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Molybdenum isotope records as a potential new proxy for paleoceanography

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Abstract

New high-precision isotope ratios of dissolved Mo in seawater from different ocean basins and depths show a homogeneous isotope composition ('mean ocean water $^{98}\text{Mo}/^{95}\text{Mo}$ ' (MOMO)), as expected from its long ocean residence time (800 kyr). This composition appears to have been constant for the past 60 Myr at a 1–3 Myr time resolution as indicated from thick sections of Fe–Mn crusts from the Atlantic and Pacific. These records yield a constant offset from MOMO (average of -3.1 and -2.9%). They are similar to our new data on recent oxic Mo sinks: pelagic sediments and six Fe–Mn crust surface layers range from -2.7 to -2.9% and -2.7 to -3.1% , respectively. Recent suboxic Mo sinks from open ocean basins display heavier and more variable isotope ratios (-0.7 to -1.6% relative to MOMO). Crustal Mo sources were characterized by measuring two granites (and a mild acid leach of one granite), seven volcanic rocks and two clastic sediments. All show a narrow range of compositions (-2.0 to -2.3%). These data indicate that isotope fractionation by chemical weathering and magmatic processes is insignificant on a global scale. They therefore represent good estimates of the composition of dissolved Mo input to the oceans and that of the average continental crust. Thus, the Mo input into the oceans appears to be distributed into lighter oxic sinks and heavier reducing sinks. This is consistent with steady-state conditions in the modern ocean. The constant isotope offset between oxic sediments and seawater suggests that the relative amounts of oxic and reducing Mo removal fluxes have not varied by more than 10% over the last 60 Myr. An equilibrium fractionation process is proposed assuming that Mo isotope fractionation occurs between (dominant) MoO_4^{2-} and (minor) $\text{Mo}(\text{OH})_6$ species in solution, of which the latter is preferentially scavenged.

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1. Introduction

Recently a number of new stable isotope systems have been investigated thanks to the advent of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Cu, Zn, Fe, Mo, e.g.

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[1–4]). The applicability of these systems to geological, environmental and biological questions requires definitions of their principal reservoirs and identification of the biochemical and geochemical processes responsible for fractionation of their isotopes. The general geochemistry of molybdenum is widely discussed in the literature (e.g. [5–10]), as it is a redox-sensitive trace metal and essential in many biological processes. Isotope fractionation of Mo by anion exchange chromatography in the laboratory has been reported [2,3], as has Mo isotope fractionation in nature [3,11,12]. The study of [12] presents the first report of natural mass-dependent Mo isotope fractionation between ocean water, Fe–Mn crusts and black shales. Mo exists in the oceans mainly in the form of the tetrahedral molybdate ion (MoO_4^{2-}) which has a high chemical inertness (e.g. [13,14]) and solubility. Consequently, Mo is a conservative trace element in the oceans with a long residence time (800 kyr; e.g. [6,8]). The oceans represent a significant Mo reservoir ($\sim 1.5 \times 10^{16}$ g), although it is small compared to the continental crust ($\sim 2 \times 10^{19}$ g). The main dissolved Mo input into the oceans is molybdate formed by weathering followed by riverine transport. Low-temperature hydrothermal input of Mo to the oceans is about 10% of the riverine input [15].

After the initial demonstration of natural Mo isotope fractionation [3,12], we proceed to explore the ocean-chemical and paleoceanographic potential of Mo. The aim of this study is threefold. First, the Mo isotope data base is expanded to include a variety of ocean water samples, Fe–Mn crusts, various types of sediments and igneous rock samples. With these data we aim to contribute to a more complete understanding of the geochemical Mo cycle and Mo reservoirs. Second, a record of Mo isotopes over the past 60 Myr was measured in hydrogenous Fe–Mn crusts to test the validity of steady-state assumptions for the oceanic Mo cycle. Third, a working hypothesis is presented to explain the observed Mo isotope fractionation. By way of synthesis, the implications for the use of Mo isotope data as a geochemical proxy for paleo-redox conditions in the oceans and basin characterization are discussed.

2. Analytical methods

A detailed description of the analytical techniques is given in [3], and only a brief summary is presented here. Molybdenum isotopic compositions were determined using a Nu instruments MC-ICP-MS. Instrumental and laboratory mass fractionation is resolved from natural mass-dependent fractionation by addition of a Mo double spike (^{100}Mo , ^{97}Mo) prior to chemical separation. With this technique, four Mo isotope ratios can be determined allowing an internal consistency check. For data presentation the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio is used. The external standard reproducibility is at or below 0.1‰ for the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio (2 S.D.).

Rock samples were spiked and then dissolved by HF–HNO₃ digestion. Water samples were evaporated and remaining salts were taken up in 2 M HCl and spiked. Fe–Mn crusts were spiked and then dissolved in 6 M HCl. All samples were purified using the chemistry described in [3].

