Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans

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How much dissolved O_2 was present in the mid-Proterozoic oceans between 1.8 and 1.0 billion years ago is debated vigorously. One model argues for oxygenation of the oceans soon after the initial rise of atmospheric O_2 ~ 2.3 billion years ago. Recent evidence for H_2S in some mid-Proterozoic marine basins suggests, however, that the deep ocean remained anoxic until much later. New Mo isotope data from modern and ancient sediments indicate expanded anoxia during the mid-Proterozoic compared to the present-day ocean. Consequently, oxygenation of the deep oceans may have lagged the atmosphere by over a billion years.

Understanding how and when the Earth's early atmosphere and oceans became rich in oxygen is essential to our understanding of early life on Earth and to the search for life beyond the Solar System (*1–3*). A large body of geochemical and sedimentological evidence points to a substantial rise in atmospheric oxygen ca. 2.3 billion years ago (Ga) (*4–6*). The history of ocean oxygenation is less clear. The occurrence of banded iron formations (BIFs) until ca. 1.8 Ga suggests deep oceans with high concentrations of ferrous iron until this time and therefore, because of the low solubilities of ferric oxides, little dissolved O_2 (*4*). The subsequent disappearance of BIFs may indicate the beginning of persistent deep-sea oxygenation, which continued with only brief interruptions to the present day (*4*). This model of ocean redox evolution is challenged by the recent proposal that euxinic (anoxic and sulfidic) conditions were common in the deep oceans from ca. 1.8 Ga to at least 1.0 Ga, after which atmospheric and deep-sea oxygen levels approached modern values (*7–9*). Euxinic conditions could also account for the disappearance of BIFs because of the low solubilities of ferrous sulfides (*8*). This debate has important implications for evolution linked to the availability of redox-sensitive, bioessential trace metals (*2*) and for climate, because the flux of biogenic methane from oceans to atmosphere is sensitive to ocean oxygenation (*10*, *11*).

Sulfur isotopes and sedimentary iron chemistry indicate that some mid-Proterozoic sedimentary basins were oxic at the surface and euxinic at depth (*9*, *12*, *13*). Sulfur isotope data further suggest that sulfate concentrations in mid-Proterozoic oceans were < 1/10th the modern value (*9*, *12–14*). However, low sulfate does not uniquely indicate anoxic or sulfidic oceans, and redox-stratified basins exist even today although > 99% of the oceans are oxygenated to the seafloor. Hence such data cannot directly address the extent of ocean anoxia.

Molybdenum stable isotopes may clarify this issue. Molybdenum enters the oceans largely via rivers. In oxygenated waters, Mo speciation is dominated by the molybdate anion (MoO_4^{2-}), which is so unreactive that Mo is the most abundant transition metal in modern oceans. However, under euxinic conditions, such as in the modern Black Sea where H_2S is > 100 µM in bottom waters, Mo is readily removed from solution (*15–18*). As a result, ocean sediments accumulating today beneath euxinic waters account for 10 - 50% of the annual removal flux of Mo from the oceans even though such waters cover an extremely small percentage of the modern seafloor (< 0.5%) (*15*, *18*, *19*). The remainder of marine Mo is primarily removed in association with sedimentary Mn oxides in oxygenated environments (*18*, *19*). It is not known if sediments accumulating under bottom waters with < 5 µM O_2 but lacking sulfide ("suboxic" sediments) constitute a net source or sink of Mo from the oceans (*18*, *20*), but they probably account for < 10% of Mo cycling today (*18*). The ocean Mo budget is therefore highly sensitive to the extent of euxinic bottom waters (*15*).

The marine Mo isotope budget also appears to be redox-sensitive. In previous studies (table S1, Fig. 1A), values for $\delta^{97/95}$Mo in granite, basalt and continental molybdenite ores were found to be –0.03 +/- 0.23 ‰ (*21–24*). Molybdenum in Holocene euxinic Black Sea sediments is significantly heavier: values for $\delta^{97/95}$Mo are 1.52 +/- 0.23 in the surface-most microlaminated sediments (Unit I) and 1.14 +/- 0.08 in the underlying sapropel (Unit II) (*22*). In contrast, $\delta^{97/95}$Mo in Mn oxide sediments, represented by Atlantic and Pacific ferromanganese nodules (*22*) and ferromanganese crusts from

the Atlantic, Pacific and Indian oceans (23), is lighter: $\delta^{97/95}$Mo = -0.47 +/- 0.17 ‰.

