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Identification of a matrix effect in the MC-ICP-MS due to sample purification using ion exchange resin: An isotopic case study of molybdenum

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Abstract

Multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become the preferred method for precise and accurate measurements of the relative abundances of many radiogenic and stable isotopes in natural materials. Isotopic analyses by MC-ICP-MS require a correction for instrumental mass-dependent isotopic fractionation ("instrumental mass bias"). Two techniques have been used to correct for instrumental mass bias in the MC-ICP-MS: (1) standard-sample bracketing (SSB) or (2) double spiking. SSB is often cited as the preferred method, but it is more susceptible to matrix effects. Here we demonstrate that a matrix effect in the MC-ICP-MS may arise indirectly from the chemical separation and purification of molybdenum using anion exchange resin. The results of our experiments show that a Mo standard passed through a column of anion exchange resin or a Mo standard added to a Mo-free solution that had been collected from anion exchange resin appears to be isotopically lighter than expected from direct analysis of the same standard. Using amounts of Mo similar to what might be expected from most natural samples (~3 μg per column cut), these offsets span a significant fraction (~10–60%) of the total known range of mass-dependent Mo isotopic variation in nature. This "column matrix effect" appears to be caused by organic material stripped from the resin. All of our attempts to eliminate or control this column matrix effect have failed, making it difficult (if not impossible) to obtain accurate measurements of mass-dependent Mo isotopic variations in natural materials using the anion exchange resin procedure described in this study and SSB techniques to correct for instrumental mass bias in the MC-ICP-MS. It is currently unknown if this type of column matrix effect will affect measurements of other stable or radiogenic isotopes by MC-ICP-MS when SSB is used to correct for instrumental mass bias.

Keywords: Molybdenum; Isotope; Mass spectrometry; MC-ICP-MS; Matrix effect

1. Introduction

Multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become the preferred method for precise and accurate measurements of the relative abundances of many radiogenic (e.g., lead [1,2] and thorium [3,4]) and stable (e.g., molybdenum [5–9] and iron [10–15]) isotopes in natural materials. MC-ICP-MS offers two main advantages compared to previous techniques using thermal ionization mass spectrometry (e.g., ref. [16]): (1) the nearly complete ionization of elements in the plasma source that are difficult to ionize thermally, and (2) the more efficient throughput of samples. However, MC-ICP-MS requires a larger correction for instrumental mass-dependent isotopic fractionation ("instrumental mass bias") compared to TIMS. The correction for instrumental mass bias (for both TIMS and MC-ICP-MS) is particularly difficult for stable isotopic systems and for radiogenic isotopic systems that lack at least two non-radiogenic isotopes (required for a completely internal correction for instrumental mass bias). Two techniques have been used to correct for instrumental mass bias in the MC-ICP-MS: (1) a comparison of the measured isotope ratios of the sample with a bracketing standard (standard-sample bracketing, or SSB), with or without the addition of another element to externally monitor instrumental mass bias (e.g., "thallium doping" for Pb isotopic measurements [1,2]), or (2) the addition of a mixture of two enriched isotopic tracers of the element of interest to the sample for an internal correction for instrumental mass bias (e.g., "double spiking" for Mo isotopic measurements [6,7]). SSB is

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often cited as the preferred method because it provides a similar precision to double spiking and is less susceptible to memory effects (e.g., ref. [16]). However, SSB is more susceptible to matrix effects.

Several types of matrix effects in the MC-ICP-MS have been identified. Spectral matrix effects (e.g., isobaric interferences [17]) occur when an element or molecule (possibly doubly charged) overlaps in mass with the isotope of interest. Non-spectral matrix effects include changes in instrumental sensitivity and/or mass bias [17] due to (1) the presence of matrix elements in the analyte inherited from the natural sample [8,15,18] that are not found in the bracketing standard, (2) differences in the concentration of the elements in the sample and the bracketing standard (both the element of interest and any element added to correct for instrumental mass bias [4,8,13,18]), (3) differences in the oxidation state of the element in the sample and the bracketing standard [19], and (4) the presence of organic material from the natural sample [15] that is not found in the bracketing standard. Non-spectral matrix effects in the MC-ICP-MS are of particular concern for stable isotopic systems because they may cause a mass-dependent bias on the isotopic composition of an element in a sample when SSB is used to correct for instrumental mass bias. Many studies (e.g., refs. [4,8,13,15,18,19]) have shown that these spectral and non-spectral matrix effects in the MC-ICP-MS can be eliminated by careful separation, purification, and treatment of the element of interest or controlled by equalizing the relative concentrations of the element(s) in the sample and bracketing standard. Here we examine the possibility that a seemingly uncorrectable type of non-spectral matrix effect in the MC-ICP-MS may arise indirectly from the chemical separation and purification of Mo using anion exchange resin.