3. Results

3.1. Recent Mo reservoirs

3.1.1. Seawater

Water samples from the Atlantic ($n=3$, 0–2400 m depth), the Pacific and the Indian oceans (deep water) were analyzed to constrain the Mo isotope composition of ocean water. Molybdenum concentrations are 0.011 ppm for all samples (Table 1). The samples yield a uniform isotope composition (Fig. 1) as expected from the long residence time of Mo in the oceans. Ocean water has the second heaviest Mo isotopic composition measured to date ($+2.3 \pm 0.1$ (2 S.D.)‰) on the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio relative to our Johnson Matthey ICP standard solution, lot 602332B). The heaviest isotope compositions were measured in pore water samples and are presented in [15]. In view of the homogeneous ocean water ratios and the persisting lack of an internationally agreed reference standard material, mean ocean Mo (MOMO) is used as reference from here on ($\delta^{98/95}\text{Mo} = [\delta^{98/95}\text{Mo}_{\text{sample}} / \delta^{98/95}\text{Mo}_{\text{MOMO}} - 1] \times 10^3$). All delta values presented are given in

Table 1
Data compilation for ferromanganese crusts and ocean water samples

Sample, depth (m)	Cruise	Latitude	Longitude	Ocean	Age (Myr)	Mo ^a (ppm)	$\delta^{98/95}\text{Mo}_{\text{Std.}}^{\text{a}}$	$\delta^{98/95}\text{Mo}_{\text{MOMO}}^{\text{a}}$
Fe–Mn crusts (profile)								
BM 1969.05 ^b 1800 m	118	39°00'N	60°57'W	Atlantic	1	7	−0.6	−2.9
					4	488	−0.5	−2.8
					5	506	−0.6	−2.9
					7	276	−0.9	−3.2
					8	260	−1.0	−3.3
					12	231	−0.8	−3.1
					15	322	−0.9	−3.2
					17	289	−1.0	−3.3
					27	316	−0.9	−3.2
					34	288	−0.9	−3.2
					48	318	−0.9	−3.2
					52	186	−0.9	−3.2
					56	94	−0.8	−3.1
					62	400	−0.7	−3.0
					237KD ^b 4830 m	VA 13/2	09°25'N	146°03'W
1	585	−0.6	−2.9					
3	579	−0.7	−3.0					
4	621	−0.6	−2.9					
6	568	−0.6	−2.9					
7	559	−0.6	−2.9					
8	646	−0.6	−2.9					
10	604	−0.6	−2.9					
15	764	−0.6	−2.9					
21	857	−0.6	−2.9					
25	866	−0.6	−2.9					
31	902	−0.7	−3.0					
38	835	−0.7	−3.0					
43	509	−0.7	−3.0					
49	563	−0.7	−3.0					
55	809	−0.6	−2.9					
60	435	−0.7	−3.0					
Fe–Mn crusts (surface)								
44 8KD, 2615 m	SO-67-1	10°15'S	161°26'W	Pacific	recent	459	−0.7	−3.0
31 22KD, 2350 m	SO-79	6°33'S	90°44'W	Pacific	recent	277	−0.5	−2.8
51 113D-D, 4513 m	DODO	23°16'S	74°59'E	Indian	recent	496	−0.7	−3.0
50 145D-C, 2700 m	Antipode	7°20'S	57°56'E	Indian	recent	296	−0.6	−2.9
63 43 DS, 1970 m	SO-84	15°08'S	8°21'W	Atlantic	recent	239	−0.8	−3.1
1965.0.35, 878 m	Atlantis II	30°59N	78°14'W	Atlantic	recent	307	−0.7	−3.0
Ocean Water								
IAPSO, Standard				Atlantic		0.011	2.3	0.0
CTD-24,				Indian		0.011	2.3	0.0
CTD-52, 1600 m				Pacific		0.011	2.4	0.1
ARI-1, Coast				Atlantic		0.011	2.3	0.0
Lab. FvB, 2400–3000 m				Labrador Sea		0.011	2.5	0.2

^a Analytical procedures see [3], external standard reproducibility <0.1‰ (2 S.D.).

^b BM 1969.05: 1.62 mm/Myr [17], 10 mm; 237KD: 3.57 mm/Myr [18], 209 mm.

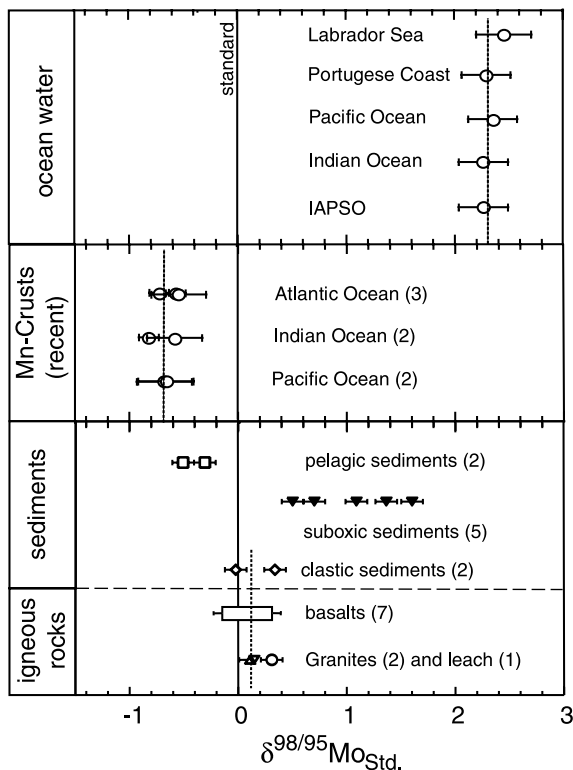


Fig. 1. Mo isotope data measured in recent natural samples. Ocean water has a homogeneous and heavy Mo isotope composition (mean ocean Mo: MOMO). Oxidic sediments (Fe–Mn crusts, pelagic sediments) show a remarkable and constant offset from ocean water and reducing sediments (see text for explanation). Igneous rocks and clastic sediments are isotopically very similar and probably represent typical crustal Mo input. This Mo input isotope composition can be balanced by the lighter oxidic and the heavier reducing Mo sink. Therefore, steady-state conditions can be assumed in the modern oceans.

permil. Tables 1 and 2 also give values relative to the Johnson Matthey ICP standard solution. We maintain this data reporting protocol until an international Mo standard becomes available for inter-laboratory comparison.

