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Molybdenum isotope fractionation during adsorption by manganese oxides

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Abstract

The isotopic composition of Mo ($\delta^{97/95}\text{Mo}$) in seawater is $\sim 2\%$ heavier than Mo in marine ferromanganese crusts and nodules [Barling et al., *Earth Planet. Sci. Lett.* 193 (2001) 447–457; Siebert et al., *Earth Planet. Sci. Lett.* 211 (2003) 159–171]. To explore this phenomenon, we have conducted an experimental investigation into the mass-dependent fractionation of Mo isotopes during adsorption onto Mn oxyhydroxide. Two series of experiments were carried out: a ‘time series’, in which adsorption proceeded for 2–96 h; and a ‘pH series’ in which pH varied from 6.5 to 8.5. The extent of Mo adsorption by Mn oxyhydroxides decreases with increasing pH, a trend typical of anion adsorption, and takes 48 h to reach steady-state. Lighter Mo isotopes are preferentially adsorbed. Experimentally determined fractionation factors ($\alpha_{\text{soln-MnOx}}$) exhibit no systematic variation with either time or experimental pH. The mean $\alpha_{\text{soln-MnOx}}$ for all experiments is 1.0018 ± 0.0005 (2 S.D.). Comparison of the Mo isotopic data for experimental solutions and Mo adsorbed to Mn oxyhydroxide with predictions for ‘closed system’ equilibrium and Rayleigh fractionation models indicates that isotope fractionation occurs as a result of ‘closed system’ equilibrium exchange between dissolved and adsorbed Mo. The isotopic offset between dissolved and adsorbed Mo is comparable to that observed between Mo in seawater and Mo in ferromanganese nodules and crusts. It is therefore likely that adsorption of Mo to Mn oxyhydroxides is a significant factor in the fractionation of Mo isotopes in the oceans.

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Keywords: molybdenum isotopes; isotope fractionation; manganese oxides; adsorption

1. Introduction

With the advent of MC-ICP-MS, it has become

possible to measure mass-dependent variations in the isotopic compositions of many transition metals to previously unattainable levels of precision. This has led to observations, for several of these elements, of ‰-scale natural variations in their isotopic compositions resulting from mass-dependent fractionation. With these observations comes the need to understand the processes producing these variations.

Natural variations in the mass-dependent fractionation of Mo isotopes span a range of $\sim 3\%$

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in $\delta^{97/95}\text{Mo}$ ($\delta^{97/95}\text{Mo}_{\text{sample}} = ({}^{97}\text{Mo}/{}^{95}\text{Mo}_{\text{sample}}/{}^{97}\text{Mo}/{}^{95}\text{Mo}_{\text{standard}} - 1) \times 1000$) for materials analyzed to date [1–4]. Mo in seawater from the Pacific, Atlantic and Indian oceans has a homogeneous isotopic composition ($\delta^{97/95}\text{Mo}_{\text{SW}} \approx 1.5\%$ relative to the Rochester in-house standard), consistent with the long ocean residence time of Mo ($\sim 800\,000$ yr [5]). Euxinic sediments have Mo isotopic compositions ($\delta^{97/95}\text{Mo}_{\text{euxinic}}$) similar to the seawater value. In contrast, Mo in marine ferromanganese nodules and crusts ($\delta^{97/95}\text{Mo}_{\text{FeMn}}$) is lighter by $\sim 2\%$. Little variation in the isotopic composition of Mo is seen in Pacific and Atlantic ferromanganese crusts spanning ~ 60 Myr. The isotopic compositions of Mo in molybdenite ores, igneous rocks and deep sea hydrothermal fluids are intermediate between those of seawater (and euxinic sediments) and ferromanganese oxide sediments. These observations are summarized in Fig. 1.

These data strongly suggest that Mo isotopes in the marine environment are fractionated as a result of incorporation into ferromanganese oxyhydroxides, producing the observed isotopic offset between Mo in seawater and Mo in ferromanganese nodules and crusts [1,2]. The constant Mo isotopic composition of marine ferromanganese crusts sampled over 60 Myr suggests that this fractionation is the result of an equilibrium isotope effect [2].

Mn oxyhydroxide phases are probably particularly important in this process. The observed correlation of Mo and Mn content in ferromanganese nodules and crusts [6–9] indicates that Mo is associated with Mn rather than Fe oxyhydroxides [10,11]. A similar correlation is observed between Mo and Mn concentrations in oxic pelagic sediments [9,12], including those that may have undergone early diagenetic processes [9]. This suggests that the association between these two elements extends to typical oxic pelagic sediments, although the extent to which diagenetic cycling of Mo due to Mn reduction and reoxidation [9,10,13,14] affects the isotopic composition of Mo preserved in oxic pelagic sediments has yet to be investigated.

Based on estimates that 47–85% of the removal of Mo from the oceans is into oxic pelagic sedi-

ments [5,12], we have proposed that Mo isotope fractionation resulting from uptake of Mo by Mn oxyhydroxides, both in oxic pelagic sediments and in ferromanganese nodules and crusts, explains the apparent $\delta^{97/95}\text{Mo}$ offset between the presumed isotopic composition of Mo entering the oceans from igneous sources (i.e. crustal weathering and hydrothermal systems) and the observed isotopic composition of Mo in seawater [1]. This hypothesis is analogous to the situation for Ca isotopes, where the isotopic offset between ocean and crust is explained in terms of fractionation during calcium carbonate precipitation [15].

Sediments accumulating under euxinic waters are also a major sink of Mo from the oceans (e.g. [5,12]). Although it seems likely that Mo isotopes are also fractionated during changes in Mo speciation associated with the removal of Mo from solution under reducing conditions, the observation of little or no fractionation between the isotopic composition of Mo in seawater and that in euxinic sediments probably reflects the near-quantitative removal of Mo from the water column in these environments. Hence, removal in such settings is unlikely to have an important impact on the isotopic composition of Mo in seawater, at least to first order.

This view of the ocean Mo isotope budget has led to suggestions that the Mo isotopic composition of seawater could be sensitive to changes in ocean redox conditions over time scales greater than the ocean residence time of Mo [1,2]; a decrease in the proportion of Mo removed to oxic pelagic sediments would result in a smaller isotopic offset between Mo in seawater and the Mo input to the oceans, and vice versa. Such changes might be directly recorded as variations in the Mo isotope composition of black shales [1,16] or, indirectly, as variations in the Mo isotopic composition of authigenic ferromanganese oxyhydroxides [2]. Both means of tracking the Mo isotopic composition of seawater require investigation of Mo isotope fractionation during incorporation of Mo into ferromanganese oxyhydroxides.

In this paper we report the results of an initial experimental investigation of Mo isotope fractionation resulting from adsorption of Mo onto Mn

oxyhydroxides. The experiments were designed to answer three critical questions arising from natural observations: (1) Does isotope fractionation occur between Mo in solution and Mo adsorbed by Mn oxyhydroxide? (2) Does this fractionation favor the incorporation of lighter isotopes into the Mn oxyhydroxide? (3) Is the magnitude of the isotopic offset between Mo in solution and Mo adsorbed by the Mn oxyhydroxide similar to the offset between Mo in seawater and Mo in ferromanganese oxide crusts and nodules? We also discuss the possible fractionation mechanism and the implications of our findings for application of the Mo isotope system to ocean paleoredox.