2. Materials and methods

The potential for a matrix effect in the MC-ICP-MS due to the chemical separation and purification of a sample using anion exchange resin was investigated in two ways. First, a high-purity Mo isotopic standard was passed through a column of anion exchange resin. The Mo was collected, analyzed for its isotopic composition by MC-ICP-MS, and the results were compared to an untreated aliquot of the same Mo isotopic standard. Second, an anion exchange column was run without adding any Mo to the column and the Mo cut (which would have contained the Mo, if any had been loaded) was collected. A high-purity Mo isotopic standard was added to this Mo-free solution, the mixture was analyzed for its isotopic composition by MC-ICP-MS, and the results were compared to an untreated aliquot of the same Mo isotopic standard. In some cases, the solutions from the column were chemically treated prior to analysis or passed through a "clean-up" column of anion exchange resin. In the absence of a matrix effect due to the column chemistry (for both types of experiments), the isotopic composition of the Mo in the solution from the column is expected to be identical within error to the Mo in the untreated standard. These experiments are described in more detail below.

Two low-blank, high-yield Teflon columns (a 10-mL column and a 0.25-mL clean-up column) of Eichrom AG1-X8

Table 1
Key to experiments performed in this study

Experiment	Mo standard[a]	Column type[b]	Mo added to column?	Mo recovery (%)	Solution collected	Treatment[c]	Mass Mo (μg)[d]
#1a	Wire	Lg.	Yes	99.5	1 M HCl + 5 M HNO_3	–	200
#1b	Wire	Lg.	Yes	99.5	1 M HCl + 5 M HNO_3	–	200
#2a	Wire	Lg.	Yes	100.0	1 M HCl + 5 M HNO_3	–	310
#2b	Wire	Lg.	Yes	99.8	1 M HCl + 5 M HNO_3	–	310
#3	Wire	Lg.	No	–	1 M HCl + 5 M HNO_3	–	67
#4a	Solution	Lg.	No	–	1 M HCl	–	24
#4b	Solution	Lg.	No	–	1 M HCl	Conc. HNO_3	20
#4c	Solution	Lg.	No	–	1 M HCl	Aqua regia	20
#4d	Solution	Lg.	No	–	1 M HCl	H_2O_2	20
#5a	Solution	Lg.	No	–	5 M HNO_3	–	24
#5b	Solution	Lg.	No	–	5 M HNO_3	Conc. HNO_3	20
#5c	Solution	Lg.	No	–	5 M HNO_3	Aqua regia	20
#5d	Solution	Lg.	No	–	5 M HNO_3	H_2O_2	20
#6	Solution	Lg. + Sm.	No	–	1 M HCl + 5 M HNO_3	–	3.3
#7	Solution	Sm.	No	–	1 M HCl	–	3.3
#8	Solution	Sm.	No	–	5 M HNO_3	–	3.3
#9a	Solution	Sm.	No	–	1 M HCl + 5 M HNO_3	–	3.3
#9b	Solution	Sm.	No	–	1 M HCl + 5 M HNO_3	Conc. HNO_3	3.3
#9c	Solution	Sm.	No	–	1 M HCl + 5 M HNO_3	Aqua regia	3.3
#9d	Solution	Sm.	No	–	1 M HCl + 5 M HNO_3	H_2O_2	3.3

[a] Wire = Mo wire standard; solution = Mo solution standard.

[b] Lg. = large anion exchange resin column; Sm. = small anion exchange resin column.

[c] After drying the solution from the column, the sample was treated by adding the listed reagent, refluxing in a closed beaker at 80 °C for >1 h, and drying completely. Conc. HNO_3 = 1 mL of 15 M HNO_3; aqua regia = 1 mL of 15 M HNO_3 + 2 mL 10 M HCl; H_2O_2 = 2 mL of 30% hydrogen peroxide.

[d] The mass of Mo added to the column (#1–2) or the effective mass of Mo (#3–9). The effective mass represents the amount of Mo that would have been added to the column (if it were treated as a normal sample). This effective mass (M_{Mo}) is calculated from the actual mass of Mo (m_{Mo}) added to the fraction (f) of the Mo-free solution collected from the column in each experiment ($M_{Mo} = m_{Mo}/f$).

(100–200 mesh) anion exchange resin were used for all of the experiments presented in this study (Table 1). Resin from Eichrom was used because it was found to have a significantly lower Mo blank than resin from Bio-Rad. The resin was pre-cleaned using the procedure described in ref. [8], and stored in H_2O. Following each pre-cleaning step with either HNO_3 or HCl, the resin was immediately rinsed with H_2O. One batch of resin was used for experiment #1, and a completely new batch of resin was purchased from Eichrom, pre-cleaned, and used for experiments #2–9. Each batch of resin was calibrated before use, and the Mo cuts were found to be essentially identical in the two batches. The Mo separation and purification procedure for the large column was previously described by ref. [8]. Briefly, a Mo-bearing sample in 6 M HCl is loaded onto the column, and the resin is washed with 6 M HCl to remove Zr and most other elements from the sample (except iron). Next, the resin is washed with a mixture of 0.1 M HF + 0.01 M HCl to remove most of the Fe. Finally, the Mo is collected in 1 M HCl followed by 5 M HNO_3. This procedure is similar to some previous studies (e.g., refs. [20,21]), with the addition of the 0.1 M HF + 0.01 M HCl and 5 M HNO_3 steps (the latter improves the recovery of Mo [8]). The procedure for the small clean-up column is identical to the large column, but all reagent volumes are scaled down by a factor of ~40. The recovery of Mo from this small column was verified at 99.2% by isotope dilution using the method of ref. [8].