New $\delta^{97/95}$Mo data are presented here for another sample from Black Sea Unit I and a suite of samples from the Cariaco Basin, Venezuela, which is second only to the Black Sea in its extent of modern anoxic-sulfidic water-column conditions (table S2) (25). Our $\delta^{97/95}$Mo data from Cariaco Basin sediments are similar to earlier measurements of euxinic sediments (tables S1 and S2), and new data for Black Sea Unit I are identical within error to previous measurements (tables S1 and S2). Collectively, $\delta^{97/95}$Mo averages 1.25 ± 0.37 ‰ in Holocene euxinic sediments, in contrast to -0.47 ± 0.17 ‰ in Mn oxide sediments. The nearly 2 ‰ offset between the average values of these redox end members encompasses almost the full range of $\delta^{97/95}$Mo variation measured to date.

Molybdenum in both euxinic and Mn oxide sediments is largely hydrogenous. The isotopic offset between these sediment types suggests that Mo entering the ocean from continental sources is isotopically fractionated during removal into one or both of these major sedimentary sinks (22, 23). As a result, the two sediment types have complementary isotopic compositions—one heavy and the other light, relative to the input (22, 23, 26, 27) (Fig. 2).

If the isotopic compositions presented here are representative of the major Mo sources and sinks (28), then to a first approximation the global ocean Mo isotope budget can be expressed in terms of an input of ~ 0 ‰ and outputs to oxic and euxinic sinks with isotopic compositions of ~ - 0.5 ‰ and 1.3 ‰, respectively (Fig. 2A). To test this hypothesis, consider the following simple steady-state mass balance model:

$$\delta^{97/95}\text{Mo}_{input} = \left(f_{ox} * \delta^{97/95}\text{Mo}_{ox}\right) + \left(f_{eux} * \delta^{97/95}\text{Mo}_{eux}\right), \quad (1)$$

where the subscripts input, ox and eux denote the riverine input and oxic and euxinic sedimentary sinks, respectively, and f_{ox} and f_{eux} represent the fraction of total Mo removed to each sediment type. Using the mean values for $\delta^{97/95}$Mo$_{ox}$ and $\delta^{97/95}$Mo$_{eux}$ and the range of literature estimates of f_{ox} and f_{eux} in the modern oceans (15, 18, 19), we can estimate the value of $\delta^{97/95}$Mo$_{input}$ needed to balance removal to oxic and euxinic sediments. Our predicted range for modern $\delta^{97/95}$Mo$_{input}$ matches well with measurements of Mo in crustal materials, used here as a proxy for riverine input (table S1; Fig. 1A) (22, 23). This agreement implies that these data provide a first-order representation of Mo sources to, and sinks from, the oceans (22, 23).

Mechanisms of Mo isotope fractionation in the ocean are best viewed in light of the $\delta^{97/95}$Mo value of seawater. The Mo isotope composition of seawater ($\delta^{97/95}$Mo$_{sw}$) is uniform with location and depth, with a present-day mean value of +1.56 ± 0.13 ‰ (table S1; Fig. 1A) (22, 23). This value is ~ 2 ‰ heavier than that of hydrogenous Mo associated with

sedimentary Mn oxides. Such uniformity is expected from the conservative behavior and ~ 800,000 year residence time of Mo in oxygenated oceans (18). Laboratory experiments document a fractionation factor, α, of 1.0018 ± 0.0005 between dissolved Mo and Mo adsorbed to Mn oxides ($\Delta_{dissolved-adsorbed} = \delta^{97/95}Mo_{dissolved}$ -$\delta^{97/95}$Mo$_{adsorbed} = 10^3 \cdot \ln(\alpha) \approx$ 1.8 ‰) (29). The similarity between experiments and observed $\delta^{97/95}$Mo$_{sw}$ - $\delta^{97/95}$Mo$_{ox}$ (Δ_{sw-ox}) and the importance of Mn oxides as a Mo sink indicate that preferential adsorption of light Mo isotopes to authigenic Mn oxides is the primary driver of Mo isotope fractionation in the modern ocean.

