

Assessment of Different Digestion Procedures for Mo Isotope Measurements of Black and Grey Shales Using the Double Spike Technique

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ABSTRACT: This study investigates the behavior of Mo and Mo isotopes ($\delta^{98}\text{Mo}$) in shales following leaching with HCl and HNO_3 with the aim of simplifying the shale dissolution procedure. Up to 6% of the Mo was lost and the Mo isotopes was unaffected when shales were leached using 9 M HCl after ashing. Bulk sample digestion or leaching by 4 M or more concentrated HCl after ashing were all found to be acceptable and reliable approaches to the analysis of Mo isotopes in shales. After black shale (CAGS-BS) was leached with 2 M HCl, 1 M HCl, and 9 M HNO_3 , the Mo concentration ([Mo]) in the leachate was lower and $\delta^{98}\text{Mo}$ was heavier than that obtained from bulk digestion. A Mo isotope mass-balance model showed that the $\delta^{98}\text{Mo}$ in the residues was lighter than the $\delta^{98}\text{Mo}$ from the bulk digestion of CAGS-BS and of crustal igneous rocks. No more Mo was lost, nor did Mo isotope fractionation, if the double spike was added before rather than after ashing and followed by bulk digestion or leaching with 9 M HCl. For efficiency, leaching using 4 M or more concentrated HCl after ashing is preferred for Mo isotope measurements.

KEY WORDS: Mo isotopes, double spike, ashing, bulk digestion, leaching.

0 INTRODUCTION

Black shales are fine-grained, organic-rich sedimentary rocks comprising a mixture of detrital and authigenic components. In the detrital component, the molybdenum (Mo) concentration ([Mo]) is low (1.5 ppm; McLennan, 2001). Removal of Mo from a water mass into sediments varies as a function of the water mass redox conditions. In oxic waters, there is generally little authigenic enrichment of Mo in the sediments above continental crustal background concentrations (1 ppm–2 ppm). However, slowly accumulating Fe-Mn nodules and crusts are sometimes enriched to hundreds of parts per million (Algeo and Maynard, 2004), with stable fractionation between Mn-adsorbed Mo and seawater ($\delta^{98}\text{Mo}_{\text{seawater}} - \delta^{98}\text{Mo}_{\text{Mn-adsorbed}} = 3\%$; Barling and Anbar, 2004) and variable fractionations between Fe-adsorbed Mo and seawater ($\delta^{98}\text{Mo}_{\text{seawater}} - \delta^{98}\text{Mo}_{\text{Fe-adsorbed}} = 0.83\%–2.19\%$; Goldberg et al., 2009). The Mo removal rate is $100\times$ to $1\,000\times$ greater in euxinic waters than in oxic waters, leading to significant authigenic enrichment that can exceed 100 ppm (Dahl et al., 2013; Scott and Lyons, 2012; Scott et al., 2008). In euxinic water, Mo isotopic fractionation is closely related to aqueous H_2S concentrations ($[\text{H}_2\text{S}]_{\text{aq}}$). When $[\text{H}_2\text{S}]_{\text{aq}}$ exceeds the threshold value of 11 μM , most aqueous MoO_4^{2-} is trans-

formed to MoS_4^{2-} and quantitatively removed to the sediment (Helz et al., 1996). Under these conditions, Mo isotopic fractionation will be zero and the sediment will acquire a Mo-isotope signature equal, or close to, $\delta^{98}\text{Mo}_{\text{sw}}$ ($\delta^{98}\text{Mo}_{\text{sw}} - \delta^{98}\text{Mo}_{\text{sediment}} \leq 0.5\%$; Nägler et al., 2011; Neubert et al., 2008; Siebert et al., 2006; Barling et al., 2001). In weakly oxygenated waters, with sulfidic conditions developed in the porewaters, Mo is mildly enriched in the underlying sediments. Therefore, Mo isotopes in shales have emerged as a powerful proxy for marine redox evolution (e.g., Dahl and Wirth, 2017; Kurzweil et al., 2015; Kendall et al., 2009).