The Nu Plasma MC-ICP-MS at San Diego State University (SDSU) was used for all of the Mo isotopic measurements. The instrumental details and methods employed for the correction of instrumental mass bias were previously described by ref. [8]. Both the simple SSB and the external normalization SSB (i.e., Zr doping) methods were compared for each analysis (the Zr that was added to each sample for external normalization SSB was simply ignored for simple SSB). Two different high-purity Mo solution standards were analyzed [8]: (1) a purchased “Mo solution standard” and (2) a “Mo wire standard” prepared from a 99.97% pure Mo wire. For all experiments, the Mo solution standard was used as the bracketing standard. In addition, a purchased high-purity “Zr solution standard” [8] was used for external normalization SSB. The final Mo isotopic data (Tables 2 and 3) are reported using “delta” notation for Mo isotope X (=97, 98, or 100), which is defined as $\delta^{X/95}\mathrm{Mo} = 1000 \times \{[(^{X}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{sample}}/(^{X}\mathrm{Mo}/^{95}\mathrm{Mo})_{\mathrm{standard}}] - 1\}$. In this report, a Mo standard analyzed as an unknown is referred to as a “sample”. The long-term reproducibility of the simple and external normalization SSB methods is reported by ref. [8], and a summary based on Mo isotopic standards is shown in Tables 2 and 3.

Two types of experiments were performed (Table 1). Experiments #1 and 2 were conducted first. The second set of experiments (#3–9) were designed to clarify the results of the first set of experiments. In all experiments (#1–9), the 1 M HCl and/or 5 M HNO_3 solutions from the columns were dried, treated by adding the reagent listed in Table 1 (if noted) and drying, and dissolved in 0.5 M HNO_3 for analysis. Ultra-pure reagents were used for all of the experiments in this study. It should be noted that experiments #1–3 are analogous to the procedure used by ref. [8].

Table 2
Mo isotopic data for experiments using the Mo wire standard

	Simple standard-sample bracketing						External normalization standard-sample bracketing					
	‰			‰/AMU			‰			‰/AMU		
	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo
Reference value [8]	0.085	0.120	0.199	0.042	0.040	0.040	0.15	0.23	0.37	0.07	0.08	0.07
±2σ (n = 11)	0.067	0.099	0.179	0.034	0.033	0.036	0.23	0.35	0.55	0.11	0.12	0.11
Experiments												
#1a	−0.161	−0.215	−0.357	−0.080	−0.072	−0.071	−0.27	−0.37	−0.57	−0.13	−0.12	−0.11
±2σ (n = 4)	0.024	0.036	0.047	0.012	0.012	0.009	0.13	0.13	0.30	0.07	0.04	0.06
#1b	−0.124	−0.191	−0.323	−0.062	−0.064	−0.065	−0.29	−0.41	−0.69	−0.14	−0.14	−0.14
±2σ (n = 3)	0.019	0.024	0.056	0.010	0.008	0.011	0.19	0.32	0.52	0.09	0.11	0.10
#2a	−0.327	−0.473	−0.789	−0.164	−0.158	−0.158	−0.39	−0.58	−0.96	−0.20	−0.19	−0.19
±2σ (n = 3)	0.024	0.014	0.032	0.012	0.005	0.006	0.16	0.22	0.42	0.08	0.07	0.08
#2b	−0.352	−0.515	−0.868	−0.176	−0.172	−0.174	−0.52	−0.78	−1.26	−0.26	−0.26	−0.25
±2σ (n = 3)	0.018	0.012	0.028	0.009	0.004	0.006	0.07	0.17	0.29	0.03	0.06	0.06
#3	−0.984	−1.468	−2.422	−0.492	−0.489	−0.484	−1.10	−1.63	−2.68	−0.55	−0.54	−0.54

The signal intensities of both Mo and Zr between the sample and the bracketing standard (and the ratio of the Mo to Zr signal intensities) were matched within 5% for each analysis. The $^{95}\mathrm{Mo}/^{90}\mathrm{Zr}$ ratio of each measurement was ≥5.2. Data in each row represent the same analyses that were corrected for instrumental mass bias using different methods. The data for experiments #1 and 2 represent the average and ±2σ of replicate analyses of each solution. Experiment #3 was analyzed twice, so only the average value is given.