2. Experimental and analytical methods

2.1. Experimental design

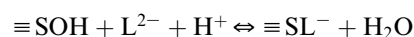
Manganese oxyhydroxides occur naturally in a variety of mineralogical forms. The slow hydro-geologic precipitation of Mn oxyhydroxide from natural waters as a result of the oxidation of Mn^{2+} weathered from the continents produces $\delta\text{-MnO}_2$ (vernadite). This form of Mn oxyhydroxide is dominant in ferromanganese crusts forming on hard-rock substrates in mid-plate environments. However, crusts and nodules from other environments can also include diagenetic and hydrothermal components such as todorokite and birnessite [17]. We have chosen to use the hydro-geologic form of Mn oxyhydroxide ($\delta\text{-MnO}_2$) in our experiments. $\delta\text{-MnO}_2$ is probably representative of the interaction of Mo and Mn oxyhydroxides in the ocean as a whole because it precipitates from seawater under unexceptional ambient conditions. However, it will be useful in the future to determine whether the interaction of Mo with diagenetic or hydrothermal Mn oxyhydroxides differs significantly from the results presented here.

$\delta\text{-MnO}_2$ can be produced in the laboratory via a variety of reactions which result in a range of surface morphologies and variable degrees of crystallinity (see review in [18]). The particular reaction used in this study was chosen because

the $\delta\text{-MnO}_2$ produced has been well characterized [18,19], is known to be amorphous, and is stable for up to 4 years when stored under refrigeration.

For practical reasons the Mo concentration in the experiments was set at $\sim 25 \mu\text{M}$. Although this concentration is much higher than the natural concentration of Mo in seawater ($0.105 \mu\text{M}$ [20,21]), it is below the threshold concentration (10^{-4} M) for the formation of polyanionic Mo complexes that are found experimentally at $\text{pH} < 6$ (e.g. [11,22,23]). We have found no evidence in the literature, either from experimental studies in the range $\text{pH} 6.5\text{--}8.5$ (i.e. our experimental conditions) or from investigations of natural waters (e.g. [24]), that Mo is likely to be present, in either case, in significant quantities as any other species than MoO_4^{2-} (dominant) and HMoO_4^- ($\leq 4\%$) and $\text{H}_2\text{MoO}_4^\circ$ ($< 1\%$).

Based on previous adsorption studies (e.g. [25]), MoO_4^{2-} is expected to form an inner sphere complex when it adsorbs to $\delta\text{-MnO}_2$:



and hence adsorption is expected to increase with decreasing pH (i.e. increasing H^+). The extent of adsorption with respect to pH for elements forming inner sphere complexes is relatively insensitive to variations in ionic strength of the solution, with variations of over an order of magnitude having little or no effect on the adsorption edge [26,27]. Therefore, natural variations in the ionic strength of seawater (typically $\sim 10\%$ or less) are likely to have a minimal effect on the adsorption behavior of Mo compared to the effect produced by variation in pH. Significantly, seawater typically varies over the range $\text{pH} 7.5\text{--}8.4$, which is in the vicinity of the adsorption edge for Mo on $\delta\text{-MnO}_2$ [25]. The experiments here therefore focus on adsorption of Mo by $\delta\text{-MnO}_2$ in solutions of constant ionic strength and variable pH. The ionic strength of the experiments was set at 0.1 M using potassium nitrate in order for the results to be readily comparable to existing adsorption studies. Potassium nitrate is used because it is expected to have a minimal effect on the interaction between ions in solution and the $\delta\text{-MnO}_2$. An additional reason for selecting an ionic strength lower than that of seawater (i.e. 0.5 M) was for

Table 1

Experimental results: Fraction of Mo adsorbed by δ -MnO₂, $\delta^{97/95}\text{Mo}$, calculated $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ and $\alpha^{97/95}\text{Mo}_{\text{soln-MnOx}}$, for experimental δ -MnO₂-solution pairs

| | pH (final) | $f(\text{Mo})$ | | $\delta^{97/95}\text{Mo}^{\text{a}}$ | | Mass balance ^b | Inferred $\delta^{97/95}\text{Mo}$ δ -MnO ₂ | $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | | $\alpha^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | |
|---|---------------|----------------|------------------------|--------------------------------------|----------------------------|---------------------------|--|--|----------|--|----------|
| | | measured | corrected ^c | solutions | δ -MnO ₂ | | | measured | inferred | measured | inferred |
| Stock Mo solution (Na ₂ MoO ₄ ·2H ₂ O) | | | | -0.59 | | | | | | | |
| Single purification | | | | -0.66 | | | | | | | |
| | | | | -0.24 | | | | | | | |
| | | | | -0.33 | | | | | | | |
| | | | | -0.46 | | | | | | | |
| | | | | Mean: -0.46 | | | | | | | |
| | | | | 2 S.D.: 0.35 | | | | | | | |
| Stock Mo solution (Na ₂ MoO ₄ ·2H ₂ O) | | | | -0.52 | | | | | | | |
| Double purification | | | | -0.48 | | | | | | | |
| | | | | -0.43 | | | | | | | |
| | | | | -0.35 | | | | | | | |
| | | | | -0.50 | | | | | | | |
| | | | | Mean: -0.45 | | | | | | | |
| | | | | 2 S.D.: 0.14 | | | | | | | |
| pH Series (time = 48 h): | | | | | | | | | | | |
| pH 6.5 | | 0.99 | | | | | | | | | |
| | | | | -0.34 | | | | | | | |
| | | | | -0.25 | | | | | | | |
| | | | | Mean: -0.30 | | | | | | | |
| | | | | 2 S.D.: 0.13 | | | | | | | |
| pH 7.5 | | 0.93 | | 1.26 | -0.58 | | | | | | |
| | | | | 1.36 | -0.55 | | | | | | |
| | | | | 1.11 | | | | | | | |
| | | | | Mean: 1.25 | -0.57 | -0.44 | -0.58 | 1.81 | 1.83 | 1.00181 | 1.00183 |
| | | | | 2 S.D.: 0.25 | 0.05 | | | | | | |
| pH 8.5 | | 0.73 | | 1.07 | -0.78 | | | | | | |
| | | | | 1.19 | -0.65 | | | | | | |
| | | | | -0.66 | | | | | | | |
| | | | | Mean: 1.13 | -0.70 | -0.20 | -1.04 | 1.83 | 2.18 | 1.00183 | 1.00218 |
| | | | | 2 S.D.: 0.17 | 0.14 | | | | | | |
| Time Series (nominal pH 8.5): | | | | | | | | | | | |
| Time = 2.3 h | 8.54 | 0.49 | 0.41 | 0.41 | | | | | | | |
| | | | | 0.39 | | | | | | | |
| | | | | Mean: 0.40 | | | -1.68 | | 2.08 | | 1.00208 |
| | | | | 2 S.D.: 0.02 | | | | | | | |
| Time = 4 h | 8.13 | 0.53 | 0.49 | 0.48 | | | | | | | |
| | | | | 0.63 | | | | | | | |
| | | | | Mean: 0.55 | | | -1.51 | | 2.06 | | 1.00206 |
| | | | | 2 S.D.: 0.22 | | | | | | | |
| Time = 6 h | 7.59 | 0.60 | 0.58 | 0.67 | | | | | | | |
| | | | | 0.57 | | | | | | | |
| | | | | 0.53 | | | | | | | |
| | | | | Mean: 0.59 | | | -1.21 | | 1.80 | | 1.00180 |
| | | | | 2 S.D.: 0.15 | | | | | | | |