3.1.2. Igneous rocks

The igneous rocks studied define a narrow range of Mo isotope values (Table 2, Fig. 1). An Archean granite and a Tertiary granite from the Himalaya yield identical $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values of -2 ± 0.1 (2 S.D.). Subduction-related basalts

from Kamchatka [16] have similar $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ with a narrow range of -2.3 to -2 . A mild leach attack (24 h, cold 0.05 M HCl) of the above Himalayan granite released 63% of its total Mo content, with an isotope composition indistinguishable from that of the whole rock. This experiment was done using a powdered sample, which favored release of Mo.

3.1.3. Fe–Mn crust surface layers

Data on surface layers of hydrogenous ferromanganese crust from the Pacific ($n=3$), Atlantic ($n=3$), and Indian ($n=2$) oceans are listed in Table 1 and shown in Fig. 1. Molybdenum concentrations are variable, ranging between 277 ppm and 493 ppm. Isotope compositions are considerably lighter than that of ocean water, displaying a very narrow range of -2.7 to -3 $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ (Table 1).

3.1.4. Sediments

Pelagic sediments show Mo isotope compositions (-2.7 and -2.9 $\delta^{98/95}\text{Mo}_{\text{MOMO}}$) similar to ferromanganese crusts and concentrations in the range of 3.4 ppm and 185 ppm. In contrast, terrigenous clastic sediments have lower Mo concentrations of 1–3 ppm and heavier isotope compositions (-2.3 and -2 $\delta^{98/95}\text{Mo}_{\text{MOMO}}$). This is in the range of the magmatic rock data (Fig. 1). Leaching of a clastic sediment using the same approach as applied to the granite (see above) released only 1% of its Mo content. Reducing sediments from recent oceanic sedimentary basins have Mo concentrations ranging from 4 ppm to 130 ppm (Table 2) and a more variable Mo isotope composition ranging from -1.8 to -0.5 $\delta^{98/95}\text{Mo}_{\text{MOMO}}$. The samples are from the San Pedro and Santa Monica basins (low oxygen < 10 μM , high carbon flux ~ 2 $\mu\text{M m}^{-2} \text{day}^{-1}$) and from the Chile margin (bottom water oxygen of < 5 μM) (McManus, personal communication) (Table 2, Fig. 1).

3.2. 60 Myr Mo isotope history

Data from depth profiles through hydrogenous Fe–Mn crusts from the Pacific Ocean (237KD) and from the Atlantic Ocean (BM1969.05), both

representing a 60 Myr time series [17,18], are listed in Table 1 and shown in Figs. 2 and 3. Fe–Mn crust profiles are sampled at mostly 1–3 Myr resolution (Fig. 2 and Table 1), similar to the maximum time resolution given by the residence time of Mo in seawater (800 kyr). In both crusts Mo isotope compositions are uniform, within error, throughout the entire 60 Myr profile, although there is a slight difference between the Atlantic and the Pacific samples (mean values of -2.9 ± 0.1 and -3.1 ± 0.1 (2 S.D.) $\delta^{98/95}\text{Mo}_{\text{MOMO}}$, respectively, Table 1, Fig. 2). This offset was tested and confirmed by alternately measuring four samples from each crust within one analytical session. It is a significant, albeit small difference compared to the large fractionation relative to seawater, and one tentative explanation will be given in Section 4.3.

In contrast to the isotope compositions that are virtually constant with time, large variations were found for Mo concentrations of the Fe–Mn

crusts. These range from 400 ppm to 900 ppm in the Pacific sample and from 100 to 500 ppm in the Atlantic (Fig. 3). Steep gradients of up to 400 ppm per 5 Myr (Fig. 3), i.e. $> 80 \text{ ppm mm}^{-1}$, are observed. These concentration variations and gradients do not correspond between the two crusts, and therefore they most probably reflect variable Mo incorporation into the Fe–Mn crust rather than secular Mo concentration changes in ocean water.

It is important to assess the possibility that the apparent uniformity of the Mo isotope ratios in the crust profiles is a result of homogenization by diffusion. From ($^{234}\text{U}/^{238}\text{U}$) profiles Henderson and Burton [19] have found effective diffusion coefficients for U in Fe–Mn crusts ($D_{\text{eff}}^{\text{U}}$) to be between $\sim 5 \times 10^{-8}$ and $\sim 10^{-6} \text{ cm}^2 \text{ yr}^{-1}$. These authors argue that such diffusion occurs essentially via pore water in the slightly porous medium, and suggest that $D_{\text{eff}}^{\text{X}}$ for a trace element X in Fe–Mn crusts is approximately inversely pro-