Table 3
Mo isotopic data for experiments using the Mo solution standard

	% Difference		Simple standard-sample bracketing						External normalization standard-sample bracketing					
	Mo[a]	Mo/Zr[b]	‰			‰/AMU			‰			‰/AMU		
			$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo	$\delta^{97/95}$Mo	$\delta^{98/95}$Mo	$\delta^{100/95}$Mo
Reference value [8]			−0.010	−0.014	−0.025	−0.005	−0.005	−0.005	0.04	0.04	0.08	0.02	0.01	0.02
±2σ ($n = 6$)			0.059	0.067	0.095	0.029	0.022	0.019	0.24	0.36	0.58	0.12	0.12	0.12
Expected value[c]			0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
Experiments														
#4a	−25	−23	−1.223	−1.830	−2.992	−0.611	−0.610	−0.598	−0.94	−1.40	−2.25	−0.47	−0.47	−0.45
#4b	−18	−25	−1.324	−1.957	−3.277	−0.662	−0.652	−0.655	−0.94	−1.34	−2.24	−0.47	−0.45	−0.45
#4c	−7	−22	−1.099	−1.660	−2.730	−0.550	−0.553	−0.546	−0.98	−1.48	−2.40	−0.49	−0.49	−0.48
#4d	−8	−14	−1.189	−1.797	−2.950	−0.595	−0.599	−0.590	−1.32	−1.99	−3.26	−0.66	−0.66	−0.65
#5a	−37	−12	−1.268	−1.901	−3.105	−0.634	−0.634	−0.621	−0.84	−1.26	−2.04	−0.42	−0.42	−0.41
#5b	−38	−13	−1.203	−1.774	−2.953	−0.601	−0.591	−0.591	−0.33	−0.49	−0.78	−0.16	−0.16	−0.16
#5c	−25	−10	−1.137	−1.703	−2.793	−0.569	−0.568	−0.559	−0.72	−1.06	−1.75	−0.36	−0.35	−0.35
#5d	−32	−21	−1.378	−2.063	−3.380	−0.689	−0.688	−0.676	−0.68	−1.01	−1.66	−0.34	−0.34	−0.33
#6	−17	14	−0.864	−1.298	−2.153	−0.432	−0.433	−0.431	−0.27	−0.38	−0.66	−0.13	−0.13	−0.13
#7	−2	−6	−0.596	−0.881	−1.463	−0.298	−0.294	−0.293	−0.65	−0.96	−1.60	−0.32	−0.32	−0.32
#8	−22	−13	−1.131	−1.678	−2.765	−0.565	−0.559	−0.553	−0.43	−0.66	−1.03	−0.22	−0.22	−0.21
#9a	−23	−7	−1.096	−1.616	−2.675	−0.548	−0.539	−0.535	−0.54	−0.78	−1.31	−0.27	−0.26	−0.26
#9b	−17	−22	−0.954	−1.416	−2.328	−0.477	−0.472	−0.466	−0.88	−1.34	−2.21	−0.44	−0.45	−0.44
#9c	−16	−20	−0.954	−1.430	−2.371	−0.477	−0.477	−0.474	−1.03	−1.54	−2.56	−0.52	−0.51	−0.51
#9d	−34	−18	−1.351	−2.015	−3.327	−0.675	−0.672	−0.665	−0.56	−0.83	−1.39	−0.28	−0.28	−0.28

For each experiment, Mo-free solutions collected from the column(s) listed in Table 1 were added to the mixed Mo–Zr solution standard prior to analysis as described in the text. Data in each row represent the same analyses that were corrected for instrumental mass bias using different methods. The ^{95}Mo/^{90}Zr ratio of each bracketing standard was ≥5.1. Experiments #4–9 were analyzed once.

[a] The % difference between the signal intensity of Mo in the sample compared to the average of the two bracketing standards. A negative value indicates that the Mo signal intensity was lower in the sample compared to the bracketing standards.

[b] The % difference between the ratio of the Mo to Zr signal intensities in the sample compared to the average of the two bracketing standards. A negative value indicates that the Mo/Zr intensity ratio was lower in the sample compared to the bracketing standards.

[c] The expected value for the Mo solution standard is zero because it was also used as the bracketing standard.

In the first set of experiments (#1–2), a relatively large amount of the Mo wire standard (200–310 μg) was passed through the large column and the Mo was collected in both 1 M HCl and 5 M HNO_3. Given the large amount of Mo used, these experiments would be expected to minimize any potential matrix effects due to the anion exchange resin. For the analyses of experiments #1–2, the signal intensities of both Mo and Zr between the sample and bracketing standard (and the ratio of the Mo to Zr signal intensities) were matched within 5% to help control matrix effects due to different Mo and Zr concentrations between the sample and bracketing standard [8].

