR-2 3#	294.2		0.36	0.22	0.15	
		Average	**329 ± 60.5**		**0.35 ± 0.11 (*n* = 3, 2*s*)**	**0.21 ± 0.07 (*n* = 3, 2*s*)**	**0.14 ± 0.04 (*n* = 3, 2*s*)**	
			248 ± 34	USGS Certificate of Analysis (BCR-2)				
Shale	SCo-1	Sco-1 1#	1.6		-0.39	-0.24	-0.16	This study
		Sco-1 2#	1.5		-0.4	-0.25	-0.16	
		Sco-1 3#	1.5		-0.42	-0.26	-0.17	
		Sco-1 4#	1.2		-0.30	-0.19	-0.12	
		Sco-1 5#	1.2		-0.38	-0.24	-0.16	
		Average	**1.4 ± 0.4**		**-0.38 ± 0.09 (*n* = 5, 2*s*)**	**-0.24 ± 0.06 (*n* = 5, 2*s*)**	**-0.16 ± 0.04 (*n* = 5, 2*s*)**	
			1.4 ± 0.4	USGS Certificate of Analysis (SCo-1)				
Shale	SGR-1b	SGR-1b 1#	44.6		1.07	0.65	0.44	This study
		SGR-1b 2#	44.7		1.05	0.63	0.42	
		SGR-1b 3#	44.8		1.04	0.62	0.43	
		Average	**44.7 ± 0.2**		**1.05 ± 0.04 (*n* = 3, 2*s*)**	**0.63 ± 0.02 (*n* = 3, 2*s*)**	**0.43 ± 0.01 (*n* = 3, 2*s*)**	
			35 ± 1.8	USGS Certificate of Analysis (SGR-1b)				

The bold values are the average and 2s of it's above (three value).

All reported data were renormalised to $\delta^{98/95}$Mo $_{\text{NIST 3134}}$ = 0.25‰. *n* is the number of separate dissolution and analyses, 2*s* is 2 standard deviations). There is no Mo concentration for IAPSO because the volume of IASPO was not known accurately.

[a] $\delta^{98/95}$Mo was calculated from $\delta^{97/95}$Mo.

0.06‰ ($n = 5$, $2s$), and $\delta^{98/95}Mo_{SGR\text{-}1b} = 0.63 \pm 0.02$‰ ($n = 3$, $2s$) (Table 3).

As shown in Table 3, the $2s$ values of measurements for all seven reference materials are within the intermediate precision described above. Each of these seven geochemical reference materials is homogeneous with respect to their Mo isotopic composition. It is possible that the Mo composition of BCR-2 is not representative of all basaltic materials, but it is still useful to qualify chromatographic separation, the total procedure of measurement and intermediate precision in mass spectrometry performance, and enable inter-laboratory comparisons.

Improvement in analytical techniques

The mass spectrometer measurement protocol used to quantify Mo isotopes in this study differs from a previous technique described by Pearce *et al.* (2009), which consisted of ten blocks with ten cycles, with an integration time of 8 s and a magnet settling time of 2 s between cycles. The protocols of this study used a single block of twenty cycles, with a integration time of 10 s for each cycle and a magnet settling time of 6 s. Another difference was the measurement and offset of the average of the spiked NIST SRM 3134 calibration value before and after every three samples. This approach was taken to provide a more regular factor, applying only to the bracketed samples, instead of using a single factor calculated from the offset of the daily mean of the spiked NIST SRM 3134 calibration values and applying it to all analyses made during the same session (Pearce *et al.* 2009). The measurement output is about four times more efficient relative to previous techniques (Pearce *et al.* 2009).

Conclusions

The procedure using Bio-Rad AG® 1-X8 anion exchange resin can separate Mo from matrix elements (Fe, Mg, K, Na, Ca, Al, Cu, Sr, Mn, Ti and Zr) effectively in black shales and other common geological materials. The Mo isotope measurement protocol of this study saves time and has a precision comparable to that reported by Pearce *et al.* (2009).

In addition, we report the Mo isotopic compositions of the BCR-2, SCo-1 and SGR-1b reference materials for the first time as follows: $\delta^{98/95}Mo_{BCR\text{-}2} = 0.21 \pm 0.07$‰ ($n = 3$, $2s$), $\delta^{98/95}Mo_{SCo\text{-}1} = -0.24 \pm 0.06$‰ ($n = 5$, $2s$) and $\delta^{98/95}Mo_{SGR\text{-}1b} = 0.63 \pm 0.02$‰ ($n = 3$, $2s$).

The reference materials measured in this study are representative of the range of sample types currently analysed for Mo isotopes in the field of geosciences. The data obtained in this study are suitable for sample calibration, and provide a better baseline for quality assurance and inter-laboratory comparison.

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Appendix A

Information on reference materials IAPSO, NOD-P-1, NOD-A-1, HV-2, BCR-2, SCo-1 and SGR-1b

IAPSO is an Atlantic seawater reference material of International Association for the Physical Sciences of the Oceans (IAPSO), prepared from natural open-ocean surface waters of the mid-Atlantic. It was treated with ultra-violet light and filtered to 0.2 µm to minimise microbial contamination.