When shale Mo isotopes are analyzed, organic matter can negatively affect the performance of the subsequent ion-exchange purification of Mo (Malinovsky et al. 2005). Ashing is one of the most common methods used to remove organic matter (e.g., Goldberg et al., 2013; Herrmann et al., 2012; Nägler et al., 2005) because it can quickly destroy organic matter. Bulk sample digestion for Mo isotope measurement has been used after ashing in previous studies (e.g., Dickson et al., 2020; Ostrander et al., 2019; Gordon et al., 2009; Zhou et al., 2007), however, bulk digestion requires large amounts of acid, including HF, HNO_3 , and HCl, and is time consuming.

This study investigates the behaviour of Mo and Mo isotopes in shales when leached with different concentrations of HCl and 9 M HNO_3 and compares the results with those obtained using bulk digestion. Our aim was to simplify the procedure used for the dissolution of black shales in Mo isotope measurements and reduce the volume of acid required. Our approach differs from the leaching experiments performed by

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both Liermann et al. (2011), who investigated black shales in the presence of organic ligands and bacteria, and Voegelin et al. (2012), who studied crustal igneous rocks (basalt, granite, and orthogneiss), because their purpose was to investigate Mo isotope fractionation processes during weathering and quantify the enrichment of heavy Mo isotopes in the leachate.

1 SAMPLE PREPARATION

We prepared the samples under Class 100 laminar flow hoods in a Class 1000 clean room at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of Geological Sciences, Beijing, China. A Savillex® DST-1000 acid-purification system was used to purify the acids (HCl, HNO₃, and HF). The Savillex® PFA containers were soaked overnight in 5 M HNO₃ at ~100 °C, rinsed with water (resistivity 15 MΩ·cm), then soaked in 1.5 M purified HNO₃ overnight and rinsed with pure water (resistivity 18.2 MΩ·cm) three times, before finally being dried and used in the experiments.

In this study, we analyzed shale reference materials from the USGS (SGR-1b) as well as in-house “α” Mo standard solution (Lot 13-15044B) from Johnson Matthey and black shale reference materials (CAGS-BS), together with four black shale samples (Datangpo-1, Datangpo-2, Datangpo-3, and Datangpo-4) and one grey shale sample (Datangpo-5) from the Datangpo Formation in southern China.

2 EXPERIMENTAL DESIGN

To assess the reliability and repeatability of the full analytical and instrumental procedures, each sample for each procedure was processed three times, which involved ashing, bulk sample digestion, leaching with acids, chromatographic separation, and mass spectrometry measurements.

A ⁹⁷Mo-¹⁰⁰Mo double spike was used when analyzing the Mo isotopes (Li et al., 2016). With the double spike, corrections can be made for the mass fractionation that occurs during chemical separation (Rudge et al., 2009). Normally, the double spike is added after ashing (e.g., Ostrander et al., 2019; Goldberg et al., 2013; Nägler et al., 2005).

2.1 Adding Double Spike after Ashing, with Bulk Digestion (Procedure I)

Powdered samples SGR-1b, CAGS-BS, Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 were weighed accurately into 50 mL quartz crucibles (up to 1 g) and ashed at 600 °C for 6 h in a muffle furnace to burn off organic matter. After cooling, the samples were transferred to 15 mL Savillex® beakers, to which the ¹⁰⁰Mo-⁹⁷Mo double spike solution was added, and then bulk digested using 10 mL of a 4 : 1 mixture of 17 M HF and 12 M HNO₃ on a hot plate at 130 °C for approximately 3 days to ensure complete digestion.

2.2 Adding Double Spike after Ashing, with Leaching Using HCl or HNO₃ (Procedure II)

Powdered samples CAGS-BS, Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 were weighed accurately into 50-mL quartz crucibles (up to 1 g), and ashed at 600 °C for 6 h in a muffle furnace to burn off organic matter. After cooling, the samples were transferred to 15-mL Savillex®

beakers, to which the ¹⁰⁰Mo-⁹⁷Mo double spike solution was added. The Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 samples were immersed in 10 mL of 9 M HCl on a hot plate at 130 °C for approximately 1 day. The CAGS-BS samples were leached with 8 M HCl, 6 M HCl, 4 M HCl, 2 M HCl, 1 M HCl, and 9 M HNO₃ on a hot plate at 130 °C for approximately 1 day.