In the second set of experiments (#3–9), the large and/or small columns were run without adding any Mo to the column, and the 1 M HCl and/or 5 M HNO_3 solutions (which would have contained the Mo, if any had been loaded) were collected and in some cases chemically treated prior to being added to either the Mo wire standard (#3) or the Mo solution standard (#4–9) immediately before analysis. In several experiments (#4, 5, 7 and 8), the 1 M HCl and 5 M HNO_3 solutions were collected and analyzed separately to isolate any potential matrix effects specific to each reagent. The signal intensities of Mo and Zr were matched for the analysis of experiment #3, as described above. Matching of signal intensities was not performed for experiments #4–9. Instead, a single aliquot of the Mo solution standard (to which the Zr solution standard had been previously added) was split into two portions for each analysis. Next, a fraction of the prepared solution from the column experiment (now in 0.5 M HNO_3) was added to one split of the mixed Mo–Zr solution standard, and an identical amount of pure 0.5 M HNO_3 was added to the second split of mixed Mo–Zr solution standard (to ensure the same Mo and Zr concentrations in the final two solutions). The aliquot of the Mo–Zr solution standard to which pure 0.5 M HNO_3 had been added was used as the bracketing standard for the concentration-matched Mo–Zr solution standard to which the solution from the column experiment had been added (i.e., the "sample").

3. Results

In all cases, a Mo standard passed through anion exchange resin or a Mo standard added to a Mo-free solution that had been collected from anion exchange resin appears to be isotopically lighter than expected from direct analysis of the same standard (Tables 2 and 3). All of the offsets in the Mo isotope ratios between the samples and the bracketing standards are mass dependent (as shown by the essentially identical $\delta^{X/95}$Mo values in units of ‰/AMU for a given experiment and both methods of correcting for instrumental mass bias). We also evaluated the graphical method of correcting for instrumental mass bias developed by Maréchal et al. [22]. The results using this method (not shown) are similar to both the simple and external normalization SSB methods. These observations strongly suggest that the anion exchange resin used to separate and purify Mo may lead to a mass-dependent bias on the isotopic composition of the sample (when analyzed by MC-ICP-MS using SSB).

In the first set of experiments (#1–2), the differences between the Mo wire standard passed through the column and the reference value for this standard [8] range from −0.21 to −0.44‰ for $\delta^{97/95}$Mo when corrected using simple SSB (Table 2). These results are significant outside of the $\pm 2\sigma$ errors. Although relatively small, these offsets are particularly significant given the large amount of Mo used for these experiments (equivalent to passing a sample with 200–310 μg of Mo through the column with a large dilution factor of ∼290–440 prior to analysis). For experiment #3, with a smaller proportion of the Mo wire standard added to the solution collected from the column (67 μg, with a dilution factor of ∼100), a larger −1.07‰ offset for $\delta^{97/95}$Mo is observed (when corrected using simple SSB). Thus, relatively large discrepancies in the isotopic composition of a standard passed through the anion exchange resin (relative to the untreated standard) are observed even when a large amount of Mo is passed through the column and strongly diluted prior to analysis.

In the second set of experiments (#4–9) using effectively smaller amounts of Mo (3.3–24 μg; Table 1), the following attempts were made to better understand and eliminate the mass-dependent bias observed in experiments #1–3: (1) the 1 M HCl vs. 5 M HNO_3 solutions from the large column were analyzed separately (#4a vs. 5a), (2) the 1 M HCl vs. 5 M HNO_3 solutions from the large columns were treated with concentrated HNO_3, aqua regia, or H_2O_2 prior to analysis (#4b–d and 5b–d), (3) the 1 M HCl + 5 M HNO_3 solution from the large column was passed through a small clean-up column of anion exchange resin (#6), (4) the 1 M HCl vs. 5 M HNO_3 solutions from the small column were analyzed separately (#7–8), (5) the 1 M HCl + 5 M HNO_3 solution from the small column was analyzed (#9a), and (6) the 1 M HCl vs. 5 M HNO_3 solutions from the small column were treated with concentrated HNO_3, aqua regia, or H_2O_2 prior to analysis (#9b–d). All of these experiments display a significant difference between the Mo solution standard added to the Mo-free solution collected from the column and the expected value for this standard, with an offset on $\delta^{97/95}$Mo ranging from −0.60 to −1.38‰ (when corrected using simple SSB). Unlike the first series of experiments, no attempt was made to match the signal intensities of Mo and Zr between the sample and bracketing standard, because both were split and diluted identically from the same mixed Mo–Zr solution standard for each analysis (and thus, similar signal intensities were expected). Surprisingly, large differences in the signal intensities of Mo and Zr between the sample and bracketing standards were observed (Table 3). The signal intensities of Mo were 2–38% lower in the samples compared to the bracketing standard. In contrast, the signal intensities of Zr were more variable (29% lower to 20% higher in the sample). This also resulted in a large range of the Mo/Zr intensity ratio between the samples and the bracketing standards (Table 3) from 25% lower to 14% higher in the sample.