Table 2
Data compilation for bulk rock samples and sediments

Sample	Description	Mo ^a (ppm)	$\delta^{98/95}\text{Mo}_{\text{Std.}}^{\text{a}}$	$\delta^{98/95}\text{Mo}_{\text{MOMO}}^{\text{a}}$
Pelagic clays (Quaternary)				
53-45-2	11°44'N, 138°22.2'W	3.4	−0.30	−2.6
48-19-17	08°16.5'N, 151°07.3'W	185.0	−0.50	−2.8
Subduction volcanics				
KOM-96-6	Kamchatka	0.7	−0.09	−2.4
KLU-96-11	Kamchatka	0.7	0.25	−2.1
ICH-96-05	Kamchatka	1.4	0.00	−2.3
KOM-96-02/2	Kamchatka	0.8	0.19	−2.1
KLU-96-14	Kamchatka	0.8	0.02	−2.3
ICH-96-02	Kamchatka	1.2	0.02	−2.3
Granites				
99/112	Archean (South Africa)			
103B (bulk)	Himalaya	19.1	0.14	−2.2
103B (leach)	Himalaya	12.1	0.10	−2.2
Suboxic sediments				
Teflon94 SP2 25	San Pedro Basin	4.0	0.72	−1.6
Teflon94 SP2 1	San Pedro Basin	3.4	0.52	−1.8
Teflon 8B-17	Santa Monica Basin	4.9	1.11	−1.2
RR97 82 MC A15	Chile margin	131.9	1.39	−0.9
RR97 80 MC03 A10	Chile margin	40.8	1.62	−0.7
Clastic sediments				
GUA-4	Spain	1.2	0.36	−1.9
FON-1	Spain	2.7	0.00	−2.3
GUA-4 (leach)		0.01		
FON-1 (leach)		0.01		

^a Analytical procedures see [3], external standard reproducibility $< 0.1\%$ (2 S.D.).

portional to K_c^X , the ratio of its concentrations in the crust to that in seawater. $K_c^{Mo} \approx 30\,000$, roughly an order of magnitude greater than K_c^U . Therefore, $10^{-7} \text{ cm}^2 \text{ yr}^{-1}$ is a reasonable estimate for an upper limit for D_{eff}^{Mo} . A useful parameter to assess potential smoothing of an isotope ratio profile in a Fe–Mn crust is the ‘half-preservation time’ of an isotope anomaly representative of a layer within the crust. This ‘half-preservation time’ is proportional to the square of the thickness of the layer. Given a value of $10^{-7} \text{ cm}^2 \text{ yr}^{-1}$ for D_{eff}^{Mo} , the magnitude of a Mo isotope anomaly in a 1 mm thick layer would be halved in ~ 6 Myr. Similarly, half the amplitude of an anomaly in the oldest portion of the crust (60 Ma) would be preserved if it represented a ~ 3 mm thick layer. Therefore, because the spacing of our sampling throughout most of the profiles exceeds the smoothing length, it can be assumed that Mo isotope variations would still be visible, even if somewhat attenuated (Fig. 2). In addition, modern seawater percolating through the crust after its formation would have a Mo isotope composition that is 3‰ heavier than the crust itself. We are aware of the fact that a perturbation of the initial

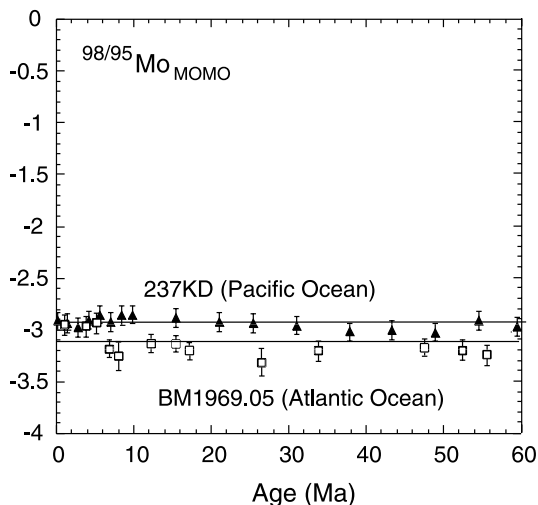


Fig. 2. Mo isotope time series from thick sections of Fe–Mn crusts (237KD, Pacific and BM1969.05, Atlantic). The offset to light Mo isotope compositions relative to ocean water in the Fe–Mn crust is constant for the last 60 Myr, indicating that the ratio of oxic to reducing Mo removal fluxes in the oceans was similar on a global scale over the last 60 Myr.

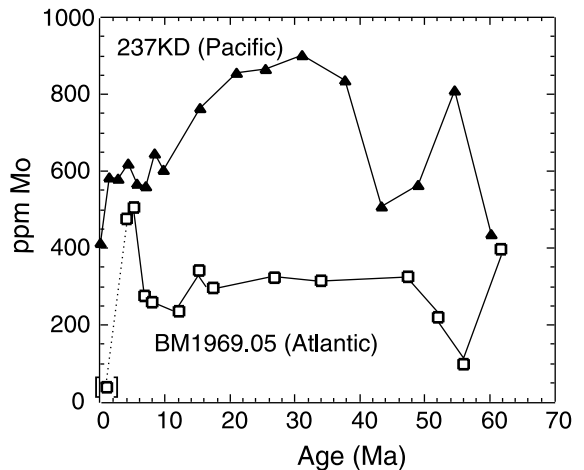


Fig. 3. Mo concentration profiles from thick sections of Fe–Mn crusts (237KD and BM1969.05).

isotope distribution by diffusion might still be a possibility. However, for the reasons discussed above, we consider it unlikely that the observed constancy of the Mo isotope compositions has resulted entirely from smoothing and below we discuss the Mo isotope ratios in terms of a real secular invariance.