2.3 Adding Double Spike before Ashing, with Bulk Digestion (Procedure III)

Powdered samples Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 were weighed accurately into 50-mL quartz crucibles, to which the ¹⁰⁰Mo-⁹⁷Mo double spike solution was added, and evaporated to dryness on a hot plate at 130 °C. The samples were then ashed at 600 °C for 6 h in a muffle furnace to burn off the organic matter. After cooling, the samples were transferred to 15-mL Savillex® beakers and digested using 10 mL of a 4 : 1 mixture of 17 M HF and 12 M HNO₃. The mixtures were bulk digested on a hot plate at 130 °C for approximately 3 days to ensure complete digestion.

2.4 Adding Double Spike before Ashing, with Leaching (Procedure IV)

Powdered samples Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 were weighed accurately into 50-mL quartz crucibles, to which the ¹⁰⁰Mo-⁹⁷Mo double spike solution was added, and evaporated to dryness on a hot plate at 130 °C. The samples were then ashed at 600 °C for 6 h in a muffle furnace to burn off organic matter. After cooling, these samples were transferred to 15-mL Savillex® beakers and immersed in 10 mL of 9 M HCl on a hot plate at 130 °C for approximately 1 day.

The dissolved samples from procedures I and III were evaporated to dryness, taken up in 12 M HNO₃ and evaporated to dryness three times, then taken up in 9 M HCl and evaporated to dryness three times. The residues were then dissolved in 7 mL of 1 M HF/0.5 M HCl and centrifuged for 5 min at 4 000 rpm to remove any residual solids. The sample solutions leached with different concentrations of HCl were centrifuged for 5 min at 4 000 rpm to separate the leachates from the residual solids. The leachates were evaporated to dryness, and then dissolved in 7 mL of 1 M HF/0.5 M HCl and centrifuged for 5 min at 4 000 rpm to remove any residual solids. The sample solutions leached with 9 M HNO₃ were centrifuged for 5 min at 4 000 rpm to separate the leachates from the residues. The leachates were evaporated to dryness, then taken up in 9 M HCl and evaporated to dryness three times, and then dissolved in 7 mL of 1 M HF/0.5 M HCl and centrifuged for 5 min at 4 000 rpm to remove any residual solids. All of the supernatant liquids were then ready for the chromatographic separation of Mo.

3 ANALYTICAL METHODS

3.1 Chromatographic Separation

For the chromatographic procedure, as described by Pearce et al. (2009) and Li et al. (2016), we used 2 mL of Bio-Rad AG® 1-X8 anion-exchange resin in a 10 mL Poly-Prep® column. The sample is loaded onto the preconditioned columns in 6 mL of a 1 M HF/0.5 M HCl solution. The column was

washed with 8 mL of 1 M HF/0.5 M HCl, followed by 8 mL of 4 M HCl to remove the matrix. Finally, 10 mL of 3 M HNO₃ was used to elute the Mo. The Mo fraction was then evaporated to dryness and re-dissolved in 0.3 M HNO₃ for determination by multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS).

3.2 MC-ICP-MS Analysis

All Mo isotope measurements were made at the Laboratory of Isotopic Geology, Institute of Geology, Chinese Academy of Geological Sciences, Beijing, China, using a Nu Plasma HR MC-ICP-MS equipped with a DSN^o 100 desolvating nebuliser. Samples were aspirated in 0.3 M HNO₃ at a rate of ~100 µL/min, with Mo concentrations of ~100 ng/mL (Li et al., 2016; Table 1).

The Mo isotope data were standardized following Nögler et al. (2014), where the $\delta^{98}\text{Mo}$ of the reference material NIST SRM 3134 (Lot No. 891307) was set to 0.25‰ and defined as follows.

$$\delta^{98}\text{Mo}(\text{‰}) = \left(\left(\frac{{}^{98}\text{Mo}}{{}^{95}\text{Mo}} \right)_{\text{sample}} / \left(\frac{{}^{98}\text{Mo}}{{}^{95}\text{Mo}} \right)_{\text{NIST SRM 3134}} - 1 \right) \times 1000$$

where $\delta^{97}\text{Mo} = 0.667 \times \delta^{98}\text{Mo}$, and $\delta^{100}\text{Mo} = 1.667 \times \delta^{98}\text{Mo}$.