In contrast to the fractionation associated with Mn oxides, $\delta^{97/95}$Mo$_{sw}$ is within 0.3 ‰ of $\delta^{97/95}$Mo$_{eux}$, indicating relatively little net fractionation when Mo is removed from the water column and deposited with sediments in euxinic basins. This is most likely a consequence of mass balance: Mo removal from aqueous systems when [H$_2$S] > 100 µM is nearly quantitative, and a large fraction is removed even when [H$_2$S] is lower (16, 17, 30). Hence, the $\delta^{97/95}$Mo value of sediments accumulating under euxinic conditions should be similar to the $\delta^{97/95}$Mo of the Mo source to the immediately overlying waters, even if there are large instantaneous isotope effects during Mo removal to these sediments. Small (< ± 0.4 ‰) variations in the $\delta^{97/95}$Mo of Holocene euxinic sediments may result from local effects (22, 23) (see supporting online text). However, even relatively restricted basins like the modern Black Sea, where the mean residence time of the deep water is ~ 387 years, are well mixed with the open ocean because of the long residence time of oceanic Mo (31). Consequently, the similarity of $\delta^{97/95}$Mo$_{sw}$ and $\delta^{97/95}$Mo$_{eux}$ today is not surprising, and removal of Mo to euxinic sediments is unlikely to drive global-scale Mo isotope fractionation. Instead, $\delta^{97/95}$Mo$_{eux}$ should track the Mo isotope evolution of seawater and thus the balance between oxic and euxinic marine deposition over geologic time.

The preceding systematics provide a basis for using Mo isotopes in ancient euxinic sediments (i.e., black shales) to examine changing ocean redox conditions. If Mo isotope fractionation in the oceans results from an equilibrium isotope effect between dissolved and Mn oxide associated Mo (22, 23, 29), then $\Delta_{sw-ox} = \Delta_{dissolved-adsorbed} \approx$ 1.8 ‰. Additionally, because of the near quantitative removal of Mo in euxinic settings, it seems reasonable that $\delta^{97/95}$Mo$_{eux}$ approximates $\delta^{97/95}$Mo$_{sw}$, at least in settings similar to the Black Sea and Cariaco Basin. Using these relationships and assuming $f_{ox} + f_{eux} = 1$, Eqn. 1 can be modified to obtain:

$$\delta^{97/95}\text{Mo}_{eux} = \delta^{97/95}\text{Mo}_{input} + \Delta_{sw-ox} * f_{ox}, \quad (2)$$

Hence, changes in ocean redox, which affect the relative proportions of f_{eux} and f_{ox}, should result in changes in the isotopic composition of hydrogenous Mo in euxinic sediments. Although highly idealized, this model illustrates

that expanded euxinic or contracted oxic conditions relative to the modern oceans should shift $\delta^{97/95}Mo_{eux}$ toward $\delta^{97/95}Mo_{input}$.

To examine the question of mid-Proterozoic ocean redox, we measured $\delta^{97/95}Mo$ in black shales from the Roper Group (Velkerri Formation; ~1.4 Ga; [Mo] = 11 to 60 ppm) and the Tawallah Group (Wollogorang Formation; ~1.7 Ga; [Mo] = 42 to 52 ppm) in northern Australia. Both sample suites were obtained from drill cores and are exquisitely preserved. Specifically, they have experienced no oxidative weathering and little metamorphism or deformation (25, 32, 33). Therefore, it is expected that the primary $\delta^{97/95}Mo$ of these sediments should be well preserved.

Detailed chemostratigaphic studies of sulfur isotopes and sedimentary iron chemistry have been conducted for both formations (12, 13). Based on their ratios of highly reactive Fe to total Fe and the degrees to which reactive Fe has been pyritized, our samples come from those parts of the depositional basins showing euxinic character similar to that of the modern Black Sea (12, 13, 25, 34). By analogy to modern euxinic settings, Mo sequestration into these sediments was likely quantitative, or nearly so. Sulfur stable isotopes and sedimentary features strongly suggest that during accumulation of these sediments neither basin was isolated from the global ocean (12, 13). Hence, we can be confident that our $\delta^{97/95}Mo$ data are representative of the overlying Proterozoic water column and that this water column was in contact with the open ocean.