Table 1 (Continued).

| | pH (final) | $f(\text{Mo})$ | | $\delta^{97/95}\text{Mo}^a$ | | Mass balance ^b | Inferred $\delta^{97/95}\text{Mo}$ $\delta\text{-MnO}_2$ | $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | | $\alpha^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | |
|---------------------------------------|---------------|----------------|------------------------|-----------------------------------|-----------------------|---------------------------|---|---|---|--|----------|
| | | measured | corrected ^c | solutions | $\delta\text{-MnO}_2$ | | | measured | inferred | measured | inferred |
| Time = 12 h | 8.28 | 0.65 | 0.57 | 0.64 0.68 0.66 | | | | | | | |
| | | | | Mean: 0.66 2 S.D.: 0.05 | | | -1.29 | | 1.95 | | 1.00195 |
| Time = 24 h | 8.29 | 0.68 | 0.61 | 0.82 0.73 0.63 | | | | | | | |
| | | | | Mean: 0.73 2 S.D.: 0.19 | | | -1.20 | | 1.93 | | 1.00193 |
| Time = 48 h ^d (Split 1) | 8.29 | 0.76 | 0.67 | 0.67 0.62 0.50 | | | | | | | |
| | | | | Mean: 0.59 2 S.D.: 0.18 | | | -0.97 | | 1.56 | | 1.00156 |
| Time = 48 h ^d (Split 2) | 8.29 | 0.79 | 0.68 | 0.55 0.45 0.52 | | | | | | | |
| | | | | Mean: 0.51 2 S.D.: 0.09 | | | -0.91 | | 1.41 | | 1.00141 |
| Time = 48 h (Full duplicate) | 7.70 | 0.77 | 0.72 | 0.75 0.54 0.65 | -1.06 | -0.58 | -0.89 | 1.71 | 1.54 | 1.00171 | 1.00154 |
| | | | | Mean: 0.65 2 S.D.: 0.30 | -1.06 ^e | | | | | | |
| Time = 96 h | 8.20 | 0.76 | 0.69 | 0.88 0.82 0.83 | | | | | | | |
| | | | | Mean: 0.84 2 S.D.: 0.06 | | | -1.04 | | 1.88 | | 1.00188 |
| | | | | | | Mean mass balance | | Mean $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | Mean $\alpha^{97/95}\text{Mo}_{\text{soln-MnOx}}$ | | |
| | | | | | | -0.41 | | 1.78 | 1.84 | 1.0018 | 1.0018 |
| | | | | | | 2 S.D.: 0.38 | 2 S.D.: | 0.12 | 0.49 | 0.0001 | 0.0005 |

^a For comparison with the data of Siebert et al. [2,4] and McManus et al. [3] $\delta^{98/95}\text{Mo} \sim 1.5 \times \delta^{97/95}\text{Mo}$.

^b $\delta^{97/95}\text{Mo}$ of the bulk experiment calculated as $f(\text{Mo}) \times \delta^{97/95}\text{Mo}_{\text{MnOx}} + (1-f(\text{Mo})) \times \delta^{97/95}\text{Mo}_{\text{soln}}$. Should equal $\delta^{97/95}\text{Mo}$ of the stock Mo solution.

^c Fraction of Mo adsorbed by $\delta\text{-MnO}_2$ corrected for the dead volume of the filtration apparatus. See text.

^d Experiment was split into two equal aliquots after adsorption. Subsequently, each split was processed separately.

^e $\delta^{97/95}\text{Mo}_{\text{MnOx}}$ corrected for dead volume of filter apparatus. See text.

ease of purification of the experimental solutions prior to isotopic analysis (see below).

2.2. Materials and reagents

All experiments were carried out in a clean room fitted with HEPA-filtered Class 100 air supply and laminar flow benches. All labware, including Teflon[®] and disposable plastics, was cleaned in 50% concentrated reagent-grade acids and 18 M Ω deionized H₂O prior to use. Acids used in experiments and during separation chemistry were ultra-pure and were either commercial sub-boiling, quartz-distilled acids (Seastar[™]) or acids purified in-house by sub-boiling distillation in a Teflon[®] still. Water used is 18 M Ω deionized H₂O. All other reagents were 'reagent grade' and better than 99.5% pure. Mo-containing solutions were stored in Teflon[®], except during agitation. δ -MnO₂ was separated from experimental suspensions by filtration through a 0.1 μ m Supor[®]-100 (hydrophilic polyethersulfone) membrane in a Savillex[®] Teflon[®] PFA filtration assembly attached to a Savillex[®] Teflon[®] PFA container. The filtration apparatus was rinsed in 18 M Ω water, heated in 50% concentrated nitric acid overnight, and rinsed again in 18 M Ω water between experiments. The pH of the various experiments was monitored using a Mettler-Toledo MP 120 pH meter fitted with a combination electrode.

2.3. Preparation of δ -MnO₂ and Mo solution

δ -MnO₂ was produced by addition of concentrated hydrochloric acid to potassium permanganate dissolved in a small volume of water [19]. The reaction was allowed to proceed for 3 h, at which time the product was diluted with 18 M Ω water. The resulting δ -MnO₂ suspension (pH 1.7–1.9) was adjusted to a pH of 7 by addition of potassium hydroxide. The suspension was then filtered. The δ -MnO₂ was then repeatedly resuspended and filtered until it had been washed by a volume of water equivalent to four times that of the original suspension. The remaining δ -MnO₂ was then resuspended in 18 M Ω water, the suspension weighed and refrigerated until use. The amorphous nature of the δ -MnO₂ produced was

confirmed by examination of a small aliquot of the δ -MnO₂ suspension using X-ray diffraction.

The proportions of potassium permanganate and hydrochloric acid used result in a slight stoichiometric excess of potassium permanganate. Assuming that all the hydrochloric acid was consumed in the reaction, the final suspension used in the two experimental series presented here contained approximately 0.22 g (2.53×10^{-3} mol) of δ -MnO₂. For each experiment approximately 8% of the stock suspension was used, i.e. approximately 0.018 g (2.02×10^{-4} mol) of δ -MnO₂.