In retrospect, the observation of relatively large differences in the signal intensities of Mo and Zr between the samples and bracketing standards for the second set of experiments (#4–9) means that the Mo and Zr concentrations of the samples and bracketing standards for the first set of experiments (#1–3) were probably not precisely matched (even though the signal intensities were matched within 5%). Pietruszka et al. [8] showed that differences in either the Mo concentration or Mo/Zr concentration ratio between a sample and the bracketing standard may bias the $\delta^{X/95}$Mo values of the sample (when analyzed using either simple or external normalization SSB). Based on the data in Table 3, the maximum differences in the Mo signal intensity and Mo/Zr intensity ratio between a concentration-matched sample and standard were 38 and 25%, respectively. By analogy, the mismatch between the Mo concentrations and Mo/Zr concentration ratios for the first set of experiments (Table 2) are likely to be less than this amount because larger amounts of Mo, and thus, greater dilutions were used (Table 1). A worst-case mismatch in the Mo concentration of 38% would translate to a bias of only −0.08‰ on the $\delta^{97/95}$Mo value of the samples in Table 2 based the experiments of ref. [8]. Similarly, a worst-case mismatch of 25% on the Mo/Zr concentration ratio is expected to be similarly insignificant (based on the experiments of ref. [8]) given the high ^{95}Mo/^{90}Zr intensity ratios used in this study (>5). In any case, it is important to note that the Mo and Zr concentrations were matched for the second set of experiments and relatively large offsets in the $\delta^{X/95}$Mo values were still observed.

Interestingly, similar offsets on the $\delta^{97/95}$Mo values are observed when the analyses are corrected for instrumental mass bias using external normalization SSB (Tables 2 and 3), although these $\delta^{97/95}$Mo values do not necessarily agree with the results from simple SSB. For the second series of experiments, the level of disagreement increases as the difference in the signal intensity of Mo between the sample and the bracketing standard increases (Fig. 1). However, even when the two methods of correcting for instrumental mass bias give similar results, the $\delta^{97/95}$Mo values of both methods still disagree with the value expected when the untreated Mo isotopic standard is run directly.

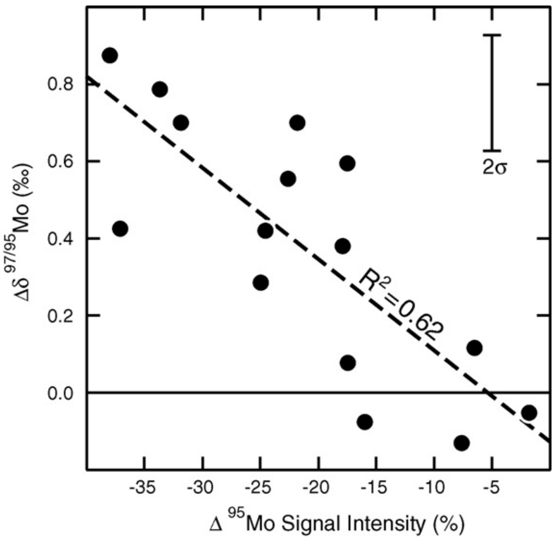

Fig. 1. Plot of the % difference in the signal intensity of Mo between the sample and the average of the bracketing standards ($\Delta^{95}\mathrm{Mo} = {}^{95}\mathrm{Mo}_{\mathrm{Sample}} - {}^{95}\mathrm{Mo}_{\mathrm{Standard}}$) vs. the difference (in ‰) between the $\delta^{97/95}$Mo value of the sample corrected using the two SSB methods ($\Delta\delta^{97/95}\mathrm{Mo} = \delta^{97/95}\mathrm{Mo}_{\mathrm{External\ Normalization\ SSB}} - \delta^{97/95}\mathrm{Mo}_{\mathrm{Simple\ SSB}}$). The data are from Table 3. The expected $\Delta\delta^{97/95}$Mo value (zero) is shown by the solid line. The 2σ error bar is based on the uncertainties for the Mo solution standard listed in Table 3. The dashed line is a best-fit linear regression through the data.

4. Discussion and conclusions

There are three possible explanations for the observations presented in this study: (1) mass-dependent fractionation of Mo occurs during the anion exchange resin column chemistry, (2) material introduced to the sample during the column chemistry subsequently causes one or more isobaric interferences during analysis, or (3) the column chemistry may lead indirectly to a matrix effect in the MC-ICP-MS. In this section, we consider these possibilities and discuss the implications of our experiments for the determination of mass-dependent Mo isotopic variations by MC-ICP-MS.