NOD-P-1 is a manganese nodule reference material from the USGS, collected from the Pacific Ocean (14°50′N, 124°28′W) at a depth of 4300 m.

NOD-A-1 is a manganese nodule reference material from the USGS, collected from the Atlantic Ocean along the Blake Plateau (31° 02′N, 78° 22′W) at a depth of 788 m (Flanagan and Gottfried 1980).

HV-2 is a copper-molybdenum ore reference material from Canada's Center for Mineral and Energy Technology (CANMET) Mining and Mineral Sciences Laboratories, donated by Teck Highland Valley Copper Partnership in British Columbia, Canada.

BCR-2 is a USGS basalt reference material, collected in 1996 from the Bridal Veil Flow Quarry under the direction of Stephen A. Wilson (USGS). The quarry is located approximately 29 miles east of Portland, Oregon.

SCo-1 is a USGS shale reference material, from Natrona County, Wyoming, near the Naval Petroleum Reserve at Teapot Dome. It is typical of the Upper Cretaceous silty marine shales, intermediate between fine-grained offshore shales and coarser nearshore marine siltstones. The rock is medium dark-grey (Munsel N-4) silty shale having thin lighter coloured silty laminations (Flanagan 1976).

SGR-1b is a USGS shale reference material, collected from the Mahogany zone of the Green River Formation. It is a petroleum and carbonate-rich shale.

Appendix B

$\delta^{98/95}$Mo results for Alfa Mo standard solutions (relative to NIST SRM 3134 = 0.25‰) measured during eighteen measurement sessions

Session	$\delta^{98/95}$Mo																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	-0.16	-0.21	-0.23	-0.13	-0.22	-0.22	-0.21	-0.18	-0.27	-0.23	-0.21	-0.22	-0.26	-0.22	-0.28	-0.3	-0.3	-0.31
2	-0.18	-0.23	-0.21	-0.24	-0.24	-0.19	-0.2	-0.27	-0.33	-0.22	-0.27	-0.24	-0.27	-0.24	-0.25	-0.27	-0.31	-0.32
3	-0.31	-0.27	-0.24	-0.32	-0.23		-0.21	-0.19	-0.23	-0.24	-0.25	-0.19	-0.27	-0.25	-0.32	-0.27	-0.32	-0.35
4	-0.22	-0.21	-0.25	-0.17	-0.23		-0.17	-0.25	-0.27	-0.2	-0.22	-0.24	-0.25	-0.2	-0.19	-0.32	-0.28	-0.25
5	-0.24	-0.21	-0.29	-0.26	-0.32		-0.23	-0.25		-0.24	-0.28	-0.24	-0.23	-0.2	-0.17	-0.34	-0.32	-0.22
6	-0.28	-0.25	-0.27	-0.25	-0.26		-0.21	-0.19		-0.24	-0.22	-0.21	-0.26	-0.23	-0.23	-0.35	-0.31	
7	-0.21	-0.26	-0.27	-0.26	-0.29		-0.23	-0.2		-0.21	-0.3		-0.28	-0.3	-0.25	-0.3	-0.33	
8	-0.33	-0.25	-0.27	-0.21	-0.21		-0.23	-0.2		-0.25	-0.27		-0.26	-0.27	-0.28	-0.29		
9	-0.18	-0.28	-0.28	-0.17	-0.24		-0.14	-0.25		-0.23	-0.23		-0.28	-0.27	-0.26			
10		-0.18	-0.21	-0.24	-0.25		-0.14	-0.2		-0.17	-0.26		-0.3		-0.28			
11		-0.22	-0.25				-0.31	-0.21			-0.25		-0.34		-0.29			
12		-0.19	-0.23				-0.31	-0.24			-0.25		-0.27		-0.32			
13		-0.23	-0.26				-0.22	-0.11			-0.26							
14		-0.26	-0.28				-0.16	-0.21			-0.22							
15		-0.25	-0.14				-0.09				-0.22							
16		-0.2	-0.22				-0.19				-0.24							
17		-0.24	-0.27				-0.15				-0.19							
18			-0.31				-0.24				-0.24							
19			-0.28				-0.09				-0.24							
20			-0.21				-0.16				-0.21							
21			-0.28															
22			-0.17															
23			-0.22															
24			-0.19															
25			-0.14															
Average	**-0.23**	**-0.23**	**-0.24**	**-0.23**	**-0.25**	**-0.20**	**-0.20**	**-0.21**	**-0.27**	**-0.22**	**-0.24**	**-0.22**	**-0.27**	**-0.24**	**-0.26**	**-0.30**	**-0.31**	**-0.29**
2s	**0.12**	**0.06**	**0.09**	**0.11**	**0.07**	**0.04**	**0.12**	**0.08**	**0.08**	**0.05**	**0.05**	**0.04**	**0.05**	**0.07**	**0.09**	**0.06**	**0.03**	**0.11**