A stock solution of Mo was prepared specifically for these experiments by dissolving sodium molybdenum oxide (Na₂MoO₄·2H₂O) in water. The Mo concentration and isotopic composition of this solution were determined. A precisely weighed aliquot of this solution, containing ~ 100 μ g (1.04 μ mol) of Mo, was used for each experiment. The resulting Mo concentration in these experiments was ~ 25 μ M.

2.4. Experimental procedures

Two experimental series were carried out: a 'pH series' consisting of three parallel experiments at pH 6.5, 7.5 and 8.5; and a 'time series' of eight parallel experiments at pH 8.5 that were run for various lengths of time between 2 and 96 h.

At the start of each experimental series, aliquots of the δ -MnO₂ suspension and Mo solution were weighed and their ionic strength matched at 0.1 M by addition of potassium nitrate. After this addition, the pH of both the δ -MnO₂ suspensions and Mo solutions was ~ 5 . Therefore, prior to mixing, the pH of each suspension–solution pair was adjusted by multiple additions of μ l quantities of 0.1 M sodium hydroxide (i.e. matched to experimental ionic strength) each of which was allowed to equilibrate before any further addition. Since the experiments were carried out in containers open to exchange with atmospheric CO₂, equilibration after each sodium hydroxide addition was slow. Once stable experimental pH was reached for a suspension–solution pair, the two were mixed and the pH monitored. In all cases an initial drop in pH was observed on mixing, followed by a slow return to roughly the desired

pH. Final pH adjustment was achieved by further additions of μl quantities of 0.1 M sodium hydroxide and/or 0.1 M perchloric acid at which point the experimental suspensions were transferred to 50 ml centrifuge tubes, sealed with Parafilm[®], enclosed in a plastic bag and put on a wrist-action agitator for the duration of the experiment.

For the pH series experiments, three separate suspension–solution pairs were set up at pH 6.5, 7.5 and 8.5. These were then mixed and agitated for 48 h. For the time series experiments, a single large-volume suspension–solution pair was adjusted to an experimental pH of 8.5. The $\delta\text{-MnO}_2$ suspension and Mo solution were then mixed and the mixture divided by weight into eight aliquots of similar size to the individual pH series experiments. These eight parallel experiments were then sealed and agitated for lengths of time that varied from 2.3 to 96 h. Individual experimental details are summarized in Table 1.

At the end of each experiment, the pH of the suspension was measured and the $\delta\text{-MnO}_2$ separated from the solution by filtration. After filtration, the solution was weighed and the ‘dead volume’ of solution trapped in the filter assembly calculated by difference from the starting weight of the experiment (the weight of the $\delta\text{-MnO}_2$ being negligible by comparison). The $\delta\text{-MnO}_2$ was then resuspended in 18 M Ω water and poured out of the filter top. Any $\delta\text{-MnO}_2$ remaining in the filter top or on the filter membrane was then dissolved in 6 M hydrochloric acid and passed through the filter. The dissolved $\delta\text{-MnO}_2$ was then added to the recovered $\delta\text{-MnO}_2$ and the suspension gently heated until the $\delta\text{-MnO}_2$ was completely dissolved. The separated $\delta\text{-MnO}_2$ and solution of each experiment will be referred to subsequently as ‘experimental $\delta\text{-MnO}_2$ –solution pairs’.

The significance of the filter dead volume of the filtration apparatus (10 ml) was not appreciated until the separated experimental solutions from the pH series experiments were weighed after filtration and found to be smaller than expected. Since these experiments were not re-weighed once mixed, the amount of residual solution Mo flushed through the filter assembly during collec-

tion of the $\delta\text{-MnO}_2$ fraction could not be calculated and thus no correction for the dead volume could be made for the pH series.

Importantly, the dead volume correction has no effect on the Mo isotopic composition of the experimental solutions and it is these data that are used, via mass balance, to infer the Mo isotopic composition of the $\delta\text{-MnO}_2$ for most of the experiments. The dead volume correction does however affect our estimates of the fraction of Mo adsorbed by the $\delta\text{-MnO}_2$ ($f(\text{Mo})$), and hence the inferred Mo isotope composition of the $\delta\text{-MnO}_2$. The measured Mo isotope composition in $\delta\text{-MnO}_2$ is also modified by the presence of dissolved Mo from the dead volume; these data also require a dead volume correction. Both the measured and corrected $f(\text{Mo})$ for the time series experiments are listed in Table 1. The difference between the two values is variable and depends on the actual dead volume measured for each experiment (1.4–7.7 g) and the Mo concentration of the residual solution. However, the net importance of these corrections is negligible. The Mo isotopic composition of the $\delta\text{-MnO}_2$ was only measured in one of the time series experiments (48 h duplicate: Table 1). For this experiment the measured $\delta^{97/95}\text{Mo}$ of the $\delta\text{-MnO}_2$ was corrected from -0.94 to -1.06 . These values are identical within our stated external reproducibility.

An estimate of the maximum effect of the uncorrected dead volume for the pH series experiments can be made by assuming a 7.7 g dead volume (i.e. the maximum measured for a time series experiment). For the pH 6.5 and 7.5 experiments the amount of Mo remaining in solution is so small that the difference between measured and corrected $f(\text{Mo})$ is insignificant ($f(\text{Mo})_{\text{corrected}} = 0.99$ and 0.91 compared to measured values of 0.99 and 0.93 respectively). For the pH 7.5 experiment, where $\delta^{97/95}\text{Mo}$, $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ and $\alpha_{\text{soln-MnOx}}$ can be calculated ($\delta^{97/95}\text{Mo} = -0.604$; $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}} = 1.85$; $\alpha_{\text{soln-MnOx}} = 1.0018$), these values calculated for the maximum estimated correction are not significantly different from those reported in Table 1.

For the pH 8.5 experiment the correction to $f(\text{Mo})$ is more significant ($f(\text{Mo})_{\text{corrected}} = 0.65$ compared to measured value of 0.73) due to the

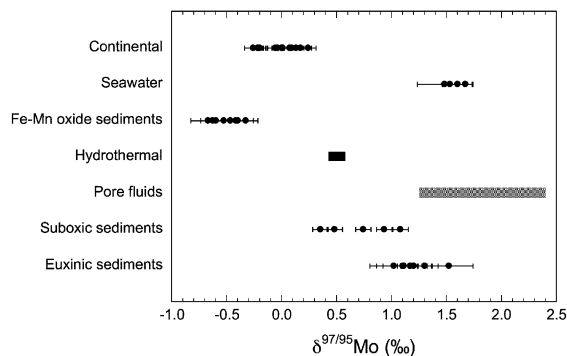


Fig. 1. Range of $\delta^{97/95}\text{Mo}$ values observed in natural materials. Continental: granites, molybdenites, clastic marine sediments. Seawater: Atlantic, Pacific and Indian oceans. Fe–Mn oxide sediments: Atlantic, Pacific and Indian ocean ferromanganese crusts and nodules. Hydrothermal: end-member fluid composition inferred from data in low- T ridge flank system (100 km east of Juan de Fuca). Pore fluids: range of values in reducing porewaters from Santa Monica basin, <25 cm depth. Suboxic sediments: Santa Monica and San Pedro basins, Chile margin. Euxinic sediments: Cariaco basin and Black Sea. Uncertainties $\pm 2\sigma$. Data sources: [1–4].