The elution of Mo from anion exchange resin in 1 M HCl is known to significantly fractionate Mo isotopes, with the first Mo from the column enriched in the heavier isotopes and the last Mo from the column enriched in the lighter isotopes [5]. However, mass-dependent isotopic fractionation of Mo during the column chemistry cannot explain the observations in this study for three reasons. First, for experiments that display the largest offsets (#3–9), the Mo was never passed through the column. Second, for experiments #1 and 2 (in which Mo was added to the column), the yields of Mo were verified by isotope dilution (as described by ref. [8]) to be >99.5%. Mass-dependent isotopic fractionation of Mo on the column is expected to be insignificant when the recovery is ∼100% (e.g., ref. [5]). Third, even if the Mo was significantly fractionated on the column at yields >99.5%, the Mo eluted from the resin would be expected to be isotopically heavy due to the loss of the last bit of isotopically light Mo (which would presumably be retained on the resin). This is opposite to the data in Tables 2 and 3.

It is also possible to rule out the presence of isobaric interferences as a cause of the observations. To examine this possibility, aliquots of the 1 M HCl and 5 M HNO_3 cuts were collected from the large column (as part of experiments #4 and 5), diluted in proportions similar to experiments #4b–d and #5b–d, and analyzed by scanning over the Zr and Mo mass range. No peaks were visible above the baseline of the Faraday collector (<0.25 mV) in the 5 M HNO_3 cut. In contrast, small peaks in the Mo and Zr mass range (in approximately natural proportions for these elements) were observed in the 1 M HCl cut. However, these peaks were all <2 mV, which is consistent with the typical blank for the large anion exchange resin column [8] and is insignificant relative to the typical Mo signal intensity (<0.03% contribution from the blank). As another test for the presence of one or more isobaric interferences, all of the data from Table 3 were re-reduced using an internal normalization for instrumental mass bias relative to an assumed true ^{97}Mo/^{95}Mo ratio of 0.60208 [23]. Both the samples and bracketing standards gave identical results (0.04–0.09‰, $\pm 2\sigma$) for all permutations of the Mo isotopes that lack Zr interferences (^{98}Mo/^{95}Mo, ^{100}Mo/^{95}Mo, ^{100}Mo/^{98}Mo, ^{100}Mo/^{97}Mo, and ^{98}Mo/^{97}Mo), when corrected using the exponential law [24]. This would not be the case if one or more isobaric interferences were present in the samples (and not in the standard). Finally, it is important to emphasize that the variations in the Mo isotope ratios are strongly mass-dependent for both simple and external normalization SSB, which can be seen when the $\delta^{X/95}$Mo values are compared on a ‰/AMU basis

(Tables 2 and 3). The strong mass dependence of the $\delta^{X/95}$Mo values would tend to be destroyed by an isobaric interference. For example, mass-balance calculations show that addition of an interference at mass 95 sufficient to reduce the $\delta^{97/95}$Mo value of a sample by 0.5‰/AMU would decrease the $\delta^{100/95}$Mo value by only 0.2‰/AMU.

Instead, we conclude that the anion exchange resin column chemistry indirectly leads to a matrix effect in the MC-ICP-MS. The most likely culprit for this effect is organic material stripped from the resin during the collection of the Mo in 1 M HCl and 5 M HNO_3. All solutions collected from the large column (experiments #1–5 and #6 before the clean-up column) were visibly sticky in clean Teflon beakers (prior to any chemical treatment), and the 5 M HNO_3 cut was always slightly worse than the 1 M HCl cut. Although the solutions from the small columns (experiments #7–9 and #6 after the clean-up column) and chemically treated solutions from the large column (experiments #4b–d and #5b–d) lacked any visible signs of organics in clean Teflon beakers, they still produced relatively large matrix effects (Table 3). The visible reduction in the organics following the clean-up column is thought to result from the lack of adherence of the organics to the resin while the Mo sticks in 6 M HCl and 0.1 M HF + 0.01 M HCl. Thus, elution of the Mo in 1 M HCl and/or 5 M HNO_3 would probably add only ∼1/40 of the original amount of organics.

The presence of organics in the 1 M HCl and 5 M HNO_3 cuts from the large column was verified by monitoring the UV spectrum of each cut in a 1-cm cell between 220 and 350 nm (where organics cause significant absorption) using a Cary 50 UV–vis spectrophotometer at SDSU. Both the 1 M HCl and 5 M HNO_3 cuts were dried and re-dissolved in 1 M HCl prior to scanning their UV spectra. Strong absorption (relative to a pure 1 M HCl reference solution) consistent with the presence of organics was observed in both solutions collected from the column, although the absorption was greater in the 5 M HNO_3 cut than the 1 M HCl cut (consistent with the visual appearance of the solutions).

To our knowledge, this type of non-spectral matrix effect due to column chemistry (hereafter called a "column matrix effect") has not been previously documented. However, two earlier studies [5,9] presented Mo isotopic data that may indirectly relate to this issue.