4 RESULTS AND DISCUSSION

The $\delta^{98}\text{Mo}$ of sample SGR-1b obtained from the bulk digestion was $0.69\text{‰} \pm 0.08\text{‰}$ (i.e., $\pm 2\text{sd}$; Table 2), which is consistent, within error, with the values reported by Gaspers et al. (2020), Li et al. (2016), and Zhao et al., (2016).

The [Mo] and Mo isotopes of the six samples obtained us-

ing the various procedures are presented in Table 3. [Mo] was calculated by isotope dilution and using the average of the calibrated ⁹⁷Mo and ¹⁰⁰Mo spike solution. In general, the precision of isotope dilution ICP-MS for trace element measurement is ~5% (Wang et al., 2015). The precision of our Mo isotope measurements in terms of $\delta^{98}\text{Mo}$ was $\pm 0.10\text{‰}$ and the total procedure blank was < 2.5 ng (Li et al., 2016).

4.1 Mo Lost and Mo Isotope Fractionation during Leaching with the Different Acids

The [Mo] values obtained from Procedure I from Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 were 8.56 ppm, 8.99 ppm, 2.52 ppm, 1.56 ppm, and 0.83 ppm, respectively, and those obtained from these five shales leached with 9 M HCl using Procedure II were 8.44 ppm, 8.90 ppm, 2.46 ppm, 1.50 ppm, and 0.78 ppm, respectively. The Mo losses from these five samples during leaching, which were calculated as the difference in [Mo] between procedures I and II, were 0.12 ppm (1.40%), 0.09 ppm (1.00%), 0.06 ppm (2.38%), 0.06 ppm (3.85%), and 0.05 ppm (6.02%), respectively. The [Mo] values of Datangpo-1, Datangpo-2, Datangpo-3, and Datangpo-4 obtained from procedures I and II were all within 5% of each other, but those from Datangpo-5 differed by 6.02%.

However, the Mo losses from these five samples during leaching were similar (0.05 ppm–0.12 ppm), which indicates that the Mo loss was caused mainly by leaching rather by isotope dilution during ICP-MS analysis.

The $\delta^{98}\text{Mo}$ values for Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 obtained from Procedure I were $0 \pm 0.03\text{‰}$, $0.36\text{‰} \pm 0.05\text{‰}$, $0.61\text{‰} \pm 0.08\text{‰}$, $-0.03\text{‰} \pm 0.08\text{‰}$, and $-0.26\text{‰} \pm 0.03\text{‰}$, respectively, and those of the five shales from Procedure II were $0.02\text{‰} \pm 0.03\text{‰}$, $0.33\text{‰} \pm 0.06\text{‰}$, $0.60\text{‰} \pm 0.07\text{‰}$, $-0.04\text{‰} \pm 0.05\text{‰}$, and $-0.28\text{‰} \pm 0.03\text{‰}$, respectively. The Mo isotope values of these five samples obtained from procedures I and II were all within 5% of each other. Therefore, the limited Mo loss during leaching with 9 M HCl did not affect the Mo isotopic compositions of the shale samples.

The [Mo] of the bulk CAGS-BS digestion was 73.55 ppm, and that of CAGS-BS leached with 8 M HCl, 6 M HCl, 4 M HCl, 2 M HCl, and 1 M HCl was 73.07 ppm, 73.13 ppm, 72.72 ppm, 69.20 ppm, and 53.04 ppm, respectively (Table 3), which demonstrates that [Mo] in leachate increased as the HCl concentration increased. The $\delta^{98}\text{Mo}$ of CAGS-BS obtained from the bulk sample digestion was $0.09\text{‰} \pm 0.01\text{‰}$, and that leached with 8 M HCl, 6 M HCl, 4 M HCl, 2 M HCl, and 1 M HCl was $0.08\text{‰} \pm 0.06\text{‰}$, $0.10\text{‰} \pm 0.01\text{‰}$, $0.11\text{‰} \pm 0.02\text{‰}$, $0.14\text{‰} \pm 0.01\text{‰}$, and $0.38\text{‰} \pm 0.05\text{‰}$, respectively, (Table 3), which demonstrates that $\delta^{98}\text{Mo}$ decreased as the concentration of HCl increased. When the shales were leached with 4 M or more concentrated HCl, the [Mo] and Mo isotopic compositions of the shales were the same as those obtained using bulk digestion within error. When CAGS-BS was leached with 2 M and 1 M HCl, more isotopically heavy aqueous Mo was released when compared with the bulk digestion, with 94% and 72% of the total shale Mo inventory extracted. When CAGS-BS was leached with 9 M HNO₃, 74% of the total shale Mo was released and caused a preferential release of heavy Mo iso-