greater percentage of Mo remaining in solution. However, even in this worst case scenario the $\delta^{97/95}\text{Mo}$, $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ and $\alpha_{\text{soln-MnOx}}$ calculated using the corrected data ($\delta^{97/95}\text{Mo} = -0.910$; $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}} = 2.04$; $\alpha_{\text{soln-MnOx}} = 1.0020$) are still within the range of the values reported in Table 1. Thus although the dead volume correction on the $f(\text{Mo})$ adsorbed can be significant, the change in $\delta^{97/95}\text{Mo}$ is within our external reproducibility and thus the corrections

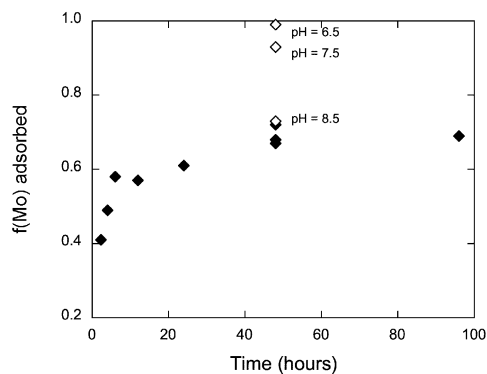


Fig. 2. Fraction of Mo adsorbed by $\delta\text{-MnO}_2$ versus time (hours). Time series experiments: closed diamonds; pH series experiments: open diamonds.

do not translate into significant changes in $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ and $\alpha_{\text{soln-MnOx}}$.

2.5. Purification of Mo and mass spectrometry

The stock Mo solution and all experimental $\delta\text{-MnO}_2$ –solution pairs were aliquoted and spiked with a ^{97}Mo -enriched spike for concentration determination by isotope dilution. These spiked aliquots and the remaining unspiked experimental $\delta\text{-MnO}_2$ –solution pairs were purified by anion exchange chemistry [1]. For the experimental solutions a single pass through the anion column was sufficient to achieve an essentially pure Mo sample. For the stock Mo solution and the experimental $\delta\text{-MnO}_2$ initial MC-ICP-MS runs indicated that matrix effects (possibly due to residual Na from the original standard salt) and/or isobaric interferences were degrading analytical reproducibility, therefore a second pass through chemistry was required to achieve a Mo cut pure enough for precise MC-ICP-MS measurement (Table 1).

At the end of each separation chemistry (except for the purification of the spiked concentration aliquots) a second aliquot was taken and spiked in order to determine the yield through the separation procedure. As previously documented [1,28] >90% yield is required if fractionation resulting from interaction of the sample Mo with the resin is to be negligible in comparison to our analytical precision.

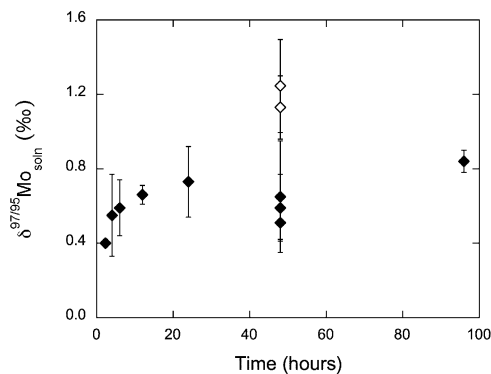


Fig. 3. $\delta^{97/95}\text{Mo}$ of Mo remaining in solution versus time (hours) for pH and time series experiments. Symbols as for Fig. 2. Error bars are $\pm 2\sigma$ on replicate analyses.

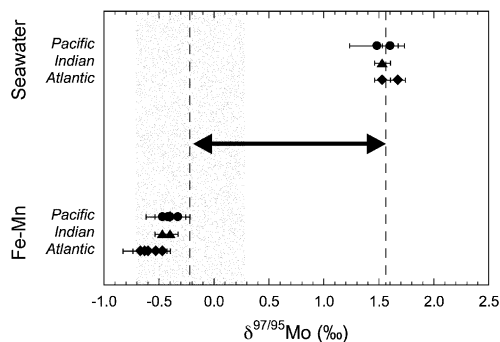


Fig. 4. Comparison of the isotopic offset between Mo in seawater and Mo in ferromanganese crusts and nodules expected from experimental findings with natural observations. The expected offset is derived from the mean seawater value (1.56‰) and $\alpha_{\text{soln-MnOx}} = 1.0018 \pm 0.0005$. The shaded region denotes the $\pm 2\sigma$ uncertainty on the expected value for adsorbed Mo. Observations are from Pacific (circles), Indian (triangles) and Atlantic (diamonds) oceans. Data sources as for Fig. 1.

Concentrations and yields were determined by isotope dilution–MC-ICP-MS on the University of Rochester VG Elemental Plasma 54. Mo isotope compositions were measured on the same instrument. Isotope composition data (Table 1) are reported as $\delta^{97/95}\text{Mo} = \left(\frac{(^{97}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{97}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right) \times 1000$ ‰ relative to an in-house laboratory standard (Johnson Matthey Specpure[®] plasma standard, Lot # 802309E, which is isotopically indistinguishable from our previous in-house standard [1]). Measurements were made using the ‘element spike’ method [29,30] with Zr as the ‘element spike’. Instrumental methods are described in detail in Anbar et al. [28] and Barling et al. [1]. Some difficulty was encountered in meeting previously stated quality control criteria. This affected measurements of $^{92}\text{Mo}/^{95}\text{Mo}$, $^{94}\text{Mo}/^{95}\text{Mo}$ and $^{96}\text{Mo}/^{95}\text{Mo}$ (i.e. the Zr interfered ratios), but not $^{97}\text{Mo}/^{95}\text{Mo}$ or $^{98}\text{Mo}/^{95}\text{Mo}$. For runs in which $\delta^{97/95}\text{Mo}/\text{amu}$ and $\delta^{98/95}\text{Mo}/\text{amu}$ (i.e. interference free ratios) agree to within better than 0.05‰, our external precision on replicate experimental samples run on multiple days is $\leq \pm 0.25$ ‰ (2σ) for all but one experimental sample (Table 1). Hence, we accepted data from runs in which this quality control criterion was met, and rejected data which failed this test.