We find that the Mo isotope compositions of these mid-Proterozoic black shales have significantly lighter $\delta^{97/95}Mo$ values than modern equivalents (table S2; Fig. 1B). Specifically, the mean mid-Proterozoic value is 1.1 ‰ lighter than the modern Black Sea sediments, which are the most obvious modern analog, and are 0.7 ‰ lighter than the average of all Holocene euxinic sediments measured to date (Fig. 1A).

It is likely that $\delta^{97/95}Mo_{sw}$ was well mixed in the mid-Proterozoic ocean and that these data are globally representative. This assumption is supported by the fact that the concentration of Mo in mid-Proterozoic euxinic sediments, while low, is within the range of Phanerozoic equivalents (which vary over a factor of ~ 10). This comparison suggests a global ocean in which the Mo concentration was probably not more than an order of magnitude lower than today (35). Unless ocean mixing times were substantially slower than today, or Mo concentrations decreased by more than a factor of ~ 50, $\delta^{97/95}Mo_{sw}$ was likely well mixed.

It follows that the mid-Proterozoic global ocean Mo isotope budget was very different compared to the present day. Equation 2 indicates that f_{ox} accounted for ~ 30% of Mo removal during the mid-Proterozoic, versus ~ 75% today (36,

37) (Fig. 2). This value probably underestimates the extent to which mid-Proterozoic ocean redox differed from the modern oceans because Eqn. 2 ignores suboxic sedimentary environments. Considerable variation in Mo isotopes is observed in such sediments today (0.35 ‰ < $\delta^{97/95}Mo$ < 1.08 ‰) (23) (table S1). In a pore-water profile beneath suboxic waters, $\delta^{97/95}Mo$ in the interstitial waters is as much as 0.8 ‰ heavier than in seawater (20). If these data are broadly representative, this relationship indicates preferential removal of light Mo isotopes to sediments in such settings. The effect of such sediments on the Mo isotope budget is semi-quantitatively similar to that of Mn oxide sediments (38). Although suboxic settings are of secondary importance in the modern Mo budget, this may not have been the case in the mid-Proterozoic. It can be reasonably hypothesized that expanded suboxic conditions would have gone hand-in-hand with contraction of oxic seafloor and expanded euxinic deposition. Because oxic and suboxic removal fractionate Mo isotopes similarly, mass balance requires that an increase in the suboxic sink could only occur at the expense of the oxic sink. Thus, it is probable that f_{ox} was < 30%.

It is difficult to account for the Proterozoic data without invoking ocean redox arguments. If the balance between oxic and euxinic sinks were unchanged, then Eqn. 2 demands $\delta^{97/95}Mo_{input}$ was ~ - 0.8 ‰ during the mid-Proterozoic. Such $\delta^{97/95}Mo_{input}$ is substantially lighter than any known crustal materials (22, 23). Regional or local influences on $\delta^{97/95}Mo$ in the studied sediments, as might result from localized hydrothermal or riverine influences, are also unlikely but less easily dismissed (see supporting online text).

Molybdenum isotope data therefore point to redox conditions in mid-Proterozoic oceans that differed from those observed today. If we assume a linear scaling of f_{ox} and f_{eux} to the areal extent of oxic and euxinic seafloor, then the ratio f_{ox}/f_{eux} can be used to assess changes in the relative extents of such environments (39). The Mo isotope data indicate that f_{ox}/f_{eux} changed from < 0.4 in the mid-Proterozoic to ~ 3 today. Hence, the area of oxic sedimentation in the mid-Proterozoic oceans was nearly a factor of 10 smaller than the modern, or the area of euxinic sedimentation approached a factor of 10 larger than the modern. Most likely, an intermediate situation occurred involving both significant contraction of the extent of oxic deposition and expansion of the euxinic deep ocean (40).