4. Discussion

4.1. Mo sources

A first important observation is that ocean water has a much heavier Mo isotope composition than any source of Mo recognized so far. The significant amount leached from igneous rocks (ca. 60% of total Mo with 0.05 M HCl) points to highly effective mobilization of Mo during weathering, erosion and sediment transport under oxidizing surface conditions. Clearly, a mild acid leach is no accurate reproduction of natural weathering processes. Yet the large fraction of Mo available for release upon weathering results in released isotope compositions identical to the source rock. The fact that various igneous rocks, the granite leach experiments and detrital sediments are isotopically very similar suggests that the net effect of weathering, erosion and transport on Mo isotope fractionation is likely to be close

to zero. Mo isotope fractionation during ground-water/riverine and estuarine transport may affect Mo isotope compositions on a local scale, but apparently does not influence the $\delta^{98/85}\text{Mo}$ value of the bulk input into the oceans. Admixture of Mo derived from extensive weathering of black shales may locally increase this value somewhat. This effect can be significant for the Os isotope composition of ocean water, because of the short residence time of Os in the oceans and the vastly more radiogenic isotope composition of Os in black shales compared to crustal rocks [20,21]. In the case of Mo, the same mass balance as discussed by the above authors would not yield a significant shift in isotope compositions on a larger scale as the difference in Mo isotope compositions is much less pronounced and Mo has a long residence time in the oceans. The input data presented here also agree with the Mo input isotope composition calculated by [12] for steady-state conditions in the modern oceans. Low-temperature hydrothermal input of Mo to the oceans contributes about 10% of the total dissolved Mo to the oceans [15]. Like Mo from suboxic sediments, low-temperature hydrothermal Mo has an isotope composition intermediate between crustal rocks and ocean water [15].

Although more data are clearly needed to evaluate the influence of various inputs, it appears reasonable to assume that the average isotope composition of Mo input into the oceans is close to that of the common igneous rocks and clastic sediments analyzed, i.e. $\delta^{98/95}\text{Mo}_{\text{input(MOMO)}} \approx -2$ (see Table 2, Fig. 1).

Moreover, as there appears to be no net Mo fractionation associated with continental input, and also hydrothermal input is a minor component, the fractionation leading to the heavy Mo isotope composition of ocean water must be sought in processes associated with Mo removal.

4.2. Mo sinks

Sinks analyzed in this study include Fe–Mn crusts, pelagic and suboxic sediments. The largest offset from ocean water is found in Fe–Mn crusts, which are about 3‰ lighter than seawater (see also [12,22]). Whereas these hydrogenous compo-

nents are important for reconstructing paleoceanographic processes, it is not yet clear whether they are sufficiently large in mass to represent a significant Mo sink [8]. However, pelagic sediments can be an important sink for Mo and seem to bear a similarly light isotope composition (Table 2). Pelagic sediments are commonly enriched in trace metals and show a strong covariance of Mo and Mn [23–26]. Mo enrichment with respect to the detrital background (1–2 ppm) is thus most likely caused by association with ferromanganese oxides in the form of grain coatings or micronodules in those sediments. If Mo removal is associated with the formation of Fe–Mn oxyhydroxides, then a similar Mo isotope composition for pelagic sediments, Fe–Mn nodules and Fe–Mn crusts is to be expected. Regardless of the precise nature of the fractionation process, the persistent preferential removal of light Mo from the ocean naturally leads to the observed enrichment of residual heavy Mo isotopes in that reservoir.

Mo isotope data from open ocean suboxic sites (low-oxygen bottom water, no free H_2S [10]) presented here show a relatively large range of Mo isotope compositions (Table 2). Their $\delta^{98/95}\text{Mo}$ values are broadly correlated with their Mo concentrations. The sediments from the Chile margin, with the lowest bottom water oxygen level, show the highest Mo concentrations and $\delta^{98/95}\text{Mo}$ values. It appears that with increasing reducing conditions the efficiency of Mo scavenging also increases. Mass balance then requires that the isotope composition in the resulting sediment approaches that of ocean water (reservoir effect). It is probably valid to state that suboxic sediments commonly contain Mo that is heavier than the ocean input. Thus they represent a net heavy Mo sink relative to the Mo input isotope composition.

In addition, sediments from anoxic basins, defined here as containing free H_2S in bottom water (e.g. Black Sea, Cariaco Trench, Framvaren Fjord, Saanich Inlet), constitute an important sink for Mo. Mo scavenging under anoxic bottom water conditions with H_2S concentrations above ca. 100 μM [9,10] should be almost complete, due to the fast formation of thiomolybdates. There-

fore, the resulting sediments are expected to contain Mo with isotope compositions identical to or close to the bulk dissolved Mo. This has indeed been observed for samples from the Black Sea by [12]. In principle, this observation implies that the paleo-Mo isotope composition of the oceans can be determined by analyzing black shales as suggested by [12]. However, truly anoxic conditions often develop under unique conditions in restricted basins, and several complications have to be taken into consideration. An important feature of the Black Sea is the contribution of a significant proportion of Mo input by riverine transport. In the surface water of the Black Sea the freshwater input represents as much as 30%. If this freshwater input bears the typical crustal isotopic composition, as shown above ($\delta^{98/95}\text{Mo}_{\text{MOMO}} = -2.3$ to -1.9), this would result in a $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value of about -0.4 for Black Sea water. Therefore, resulting anoxic sediments formed with complete Mo scavenging under anoxic conditions might record Mo isotope compositions lighter than that of coeval open ocean water. The reliability of black shales as paleo-seawater proxies for Mo isotopes is thus influenced by the paleo-setting of the preserved rock and additional parameters that are hardly known to date, e.g. the relative proportion of riverine Mo flux to the basin.