For three experimental $\delta\text{-MnO}_2$ –solution pairs (two from the pH series and one from the time series) the Mo isotopic composition was determined on both the experimental $\delta\text{-MnO}_2$ and the experimental solution. Mass balance calculations for these pairs agreed to within our stated external analytical error with the measured Mo isotopic composition of the stock Mo solution (Table 1). Therefore, for the remaining experimental pairs only the Mo isotopic compositions of the experimental solutions were measured and the Mo isotopic composition of the experimental

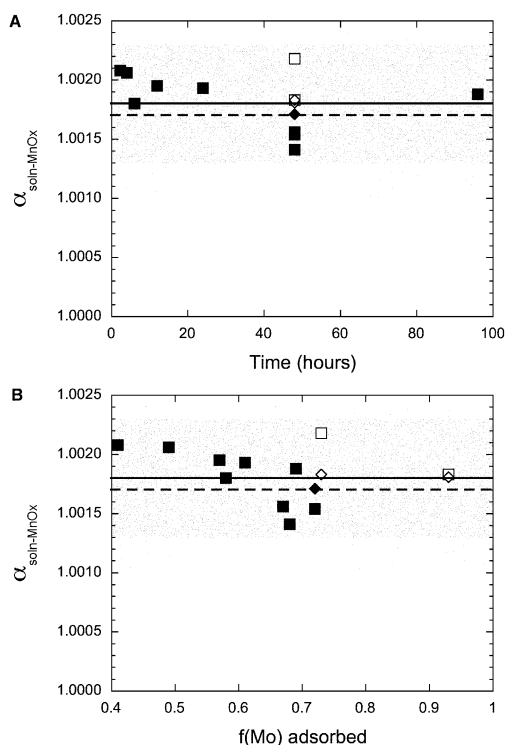


Fig. 5. Calculated $\alpha_{\text{soln-MnOx}}$ for experimental $\delta\text{-MnO}_2$ –solution pairs using both measured and inferred Mo isotopic compositions for $\delta\text{-MnO}_2$, (A) versus time in hours and (B) versus fraction of Mo adsorbed by $\delta\text{-MnO}_2$. Time series experiments in closed symbols, pH series experiments in open symbols. For both series diamonds represent values calculated using measured $\delta^{97/95}\text{Mo}_{\text{MnOx}}$ and squares represent values calculated using inferred $\delta^{97/95}\text{Mo}_{\text{MnOx}}$. Dashed lines and light shaded bands denote the mean and $\pm 2\sigma$ uncertainty on $\alpha_{\text{soln-MnOx}}$ for the four replicate 48 h-pH 8.5 experiments; solid lines and dark shaded bands denote the mean and $\pm 2\sigma$ uncertainty on $\alpha_{\text{soln-MnOx}}$ for all experiments.

δ -MnO₂ was inferred by mass balance. The measured and inferred values for experimental δ -MnO₂ are presented in separate columns in Table 1. Both sets of values for δ -MnO₂ are used and compared in all figures and in subsequent calculations.

3. Results

The time series experiments were carried out at pH 8.5. The adsorption process was not instantaneous; steady-state partitioning of Mo between experimental δ -MnO₂–solution pairs was achieved after 48 h (Fig. 2). Replicate experiments at 48 h indicate that the results for the fraction of Mo adsorbed by δ -MnO₂ are reproducible.

For the pH series of experiments, the fraction of Mo adsorbed by the δ -MnO₂ was determined 48 h after mixing. The fraction of Mo adsorbed by the δ -MnO₂ decreased with increasing pH from >99% at pH 6.5 to ~70% at pH = 8.5 (Fig. 2). Such a trend is expected from experimental studies of anion adsorption (e.g. [31–33]). The pH 8.5 experiment in the pH series reproduces 48 h–pH 8.5 experiments in the time series.

As seen in observations of the isotopic compo-

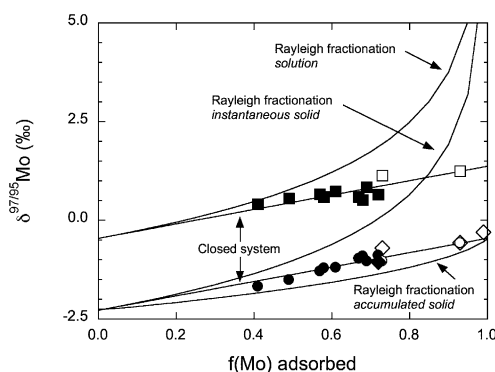


Fig. 6. $\delta^{97/95}\text{Mo}_{\text{soln}}$ and $\delta^{97/95}\text{Mo}_{\text{MnOx}}$ (both measured and inferred) versus fraction of Mo adsorbed by δ -MnO₂. Comparison of data with trends predicted for closed system equilibrium and Rayleigh fractionation models calculated using the experimentally determined $\alpha_{\text{soln-MnOx}}$. Time series experiments in closed symbols, pH series experiments in open symbols. For both series squares equal solutions, diamonds equal measured isotopic compositions of δ -MnO₂ and circles equal isotope compositions of δ -MnO₂ inferred by mass balance.

sition of Mo in ferromanganese phases relative to the isotopic composition of seawater Mo, the lighter Mo isotopes are, in all experiments, preferentially adsorbed by the δ -MnO₂, leaving the experimental solution isotopically heavy relative to the stock Mo solution (Fig. 3). Steady-state Mo isotopic composition for experimental solutions is reached by 48 h post mixing. Isotopic measurements of replicate 48 h experiments in the time series agree within error. However, the 48 h–pH 8.5 experiment in the pH series only agrees within error with one of the three time series replicates at 48 h. The reproducibility of the individual measurements, as indicated by the error bars on the symbols in Fig. 3, suggests that there may be a real difference between the two series of experiments. Such a difference might relate to changes in the character of surface adsorption sites on the δ -MnO₂ due to ageing of the δ -MnO₂ between the two experimental series (~14 days). Alternatively, the difference may indicate that dead volume complications in the pH series were more significant than estimated above.

The isotopic offset between Mo in solution and Mo adsorbed by δ -MnO₂ ($\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}} = \delta^{97/95}\text{Mo}_{\text{soln}} - \delta^{97/95}\text{Mo}_{\text{MnOx}}$), whether calculated from measured ($\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}} = 1.78 \pm 0.12$ (2 σ)) or inferred ($\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}} = 1.84 \pm 0.49$ (2 σ)) values for the $\delta^{97/95}\text{Mo}_{\text{MnOx}}$, is comparable to the isotopic offset observed between Mo in seawater and Mo in ferromanganese nodules and crusts (Fig. 4).

4. Discussion

Our results provide unequivocally affirmative answers to the three questions posed above: isotopic fractionation does occur between Mo in solution and Mo adsorbed onto Mn oxyhydroxide (δ -MnO₂); adsorption of light isotopes is favored; and the range of experimental values for $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ is comparable to the range of values observed for the isotopic offset between Mo in seawater and natural marine ferromanganese oxyhydroxides (Fig. 4). These findings demonstrate that, although simplified compared to natural systems, the experimental system fraction-

ates Mo isotopes in a manner consistent with the natural variations observed by Barling et al. [1] and Siebert et al. [2].