Such conditions may have persisted until after 1 Ga, when S isotopes suggest an increase in ocean-atmosphere oxygenation (7, 8). Subsequently, ocean anoxia was generally confined to small areas of the seafloor. While episodic anoxic events occurred during the Phanerozoic, they probably did not approach the duration or areal extent of mid-Proterozoic oxygen deficiency. For example, intervals of expanded euxinic deposition were common during the Devonian, as

documented by extensive deposition of black shales on multiple continents (*41*). However, anoxic conditions were likely confined to shallow epicontinental seas, while the vast majority of the seafloor remained oxic (*41*). Consistent with this notion, $\delta^{97/95}$Mo in Devonian black shale is not as strongly shifted from modern seawater as are mid-Proterozoic shales (*22*) (table S1).

Further research is needed to relate $\delta^{97/95}$Mo variations quantitatively to ocean redox conditions. However, based on current understanding of Mo isotope systematics, it is inescapable that seafloor anoxia was expanded compared to today during at least two mid-Proterozoic intervals separated by ~ 300 million years. The $\delta^{97/95}$Mo data are consistent with globally extensive seafloor anoxia persisting after oxygenation of the atmosphere ~ 2.3 Ga. The identification of mid-Proterozoic Mn oxides with a $\delta^{97/95}$Mo value ~ 2 ‰ lighter than in coeval euxinic sediments would strengthen these arguments. Nevertheless, the full impact of nearly a billion years of ocean anoxia on Proterozoic ecosystems and biogeochemical cycles must be seriously considered.

References and Notes

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21. Data are reported using the δ notation, relative to a JMC Mo standard (Specpure lot # 702499I) where

$$\delta^{97/95}Mo = \left(\frac{^{97}Mo/^{95}Mo_{sample}}{^{97}Mo/^{95}Mo_{standard}} - 1 \right) * 1000.$$

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24. Values reported in text are the mean ± 2 standard deviations for all analysis of each sample grouping, unless otherwise noted.

25. Details of materials, methods and sample descriptions are available as supporting material on *Science* Online.

26. Molybdenite ores are assumed to consist of Mo extracted by hydrothermal processes from surrounding crustal rocks, and hence are rough proxy for crustal Mo.

27. Siebert *et al.* (*19*) found no Mo isotope fractionation during mild acid leaching of Mo from granite and basalt. Therefore it is reasonable to hypothesize that Mo released during crustal weathering is isotopically similar to Mo in granite, basalt and molybdenite.

28. Although ferromanganese crusts and nodules themselves are not major sinks for Mo, a correlation of Mo and Mn is observed in pelagic sediments (*19*). This presumably reflects coprecipitation of Mo with Mn oxides on the seafloor. Hence, $\delta^{97/95}$Mo in crusts and nodules is probably representative of $\delta^{97/95}$Mo in Mn-oxide-associated Mo.

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35. The use of basinal Mo concentrations to infer global ocean Mo concentrations is not straightforward, as evidenced by the nearly 10-fold difference in Mo concentrations between euxinic sediments in the Cariaco Basin and Black Sea. Local effects specific to the depositional setting presumably dominate. Hence, Mo concentrations in sediments cannot easily be used alone to draw inferences about global ocean redox conditions.

36. These figures are obtained using the following values: $\delta^{97/95}Mo_{in} = -0.03$; $\Delta_{sw-ox} = 1.8$; $\delta^{97/95}Mo_{eux} = 0.54$.

37. $\delta^{97/95}Mo_{eux}$ of the mid-Proterozoic samples ranges from 0.31 to 0.67 ‰, correspondingly the euxinic sink could range from 81 to 61 %.

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39. As an illustrative model, assume that $f_{ox} = k_{ox} \cdot A_{ox} \cdot [Mo]_{sw}$ and $f_{eux} = k_{eux} \cdot A_{eux} \cdot [Mo]_{sw}$, where $[Mo]_{sw}$ is the concentration of Mo in the oceans, A_{ox} and A_{eux} are the areas of oxic and euxinic sedimentation, and k_{ox} and k_{eux} are proportionality constants that parameterize the partitioning of Mo between water and sediment (i.e., these constants parameterize diffusion coefficients, sedimentation rates, chemical partition functions, etc.). Hence, $f_{ox}/f_{eux} = k_{ox}/k_{eux} \cdot A_{ox}/A_{eux}$. If k_{ox} and k_{eux} are constant, then variations in f_{ox}/f_{eux} can be directly related to variations in A_{ox}/A_{eux}. The assumption of constant k_{ox} and k_{eux} is simplistic, but useful for schematic purposes.