4.3. Mass balance and steady state

For the discussion of mass balance and steady-state conditions in the oceans an important conclusion is that suboxic and anoxic sediments constitute a heavy Mo sink, relative to the Mo input, which could balance the light oxic sink.

Although open ocean reducing sites and anoxic basins represent only a relatively small area of the total oceans (i.e. continental margin upwelling zones, coastal bays and semi-enclosed bays), the Mo concentration in these sediments is well above the crustal background and their accumulation rate is generally much higher than that of pelagic sediments. Therefore, the Mo flux in such sediments provides a quantitative mass balance to the lighter oxic sinks and no further Mo sink is required [8,27].

The near-constant Mo isotope composition of Fe–Mn crusts over the last 60 Myr is striking. It is highly unlikely that a changing isotope fractionation exactly counteracted a changing ocean water Mo isotope composition. Therefore, this constancy indicates that the open ocean Mo isotope composition itself has remained near-constant from the early Tertiary to the present.

Two main parameters might potentially cause a shift of the Mo isotope compositions in ocean water that is preserved in a Fe–Mn crust record: the relative amount of oxic to anoxic removal fluxes in the oceans, or a rapid and large change in the Mo input flux.

4.3.1. Model 1: changes in Mo removal fluxes

In Fig. 4 the results of simple modelling of the effect of changing anoxic to oxic removal fluxes in the oceans are shown. The model assumes present-day steady-state conditions. Input parameters for model calculations include a constant mass flux of Mo to the oceans with a mean isotope composition of $\delta^{98/95}\text{Mo}_{\text{MOMO}} = -2.1$, an identical removal mass flux, and a constant oceanic Mo inventory. Further, ocean water is initially at $\delta^{98/95}\text{Mo}_{\text{MOMO}} = 0$, the oxic sink $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value is offset by -2.95 from ocean water and the anoxic sink has Mo identical to ocean water.

A first and important result from this model calculation is that the oxic fraction of total Mo removal fluxes in the modern oceans must be around 0.7 to maintain steady-state conditions (Fig. 4). This is within the range of sink fluxes published in [8], which show a wide variety of Mo fluxes into anoxic sinks. Assuming a mean Mo concentration of 8 ppm for oxic sediments [25] and 50 ppm for anoxic sediments [28], the corresponding oxic to anoxic sediment mass ratio is ca. 14. The second important observation is that any variation in the relative amounts of oxic to anoxic removal fluxes greater than 10% over the last 60 Myr should have resulted in a resolvable shift in ocean water $\delta^{98/95}\text{Mo}$. That is, the magnitude of this isotope shift as measured in a Fe–Mn crust time series would exceed analytical uncertainties (Fig. 4). Mo seawater isotope ratios would adjust to a new value within 2–3 Myr

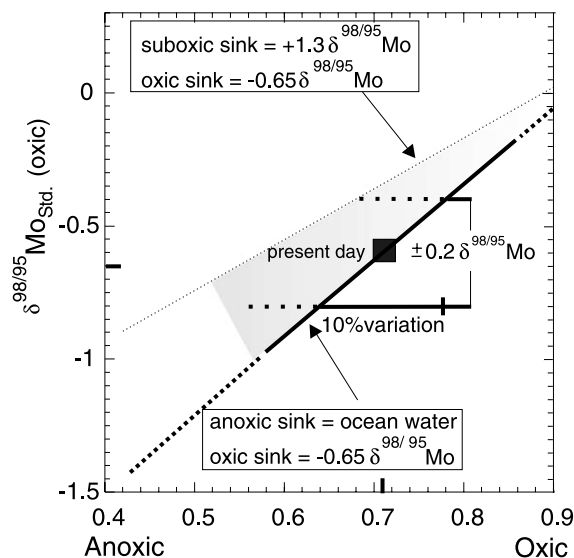


Fig. 4. Model 1: changing anoxic to oxic removal flux in the oceans under steady-state conditions. The oxic fraction of total Mo removal in the modern oceans must be around 0.7 to maintain steady-state conditions. Variations in the relative amount of oxic and reducing Mo removal flux greater than 10% should result in a shift in ocean water $\delta^{98/95}\text{Mo}$, detectable in the Fe–Mn crust time series. Shaded area: various mixtures of anoxic (ocean water Mo) to suboxic (lighter isotope compositions) fractionation result in a variety of slopes. A lighter suboxic sink results in less resolution for the detection of variations in the ratio of oxic to anoxic Mo fluxes.

after a hypothetical change in model conditions (curve 1 in Fig. 5). Therefore, at the given resolution of our Fe–Mn crust samples, the relative amounts of oxic to anoxic Mo removal fluxes can only have varied insignificantly (around 10%) over the past 10 Myr. The same conclusion roughly holds for the period from 60 Ma to 10 Ma permitting some extended variability given the lower time resolution for this period (Fig. 4).

A model calculation in which the $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ value of the reducing removal Mo flux is -1.3 (the mean value of suboxic open ocean reducing sites) yields a shallower slope of isotope compositions in Fig. 4. A variety of mixtures of anoxic to suboxic Mo isotope fractionation results in a variety of slopes (shaded area). Shallower slopes provide lower resolution for the detection of variations in the ratio of oxic to reducing Mo fluxes.