Table 1 Routine operating conditions for MC-ICP-MS

MC-ICP-MS	Nu Plasma HR
Sample introduction	DSN-100
Cup configuration	⁹² Mo: L5, ⁹⁴ Mo: L3, ⁹⁵ Mo: L2, ⁹⁶ Mo: C, ⁹⁷ Mo: H2, ⁹⁸ Mo: H4, ¹⁰⁰ Mo: H6
Resolution mode	LR
RF power (W)	1 300
Cones	Ni cone
Sample uptake	~100 µL/min
⁹⁷ Mo sensitivity	~25 V/ppm
Blocks	1
Cycles/block	10
Integration time	10 s

Table 2 Mo isotopic composition of standard solution Alfa and SGR-1b from the present and previous studies

Sample	References	$\delta^{98}\text{Mo} \pm 2\text{sd}$ (‰)
Alfa	This study	-0.21 ± 0.09
	Li et al. (2016)	-0.24 ± 0.10
SGR-1b	This study	0.69 ± 0.08
	Gaspers et al. (2020)	0.69 ± 0.06
	Li et al. (2016)	0.63 ± 0.02
	Zhao et al. (2016)	0.69 ± 0.11

Table 3 [Mo] concentrations and Mo isotope ratios obtained from the various procedures

Sample	Procedure	Before/after ashing	Bulk digestion/ leaching (leachate)	[Mo]	$\delta^{100}\text{Mo}$	$\delta^{98}\text{Mo}$	$\delta^{97}\text{Mo}$
				(ppm)	(‰)	(‰)	(‰)
Datangpo-1	I	After	Bulk digestion	8.56	0.01 ± 0.04	0 ± 0.03	0 ± 0.02
	II	After	Leaching (9 M HCl)	8.44	0.03 ± 0.05	0.02 ± 0.03	0.01 ± 0.02
	III	Before	Bulk digestion	8.63	0.05 ± 0.03	0.03 ± 0.02	0.02 ± 0.01
	IV	Before	Leaching (9 M HCl)	8.53	-0.01 ± 0.09	-0.01 ± 0.06	-0.0 ± 0.04
	Average			8.54 ± 0.15	-0.15 ± 0.07	0.01 ± 0.04	0.09 ± 0.03
Datangpo-2	I	After	Bulk digestion	8.99	0.59 ± 0.08	0.36 ± 0.05	0.24 ± 0.03
	II	After	Leaching (9 M HCl)	8.90	0.55 ± 0.10	0.33 ± 0.06	0.22 ± 0.04
	III	Before	Bulk digestion	9.05	0.61 ± 0.09	0.37 ± 0.06	0.25 ± 0.04
	IV	Before	Leaching (9 M HCl)	8.96	0.60 ± 0.05	0.36 ± 0.03	0.24 ± 0.02
	Average			8.98 ± 0.11	0.42 ± 0.08	0.36 ± 0.05	0.32 ± 0.03
Datangpo-3	I	After	Bulk digestion	2.52	1.02 ± 0.13	0.61 ± 0.08	0.41 ± 0.05
	II	After	Leaching (9 M HCl)	2.46	1.00 ± 0.12	0.60 ± 0.07	0.40 ± 0.05
	III	Before	Bulk digestion	2.53	0.99 ± 0.05	0.59 ± 0.03	0.40 ± 0.02
	IV	Before	Leaching (9 M HCl)	2.48	0.91 ± 0.14	0.55 ± 0.08	0.37 ± 0.06
	Average			2.50 ± 0.06	0.81 ± 0.13	0.59 ± 0.08	0.48 ± 0.05
Datangpo-4	I	After	Bulk digestion	1.56	-0.05 ± 0.13	-0.03 ± 0.08	-0.02 ± 0.05
	II	After	Leaching (9 M HCl)	1.50	-0.07 ± 0.09	-0.04 ± 0.05	-0.03 ± 0.04
	III	Before	Bulk digestion	1.57	0.03 ± 0.02	0.02 ± 0.01	0.01 ± 0.01
	IV	Before	Leaching (9 M HCl)	1.51	-0.05 ± 0.08	-0.03 ± 0.05	-0.02 ± 0.03