4.1. Fractionation factor

A fractionation factor (α) can be calculated from the experimental δ -MnO₂-solution pairs using both measured and inferred Mo isotopic compositions for δ -MnO₂. α is defined here as:

$$\alpha_{\text{soln-MnOx}} = (^{97}\text{Mo}/^{95}\text{Mo}_{\text{soln}})/(^{97}\text{Mo}/^{95}\text{Mo}_{\text{MnOx}}),$$

or alternatively,

$$= [1 + \delta^{97/95}\text{Mo}_{\text{soln}}/1000]/[1 + \delta^{97/95}\text{Mo}_{\text{MnOx}}/1000]$$

The calculated values for $\alpha_{\text{soln-MnOx}}$ are plotted against time and fraction of Mo adsorbed in Fig. 5. $\alpha_{\text{soln-MnOx}}$ exhibits no systematic variation with either variable, or with experimental pH. The total range of calculated $\alpha_{\text{soln-MnOx}}$ is seen in the replicate 48 h-pH 8.5 experiments, giving an indication of the experimental reproducibility of the value of $\alpha_{\text{soln-MnOx}}$ ($\alpha_{\text{soln-MnOx}} = 1.0017 \pm 0.0007$ (2σ , $n=6$; two measured, four inferred). The mean $\alpha_{\text{soln-MnOx}}$ for all experiments is 1.0018 ± 0.0005 (2σ).

The hypothesis of an equilibrium isotope effect during Mo adsorption onto Mn oxyhydroxide can be explored by comparing the isotopic data from experiments with different extents of adsorption to predictions from ‘closed system’ equilibrium and Rayleigh fractionation models, using the experimentally determined $\alpha_{\text{soln-MnOx}}$. If the data agree with a ‘closed system’ model, reversible exchange between adsorbed and dissolved Mo, and hence an equilibrium process, would be indicated. If the data agree with a Rayleigh model, then an irreversible adsorption process would be indicated. Irreversibility would suggest a kinetic isotope effect.

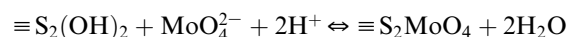
As seen in Fig. 6, the experimental δ -MnO₂ and solution data fall on single, parallel linear trends (i.e. constant $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$) that are best matched by closed system equilibrium exchange

between dissolved and adsorbed Mo. The data are therefore consistent with the suggestion that the Mo isotope fractionation during incorporation into Mn oxyhydroxides is largely the result of an equilibrium isotope effect.

4.2. Fractionation mechanism

In order to relate these findings to nature, it is helpful to have some understanding of the fractionation mechanism. The lack of any systematic variation in $\alpha_{\text{soln-MnOx}}$ with respect to experimental conditions suggests that isotopic fractionation is the result of a single mechanism. There are at least two mechanisms that could account for the data. Fractionation could occur as a result of equilibrium isotope exchange between a specific aqueous Mo species and Mo adsorbed to a single type of surface site on the δ -MnO₂. Alternatively, as proposed by Siebert et al. [2], if there is an equilibrium fractionation between co-existing aqueous species, adsorption of one of these species would shift the isotopic composition of the solution. The experimental data presented here cannot be used to distinguish between these two mechanisms. Both possibilities are briefly considered below.

Balistreri and Chao [25] investigated the adsorption behavior of Mo on δ -MnO₂ using triple layer surface complexation modelling to identify likely adsorption complexes. Two inner sphere complexes both resulted in good fits to the experimental data: the bidentate $\equiv\text{S}_2\text{MoO}_4$ complex and the monodentate $\equiv\text{SHMoO}_4$ complex:



These complexes form via the breakage of $\equiv\text{S-OH}$ bonds on the adsorbate surface and formation of a surface complex in which O atom(s) are shared between the surface and the Mo. It seems plausible that such changes in bonding could drive isotope fractionation. The $\equiv\text{S-O-Mo}$ bonds, where the O atoms are shared, could be weaker than the Mo-O bonds in the dissolved complex. Therefore, this mechanism could favor

preferential partitioning of the lighter Mo isotopes to the adsorbed phase, and the heavier to the dissolved complex, as is observed.

If Mo is adsorbing to more than one type of surface site, then either all the different Mo–surface site reactions have a similar characteristic $\alpha_{\text{soln-MnOx}}$ or the proportions of the different reactions remain constant across the range of experimental conditions. The simple single site adsorption model is preferred, since although triple layer surface complexation modelling of the adsorption of Mo on $\delta\text{-MnO}_2$ indicates that the experimental data can be modeled equally well by formation of either one of two surface complexes, only one is required for any given model [25].

Siebert et al. [2] proposed that equilibrium fractionation occurs in solution between MoO_4^{2-} and Mo(OH)_6 , with the latter, minor, species being adsorbed on Mn oxyhydroxide surfaces. This speciation hypothesis is analogous to the explanation of some Fe isotope effects (e.g. [34–36]). However, the observation that the extent of adsorption of Mo by $\delta\text{-MnO}_2$ varies inversely with pH is consistent with adsorption of an anionic (MoO_4^{2-}) species (e.g. [31–33]). Since MoO_4^{2-} is known to be by far the dominant Mo species in oxygenated natural waters with HMoO_4^- and $\text{H}_2\text{MoO}_4^\circ$ modelled as minor (<1%) equilibrium species [24] adsorption of this species would seem to be the simplest explanation of the data. This is not to say that equilibrium isotope fractionation does not occur between Mo species in solution. Indeed, since we did not determine what, if any, Mo species were present in addition to MoO_4^{2-} , it is not possible from the experimental data presented here to determine whether the observed isotopic fractionation is between isotopically homogeneous Mo species in solution and $\delta\text{-MnO}_2$ -bound Mo or between various Mo species in solution, one of which (an anion) is adsorbed onto the $\delta\text{-MnO}_2$.

The molar Mn/Mo ratio in the experimental system is much higher than in the natural system (0.0045 in seawater vs. 194 in the experiments). Experimental studies (e.g. [25]) have shown that at a given pH, adsorptive capacity of oxides tends to decrease with decreasing particle concentration. Therefore the adsorption capacity of $\delta\text{-MnO}_2$ for

Mo in the natural system is expected to be lower than in the experiments presented here. This is indeed the case. The molar Mn/Mo ratios in the experimental $\delta\text{-MnO}_2$ range from 209 at pH 7.5 to 290 at pH 8.5 (48 h) compared to molar Mn/Mo ratios ranging from 367 to 1057 calculated for Nod-P1 and Nod-A1 [37] and for a range of Pacific Ocean ferromanganese nodules reported by Calvert and Price [6]. However, if the type(s) of surface site involved do not change as a result of changing the Mn/Mo ratio, the characteristic $\alpha_{\text{soln-MnOx}}$ and $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ for the fractionation process in a low Mn/Mo system would be expected to be the same as for the high Mn/Mo system.

Another factor that might reduce the adsorption capacity of $\delta\text{-MnO}_2$ for Mo in the natural system is the presence of other anions capable of competing with molybdate ions for adsorption sites on the $\delta\text{-MnO}_2$. Balistrieri and Chao [25] investigated competition between phosphate, silicate and molybdate ions for $\delta\text{-MnO}_2$ adsorption sites. They found for experiments at pH 7 that the relative affinity sequence was molybdate \geq phosphate $>$ silicate. However, the decrease, if any, in the amount of Mo adsorbed by the $\delta\text{-MnO}_2$ in the competitive experiments was slight compared to adsorption experiments with only Mo (figs. 4 and 9 in [25]).