4.3.2. Model 2: changes in the Mo input flux

Because the continental source provides Mo different in isotope composition from seawater Mo, the effect of a change in the Mo flux into the oceans was also modeled. For this purpose, a constant ratio of oxic to anoxic sinks was maintained. The rate of change of the input flux strongly affects the resulting Mo isotope signal. We have examined a simple case to arrive at an assumption on the potential size and shape of the resulting signal. To generate a resolvable signal ($-0.2 \delta^{98/95}\text{Mo}$) in Fe–Mn crust time series, an instantaneous increase in the Mo input by a factor of 2 would be necessary. Unlike the shift caused by a change in the relative amounts of oxic and reducing sedimentation this signal would be transient, and ‘initial’ isotope compositions would be re-established in Fe–Mn crusts within 3–4 Myr.

Continental erosion has greatly increased over the last 10 Myr, as indicated by several indicators (e.g. [29,30]). Such a shift of the erosion flux

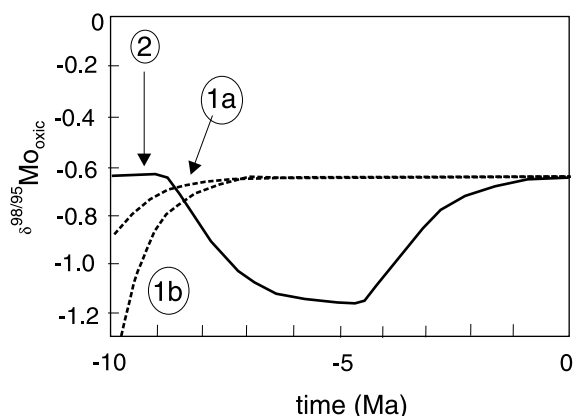


Fig. 5. Results of model calculations over time. Model 1: after a change in oxic to anoxic removal fluxes in the oceans, isotope ratios are adjusted to a new value within 2–3 Myr. (a) 10% shift modeled at 10 Ma before present, (b) 20% shift modeled at 10 Ma before present. Model 2: change in the magnitude of dissolved Mo flux into the oceans. A gradual eight-fold increase in Mo flux to the oceans would lead to a change in $\delta^{98/85}\text{Mo}$ of ca. -0.6‰ . In contrast to model 1, the resulting signal is transient, and ‘initial’ isotope compositions are re-established within 3–4 Myr. The constant offset of the $\delta^{98/95}\text{Mo}$ in Fe–Mn crust time series from modern ocean water sets limits for changes in Mo input, and the ratio of oxic to reducing sedimentation.

might also have resulted in an increase in dissolved Mo flux. For example, an instantaneous eight-fold increase in dissolved Mo input flux leads to a $\delta^{98/95}\text{Mo}$ offset of -1 in the oxic output, which would be readjusted after 4 Myr. A gradual eight-fold increase occurring over 5 Myr [30] would cause a transient Mo isotope offset of -0.6 $\delta^{98/85}\text{Mo}$ (curve 2 in Fig. 5). This is not observed in our Fe–Mn crust profiles. However, a gradual increase over 10 Myr would not be resolvable in the Mo isotope record. The apparent contradiction between an observed rapid erosion increase and the Mo isotope record remains a problem.

Thus the constant offset of the $\delta^{98/95}\text{Mo}$ in Fe–Mn crust time series from modern ocean water sets limits for both the changes in dissolved Mo input due to enhanced erosion, and the ratio of oxic to reducing sedimentation. A more detailed quantification of these effects is limited by the possibility that both types of change might occur concurrently.

4.4. Working hypothesis for a process of equilibrium Mo fractionation under oxic conditions

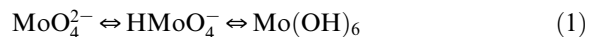
Any realistic model of Mo behavior in oxic oceanic sedimentation must provide a consistent explanation for the following basic observations. (1) Chemical sediments are depleted in heavy Mo isotopes relative to seawater and continental source Mo. (2) Contrary to other stable and radiogenic isotope systems, this offset appears to be constant through the past 60 Myr at the resolution given here. (2a) This Mo isotope offset is independent of Mo concentrations. (3) A similar large offset is absent in reducing sediments.

The question of whether the Mo isotope offset between oxic sediments and ocean water resulted from a kinetic or an equilibrium fractionation process was left open by [12]. The authors noted that at first sight kinetic fractionation during Mo scavenging might explain the light isotope composition observed in Fe–Mn crusts. For the case of Fe isotope fractionation this problem is extensively discussed in the literature (e.g. [31,32]).

Here a hypothesis is presented that invokes an

equilibrium reaction between two species of Mo in solution, of which one is predominantly scavenged. Because a chemical equilibrium reaction is involved, we regard a dominant isotope equilibrium fractionation as likely. However, fast pathways may also contribute kinetic effects.

While dominant, MoO_4^{2-} is not the only species of Mo^{6+} in the oceans. As discussed by [10], one of the most probable species of Mo in seawater to be scavenged is the octahedral $\text{Mo}(\text{OH})_6$ (molybdic acid) which is at least three orders of magnitude less abundant than MoO_4^{2-} . Being neutral, this molecule can also approach negatively charged surfaces. The axial Mo–OH bonds are weak [10,13], and once disrupted, the positive remainder of the molecule can be strongly adsorbed onto a negative surface (whether crust or colloid). This is due to the extreme field strength of Mo^{6+} . This process could be sufficient for quantitative adsorption, and no isotope fractionation is expected to occur on its adsorption. Instead, it is hypothesized here that the main fractionation occurs through the equilibrium reaction between dominant tetrahedral MoO_4^{2-} and minor octahedral $\text{Mo}(\text{OH})_6$ with the most probable reaction path [14]:



An equilibrium-dominated isotope fractionation is therefore assumed here. The Mo–O bonds of lighter isotopes are expected to be more easily disrupted due to their higher vibration energy, implying that $\text{Mo}(\text{OH})_6$ should be isotopically lighter than MoO_4^{2-} . The increase in the coordination number of Mo and the formation of weaker (more covalent) axial bonds make $\text{Mo}(\text{OH})_6$ the more reactive molecule. As a consequence, the more reactive, scavenged Mo is isotopically lighter than seawater as observed in Fe–Mn crusts. The concentration difference between MoO_4^{2-} and HMoO_4^- can be calculated after [33] as:

$$\log[\text{MoO}_4^{2-}]/[\text{HMoO}_4^-] = -\text{p}K + \text{pH} \quad (2)$$

where $-\text{p}K$ is 3.5 at ocean water pH of 8.1 resulting in a ratio of 40 000:1 for the two species. The

theoretical residence time of $\text{Mo}(\text{OH})_6$ would thus still be ca. 20 yr, long enough to allow chemical equilibration. Further, the above ratio can be decreased if particle reactivity plays a role in catalyzing the protonation of MoO_4^{2-} as recently suggested by [34]. As $\text{Mo}(\text{OH})_6$ is removed by adsorption and precipitation, Mo equilibrium in the water column will then readjust by moving reaction (1) to the right.

The working hypothesis presented above is capable of explaining the light isotope composition of Mo in the Fe–Mn crusts relative to ocean water. A further point that can be addressed is the slight but apparently consistent difference in Mo isotope composition between individual Fe–Mn crust samples. The ocean water isotope composition itself is uniform, as discussed above and as predicted by the long MoO_4^{2-} residence time. However, $\text{Mo}(\text{OH})_6$ with a much shorter apparent residence time might preserve any isotope variation superimposed or contained in the equilibrium isotope fractionation. Therefore, local differences in the degree of fractionation can be conserved. Although we will not speculate further here on possible factors affecting MoO_4^{2-} – $\text{Mo}(\text{OH})_6$ isotope fractionation, this mechanism could explain the differences observed.

4.5. Mo isotope fractionation under reducing conditions

A further issue to be addressed is the variable $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values of suboxic to anoxic sediments, which are intermediate between those of Fe–Mn crusts (and pelagic sediments) and MOMO itself. Under anoxic and sulfidic conditions, conversion of geochemically inert MoO_4^{2-} to particle-reactive thiomolybdates in aqueous solution or at mineral surfaces is a prerequisite for scavenging of Mo [10,31,35]. If the process of Mo scavenging and reduction is highly effective (i.e. there is sufficient H_2S), then the complete scavenging of Mo should lead to ocean water Mo isotope compositions as observed in black shales [12]. However, if not all Mo is scavenged, Mo isotope fractionation during formation of thiomolybdates may play a role.

Under open ocean reducing conditions (i.e.

scavenging from pore waters) a mixture of Mo derived from the formation of thiomolybdates and dissolution of Mn oxides might result in a lighter and more variable Mo isotope composition when compared to anoxic sediments. A reservoir effect may also play a role. This complication means that for reconstruction of paleo-anoxia a wider range of samples must be analyzed to enable assessment of generally higher or lower fractionation in the past.

5. Implications for the use of Mo isotope analysis

The 3‰ spread in $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values observed in the oceanic system offers a number of exciting potential applications. While Mo stable isotope geology is obviously still in its infancy, some speculations are put forward here. They concern, first, Phanerozoic basin analysis, second, tracing variations in reducing to oxic conditions in the oceans in Earth history, and third, the rise of atmospheric oxygen in the early Earth.

The heavy and uniform $^{98}\text{Mo}/^{95}\text{Mo}$ isotope signature of the oceans is, regardless of the actual fractionation mechanism, generated by the occurrence of isotope fractionation in an enormous body of water that is overwhelmingly oxygenated. Analyses of further water samples will show whether such a heavy Mo signature can be generated in more enclosed basins today or if the continental input dominates their $^{98}\text{Mo}/^{95}\text{Mo}$ ratio. High $\delta^{98/95}\text{Mo}_{\text{MOMO}}$ values in Black Sea sediments [12] may have been inherited from the open ocean, in that strong reductive Mo scavenging occurred in that basin, which might therefore ‘in toto’ have acted as a sink for oceanic Mo. If an Mo isotope composition different from the open ocean can be established to exist in modern semi-enclosed basins, then Mo isotopes become a diagnostic geological tool in basin analysis. Ideally, Mo isotopes are going to enable the identification of seawater exchange with the open ocean and a paleo-basin, i.e. the ratio of freshwater to ocean water Mo can be determined by analyzing organic- and Mo-rich shales.

Model calculations indicate that the proportion of oxic to reducing Mo removal flux in the mod-

ern oceans is about 7:3. The relatively constant Mo isotope compositions in Fe–Mn crust time series point to only small variations in this proportion over the last 60 Myr.

In pre-Cenozoic times, where no dated Fe–Mn crusts are available, bulk sediment Mo isotope compositions can potentially be used to study the same topic on a worldwide basis.

Further, following the working hypothesis presented here, the Mo fractionation observed is linked to the presence of oxidized dissolved Mo. Therefore, it is predicted that a significant fractionation of Mo relative to the average crust is absent in Archean sediments. It is thus likely that Mo isotopes will emerge as a further proxy to study the rise of atmospheric oxygen.

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