	Average			1.54 ± 0.07	-0.20 ± 0.11	-0.02 ± 0.07	0.07 ± 0.05
Datangpo-5	I	After	Bulk digestion	0.83	-0.84 ± 0.08	-0.26 ± 0.03	-0.34 ± 0.03
	II	After	Leaching (9 M HCl)	0.78	-0.88 ± 0.08	-0.28 ± 0.03	-0.36 ± 0.03
	III	Before	Bulk digestion	0.83	-0.96 ± 0.12	-0.31 ± 0.05	-0.39 ± 0.05
	IV	Before	Leaching (9 M HCl)	0.79	-0.93 ± 0.22	-0.30 ± 0.09	-0.38 ± 0.09
	Average			0.81 ± 0.05	-1.07 ± 0.15	-0.55 ± 0.09	-0.29 ± 0.06
CAGS-BS	I	After	Bulk digestion	73.55	0.15 ± 0.02	0.09 ± 0.01	0.06 ± 0.01
	II	After	Leaching (8 M HCl)	73.07	0.13 ± 0.10	0.08 ± 0.06	0.05 ± 0.04
	II	After	Leaching (6 M HCl)	73.13	0.18 ± 0.01	0.10 ± 0.01	0.07 ± 0.01
	II	After	Leaching (4 M HCl)	72.72	0.18 ± 0.03	0.11 ± 0.02	0.07 ± 0.01
	II	After	Leaching (2 M HCl)	69.20	0.24 ± 0.02	0.14 ± 0.01	0.10 ± 0.01
	II	After	Leaching (1 M HCl)	53.04	0.63 ± 0.08	0.38 ± 0.05	0.25 ± 0.03
	II	After	Leaching (9 M HNO ₃)	54.35	0.48 ± 0.05	0.29 ± 0.03	0.19 ± 0.02
	III	Before	Bulk digestion	73.45	0.14 ± 0.01	0.08 ± 0.01	0.06 ± 0.01

topes ($0.29\text{‰} \pm 0.03\text{‰}$; Table 4). The preferential release of heavy Mo isotopes when CAGS-BS was leached with 2 M HCl, 1 M HCl, and 9 M HNO₃ is consistent with the results from the leaching experiments of Liermann et al. (2011) on black shales and Voegelin et al. (2012) on crustal igneous rocks.

4.2 [Mo] and Mo Isotopes in the Residues after Leaching

A Mo isotope mass-balance model calculation, based on measured [Mo] and the Mo isotopic composition of bulk digestion and leachates, can be used to obtain [Mo] and Mo isotopic compositions in the residues after leaching. A typical equation is given below.

$$\begin{aligned}
 & [\text{Mo}]_{\text{leachate}} \delta^{98}\text{Mo}_{\text{leachate}} + [\text{Mo}]_{\text{residue}} \delta^{98}\text{Mo}_{\text{residue}} = \\
 & [\text{Mo}]_{\text{bulk digestion}} \delta^{98}\text{Mo}_{\text{bulk digestion}} \\
 & [\text{Mo}]_{\text{residual}} = [\text{Mo}]_{\text{bulk digestion}} - [\text{Mo}]_{\text{leachate}}
 \end{aligned}$$

$$\delta^{98}\text{Mo}_{\text{residue}} = ([\text{Mo}]_{\text{bulk digestion}} \delta^{98}\text{Mo}_{\text{bulk digestion}} - [\text{Mo}]_{\text{leachate}} \delta^{98}\text{Mo}_{\text{leachate}}) / ([\text{Mo}]_{\text{bulk digestion}} - [\text{Mo}]_{\text{leachate}})$$