In the first study, Anbar et al. [5] loaded ∼15 μg of Mo from a high-purity standard onto a 2-mL column of anion exchange resin (Bio-Rad AG1-X8), washed the resin with 6 M HCl, and eluted the Mo in five cuts of 1 M HCl to investigate the possibility of isotopic fractionation during column chemistry. The five cuts were analyzed by MC-ICP-MS (VG Plasma 54) using Zr-doping and the graphical method of Maréchal et al. [22] to correct for instrumental mass bias. Using mass-balance calculations for the five cuts, they showed that the cumulative isotopic composition of the Mo eluted from the column (∼95% recovery) was identical within error (±0.5‰, including the full propagation of errors) to the untreated Mo isotopic standard. This suggests that the size of a potential column matrix effect on the $\delta^{X/95}$Mo values using the procedure of Anbar et al. [5] must be less than ∼0.5‰. Our experiment #3 is approximately equivalent to the experiment of Anbar et al. [5] in terms of the proportion of Mo to resin (with the addition of the 5 M HNO_3 step in our case). The $\delta^{X/95}$Mo values for this experiment using external normalization SSB to correct for instrumental mass bias (closest to the method used by Anbar et al. [5]) are $\delta^{97/95}$Mo = −1.1‰, $\delta^{98/95}$Mo = −1.6‰, and $\delta^{100/95}$Mo = −2.7‰ (Table 2). These offsets are significantly larger than the maximum size of a potential column matrix effect permitted by the data of Anbar et al. [5], which suggests that the column matrix effect that we observed may be partially specific to our particular chemical procedure, anion exchange resin, or instrument.

In the second study, Wieser et al. [9] conducted three experiments using both anion and cation exchange resin to investigate the possibility of isotopic fractionation during column chemistry. First, an unspecified amount of high-purity Mo (from their isotopic standard) was loaded onto a column of Bio-Rad AG1-X8 anion exchange resin (of unspecified volume). The resin was washed in 4 M HCl, and the Mo was eluted in 0.5 M HCl. Second, the Mo was passed through a column of cation exchange resin (Bio-Rad AG50W-X8) in 0.5 M HCl, which is used by several laboratories to remove the residual iron from natural samples [8,20,21]. The resulting Mo cuts (∼93% recovery) were analyzed using MC-ICP-MS (ThermoFinnigan Neptune) with a procedure similar to simple SSB to correct for instrumental mass bias, and found to be ∼0.14‰/AMU lighter than the untreated Mo isotopic standard. Wieser et al. [9] interpreted this to result from isotopic fractionation of Mo on the column with less than 100% recovery. Isotopic fractionation of Mo on the column is probably dominated by the anion exchange resin procedure because Mo does not significantly interact with cation exchange resin in dilute HCl. In this case, the data of Wieser et al. [9] is probably inconsistent with isotopic fractionation on the column because the Mo eluted from the anion exchange resin would be expected to be isotopically heavy due to the loss of the last bit of isotopically light Mo (which would presumably be retained on the resin). Instead, the data of Wieser et al. [9] may be consistent with the presence of a small column matrix effect on the order of ∼0.14‰/AMU.

In any case, it is important to note that the column matrix effect observed in our study is relatively large (>0.6‰ on $\delta^{97/95}$Mo using simple SSB) when effective amounts of Mo (relative to the column cut) similar to what might be expected from most natural samples are used (e.g., experiments #6–9). Surprisingly, this column matrix effect is still observable (0.2–0.4‰ on $\delta^{97/95}$Mo using simple SSB) even when relatively large amounts of Mo are passed through the column (>200 μg). The magnitude of the column matrix effect is significant compared to the total known range of mass-dependent Mo isotopic variation in nature (e.g., ∼2.1‰ on $\delta^{97/95}$Mo [7,8,21,25]).

Attempts to remove or destroy the organics that cause this column matrix effect included (1) a clean-up column scaled down by a factor of ∼40, (2) collecting the Mo cut in different acids (1 M HCl vs. 5 M HNO_3), and (3) treating the sample with concentrated HNO_3, aqua regia, and H_2O_2 to destroy the organics. Unlike the previously identified non-spectral matrix effects in the MC-ICP-MS, all of our attempts to eliminate or control the column matrix effect for Mo have failed. Unless a means to remove this column matrix effect is found, it will be difficult (if not impossible) to obtain accurate measurements of mass-dependent Mo isotopic variations in natural materials using SSB techniques to correct for instrumental mass bias in the MC-ICP-MS (and the anion exchange resin procedure described in this study). Instead, the use of a double spike [6,7] may be required (despite the potential complications of memory effects [16]). Further study is required to determine if the column matrix effect can be eliminated or controlled using other methods for the separation and purification of Mo from natural samples (e.g., refs. [6,23]). Furthermore, it is currently unknown if this type of column matrix effect will affect measurements of other stable (e.g., Fe) or radiogenic (e.g., Pb or Th) isotopes by MC-ICP-MS when SSB (either simple or external normalization) is used to correct for instrumental mass bias.

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