40. It is important to note that although $f_{ox} + f_{eux} = 1$, it is not necessarily the case that $A_{ox} + A_{eux} = $ constant. Hence a change in A_{ox} need not be complemented by a change in A_{eux} (and vice versa). This difference arises because change in A_{ox} or A_{eux} can be compensated by change in the areal extent of suboxic seafloor, whereas the Mo mass balance model assumes that suboxic sediments are a negligible sink for Mo.

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42. We thank Y. Shen, J. Brocks, A. H. Knoll and H. D. Holland for providing samples of Proterozoic black shales, and G. Ravizza for Black Sea samples. F. Ramos, G. Williams, and S. Weyer assisted with sample analysis. Supported by NSF (EAR 0106712 and 0230183) and NASA (Exobiology program and the Astrobiology Institute).
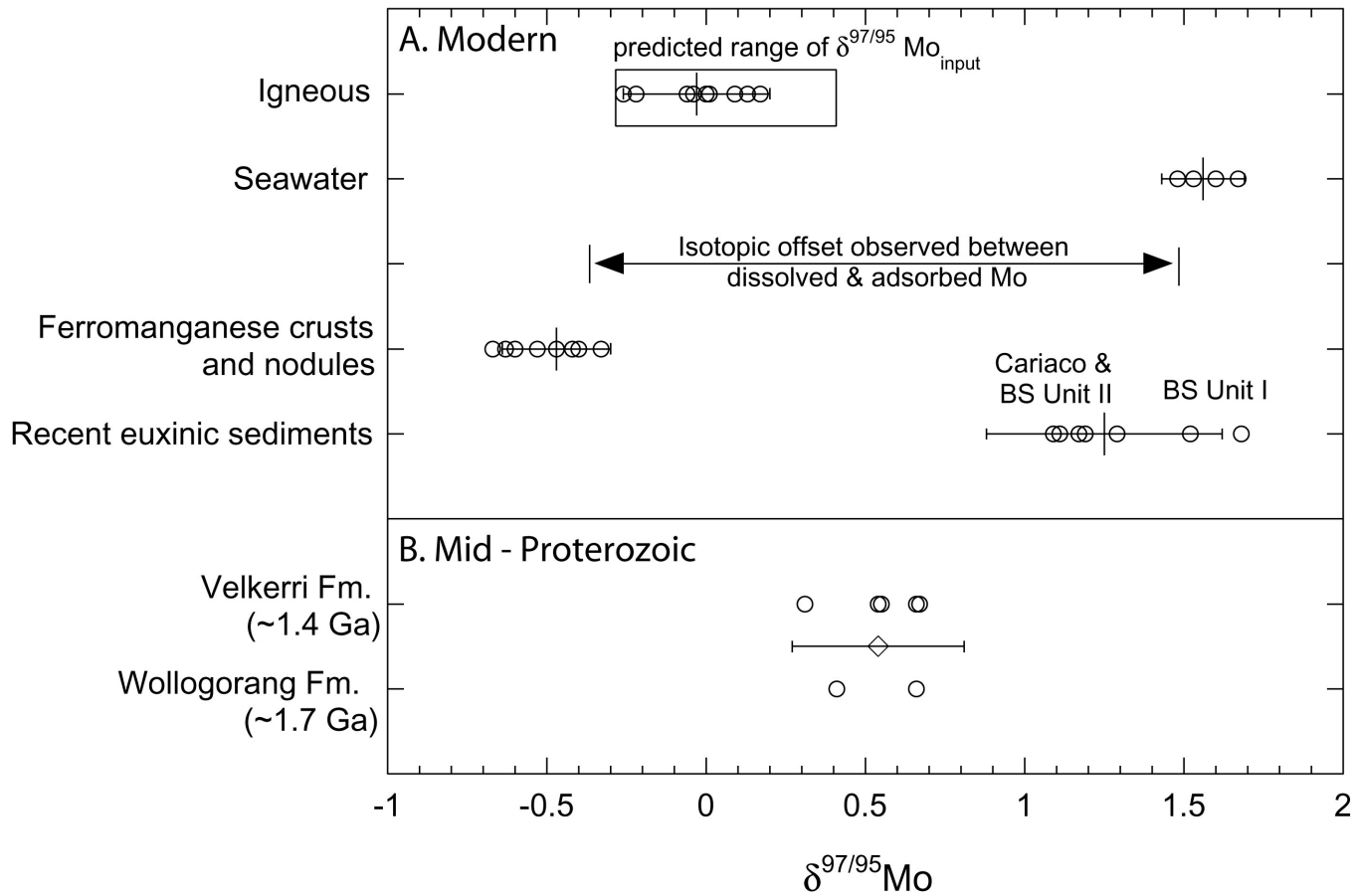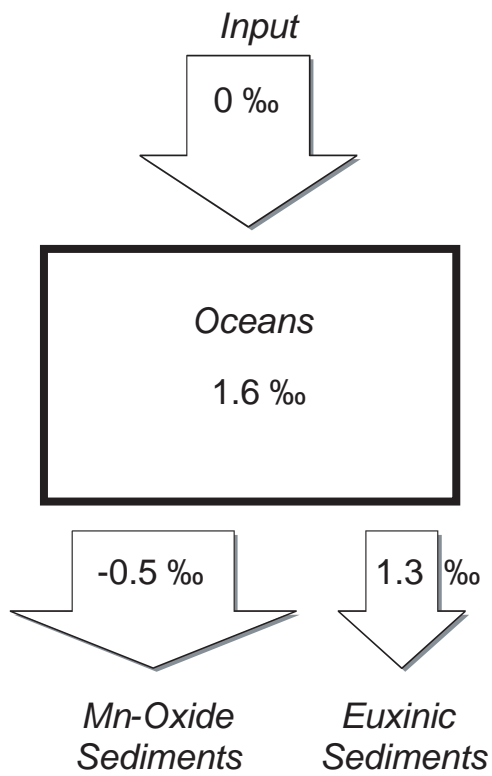
Supporting Online Material