The different leachates produced different Mo releases, and the [Mo] and $\delta^{98}\text{Mo}$ in the residue also differed (Table 4). When CAGS-BS was leached using 2 M HCl, 1 M HCl, and 9 M HNO₃, the [Mo] in the residues was 4.35, 20.51, and 19.20 ppm, respectively, and the $\delta^{98}\text{Mo}$ in the residues was -0.71‰ , -0.66‰ and -0.48‰ respectively, values that are lower than those obtained using bulk digestion of CAGS-BS and crustal igneous rocks (i.e., -0.1‰ to $+0.3\text{‰}$; Siebert et al., 2003).

4.3 Can the Double Spike be Added before Ashing?

Procedures I and III were both bulk shale digestions, the only difference being that the ^{97}Mo - ^{100}Mo double spike was added after ashing in Procedure I, but before ashing in Procedure III. The [Mo] values of the Datangpo-1, Datangpo-2, Datangpo-

Table 4 [Mo] and $\delta^{98}\text{Mo}$ in the residues after leaching with 2 M HCl, 1 M HCl, and 9 M HNO_3

Leachate	[Mo] _{residue}	$\delta^{98}\text{Mo}$ _{residue}
	(ppm)	(‰)
2 M HCl	4.35	-0.71
1 M HCl	20.51	-0.66
9 M HNO_3	19.20	-0.48

3, Datangpo-4, and Datangpo-5 samples obtained from Procedure III were 8.63, 9.05, 2.53, 1.57, and 0.83 ppm, respectively, and the $\delta^{98}\text{Mo}$ values of these samples were $0.03\text{‰} \pm 0.02\text{‰}$, $0.37\text{‰} \pm 0.06\text{‰}$, $0.59\text{‰} \pm 0.03\text{‰}$, $0.02\text{‰} \pm 0.01\text{‰}$, and $-0.31\text{‰} \pm 0.05\text{‰}$, respectively, which are similar to the values obtained from Procedure I, within error. Procedures II and IV for samples Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 both involved leaching with 9 M HCl, the only difference being that the ^{97}Mo - ^{100}Mo double spike was added after ashing in Procedure II but before ashing in Procedure IV. The [Mo] values of Datangpo-1, Datangpo-2, Datangpo-3, Datangpo-4, and Datangpo-5 obtained from Procedure IV were 8.53 ppm, 8.96 ppm, 2.48 ppm, 1.51 ppm, and 0.79 ppm, respectively, and the $\delta^{98}\text{Mo}$ values were $-0.01\text{‰} \pm 0.06\text{‰}$, $0.36\text{‰} \pm 0.03\text{‰}$, $0.55\text{‰} \pm 0.08\text{‰}$, $-0.03\text{‰} \pm 0.05\text{‰}$, and $-0.30\text{‰} \pm 0.09\text{‰}$, respectively, which are similar to the values obtained from Procedure II, within error. Therefore, our results suggest that the double spike can be added before ashing with no adverse effects on the Mo isotope compositions and no Mo losses and indicates that Mo from the ^{97}Mo - ^{100}Mo double spike solution is not lost, and the Mo isotope ratio will not change after ashing.

5 CONCLUSIONS

(1) Bulk digestion or leaching with 4 M or more concentrated HCl after ashing are appropriate and reliable approaches for Mo isotope analysis in shales.

(2) Leaching shales with 2 M HCl, 1 M HCl, or 9 M HNO_3 all released isotopically heavy aqueous Mo compared with that released from bulk digestion. According to our Mo isotope mass-balance model, the $\delta^{98}\text{Mo}$ in the residue was significantly lower than that from the bulk digestion of CAGS-BS and crustal igneous rocks.

(3) Adding the double spike before ashing is an appropriate and reliable approach to Mo isotope analysis in shales.

(4) For efficiency, leaching using 4 M or more concentrated HCl after ashing, is preferred for Mo isotope measurements.

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