Although the experimental $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ is comparable to the observed $\Delta^{97/95}\text{Mo}_{\text{SW-FeMn}}$ its mean value is slightly lower. One possible explanation for this is suggested by the 0.2‰ difference in $\delta^{97/95}\text{Mo}_{\text{FeMn}}$ observed between Pacific (−0.4‰) and Atlantic (−0.6‰) ocean ferromanganese nodules and crusts [1,2]. The Pacific Ocean ferromanganese nodules and crusts thus have a smaller $\Delta^{97/95}\text{Mo}_{\text{SW-FeMn}}$ than the Atlantic Ocean material. We propose that this may relate to the proportions of different adsorbents present in the natural material since the $\Delta^{97/95}\text{Mo}_{\text{SW-FeMn}}$ of the analyzed Pacific Ocean material, which has higher Mn/Fe ratios [37,38], more closely matches the experimental data on pure $\delta\text{-MnO}_2$. The larger $\Delta^{97/95}\text{Mo}_{\text{SW-FeMn}}$ of the Atlantic material suggests that Fe oxyhydroxides (or potentially other adsorbents) have a larger α for Mo than $\delta\text{-MnO}_2$.

4.3. Implications for paleoredox research

Previously, we proposed that $\delta^{97/95}\text{Mo}$ of seawater ($\delta^{97/95}\text{Mo}_{\text{SW}}$) may vary as a function of ocean redox conditions, and that such variations might be tracked as variations of $\delta^{97/95}\text{Mo}$ in euxinic sediments, such as black shales [1]. Siebert et al. [2] have made similar suggestions with respect to ferromanganese crusts. How do the findings of this study affect such potential applications?

The mass balance of Mo in the ocean system is approximated by:

$$\delta^{97/95}\text{Mo}_{\text{in}} = f_{\text{oxic}} \times \delta^{97/95}\text{Mo}_{\text{oxic}} + f_{\text{euxinic}} \times \delta^{97/95}\text{Mo}_{\text{euxinic}} \quad (1)$$

where $\delta^{97/95}\text{Mo}_{\text{in}}$, $\delta^{97/95}\text{Mo}_{\text{oxic}}$ and $\delta^{97/95}\text{Mo}_{\text{euxinic}}$ are the isotopic compositions of Mo entering the oceans from riverine and hydrothermal sources, and exiting via removal to oxic and euxinic sediments, respectively. f_{oxic} and f_{euxinic} are the relative proportions of these sinks, where:

$$f_{\text{oxic}} + f_{\text{euxinic}} = 1 \quad (2)$$

This model is not strictly correct because some Mo removal also occurs in environments of intermediate redox state, such as subsurface marine sediments where Mo isotopes may also fractionate [3]. The role of these suboxic sediments in the Mo ocean budget is poorly quantified (Emerson, personal communication). However, unless such settings have a much greater importance in the Mo ocean budget than presently recognized ([5]; Emerson, personal communication), they seem unlikely to exert a major influence on the isotopic composition of Mo in seawater.

Eqs. 1 and 2 may be re-arranged to yield:

$$f_{\text{euxinic}} = \frac{\delta^{97/95}\text{Mo}_{\text{oxic}} - \delta^{97/95}\text{Mo}_{\text{in}}}{\delta^{97/95}\text{Mo}_{\text{oxic}} - \delta^{97/95}\text{Mo}_{\text{euxinic}}} \quad (3)$$

Barling et al. [1] observed that $\delta^{97/95}\text{Mo}_{\text{euxinic}} \approx \delta^{97/95}\text{Mo}_{\text{SW}}$. Other studies have found similar results (Nägler, personal communication; [2]); although they observed greater variation in $\delta^{97/95}\text{Mo}_{\text{euxinic}}$, the most Mo-enriched carbona-

ceous sediments approached the seawater value. Hence:

$$f_{\text{euxinic}} = \frac{\delta^{97/95}\text{Mo}_{\text{oxic}} - \delta^{97/95}\text{Mo}_{\text{in}}}{\delta^{97/95}\text{Mo}_{\text{oxic}} - \delta^{97/95}\text{Mo}_{\text{SW}}} \quad (4)$$

The uniform $\delta^{97/95}\text{Mo}_{\text{SW}}$ observed by Siebert et al. [2] together with the likelihood that removal of Mo to oxic sediments is dominated by interaction with hydrogenous Mn oxyhydroxides suggests that $\delta^{97/95}\text{Mo}_{\text{SW}} - \delta^{97/95}\text{Mo}_{\text{oxic}} = \Delta^{97/95}\text{Mo}_{\text{SW-oxic}} \approx \Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$. Since $\Delta^{97/95}\text{Mo}_{\text{soln-MnOx}}$ is apparently governed by an equilibrium isotope exchange process, it is reasonable to presume that this fractionation will be roughly constant through space and time.

We therefore modify Eq. 4 as follows:

$$f_{\text{euxinic}} = \frac{\delta^{97/95}\text{Mo}_{\text{oxic}} - \delta^{97/95}\text{Mo}_{\text{in}}}{-\Delta^{97/95}\text{Mo}_{\text{SW-oxic}}} \quad (5)$$

This equation demonstrates that variations in f_{euxinic} (and hence f_{oxic}) may be correlated with variations in $\delta^{97/95}\text{Mo}_{\text{oxic}}$ and $\delta^{97/95}\text{Mo}_{\text{euxinic}}$. If $\delta^{97/95}\text{Mo}_{\text{in}}$ and $\Delta^{97/95}\text{Mo}_{\text{SW-oxic}}$ do not vary significantly with time, a quantitative relationship is straightforward. Although such a simple relationship is unlikely to hold in detail, these equations provide a general outline for the possible use of sedimentary Mo isotope variations to track changes in regional or global ocean redox on time scales greater than the $\sim 800\,000$ yr Mo ocean residence time.

It will be particularly important to assess the fidelity of the sedimentary Mo isotope record because equilibrium isotope exchange between dissolved and surface-bound Mo raises the possibility of exchange between Mo bound to sedimentary marine Mn oxyhydroxides and Mo in seawater or co-existing pore fluids. This process will only alter the ocean Mo isotope mass balance if the concentration of Mo in the fluid is high and if a significant volume of such fluids escape. However, such a diagenetic process could alter sedimentary records of $\delta^{97/95}\text{Mo}_{\text{oxic}}$. The possibility of Mo isotope fractionation in porewaters heightens this concern [3]. Further research is needed to assess the extent of Mo isotope exchange in natural systems as a function of diagenesis.

5. Conclusions

The results of this experimental study confirm the hypothesis that Mo isotopes are fractionated during adsorption to Mn oxyhydroxides, and provide evidence that the adsorption of Mo by Mn oxyhydroxides is a significant factor in the isotopic fractionation observed between Mo in seawater and Mo in ferromanganese nodules and crusts. Further laboratory work is needed to assess the effects of temperature and solution composition, and to examine fractionation during adsorption to other forms of Mn oxyhydroxide and other potential adsorbents (especially Fe oxyhydroxides).

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