Fig. 1. (**A** and **B**) Plot of $\delta^{97/95}Mo$ for all sample groups. Open circles represent the mean of replicate measurements for individual samples. Open diamond is the mean for all Proterozoic samples. Large vertical hash marks represent the mean of all samples for each sample group. Error bars on these means are $\pm 2\sigma$. Uncertainties of individual samples are listed in tables S1 and S2.

Fig. 2. Schematic depiction of Mo ocean isotope budget (**A**) today and (**B**) in the mid-Proterozoic, including average $\delta^{97/95}Mo$ values for reservoirs, as indicated. Widths of arrows depict proportions of Mo removed to each sediment type. Offset between oceans and Mn-oxides ($\Delta_{sw-ox} \approx 2$) is consistent with observations and laboratory experiments. Because of the possible importance of suboxic sediments to the Mo isotope budget in the mid-Proterozoic oceans, the proportion of Mo removed to Mn-oxides may have been smaller, and the proportion removed to euxinic sediments larger than indicated in (**B**).

A. Modern

Igneous

predicted range of $\delta^{97/95}$ Mo$_{input}$

Seawater

Isotopic offset observed between
dissolved & adsorbed Mo

Ferromanganese crusts
and nodules

Cariaco &
BS Unit II   BS Unit I

Recent euxinic sediments

B. Mid - Proterozoic

Velkerri Fm.
(~1.4 Ga)

Wollogorang Fm.
(~1.7 Ga)

$\delta^{97/95}$Mo

A. Modern

Input

0 ‰

Oceans

1.6 ‰

-0.5 ‰

1.3 ‰

Mn-Oxide Sediments

Euxinic Sediments

B. Mid-Proterozoic

Input

0 ‰

Oceans

0.8 ‰

-1.3 ‰

0.5 ‰

Mn-Oxide Sediments

Euxinic Sediments