

# Proterozoic ocean redox and biogeochemical stasis

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The partial pressure of oxygen in Earth's atmosphere has increased dramatically through time, and this increase is thought to have occurred in two rapid steps at both ends of the Proterozoic Eon (~2.5–0.543 Ga). However, the trajectory and mechanisms of Earth's oxygenation are still poorly constrained, and little is known regarding attendant changes in ocean ventilation and seafloor redox. We have a particularly poor understanding of ocean chemistry during the mid-Proterozoic (~1.8–0.8 Ga). Given the coupling between redox-sensitive trace element cycles and planktonic productivity, various models for mid-Proterozoic ocean chemistry imply different effects on the biogeochemical cycling of major and trace nutrients, with potential ecological constraints on emerging eukaryotic life. Here, we exploit the differing redox behavior of molybdenum and chromium to provide constraints on seafloor redox evolution by coupling a large database of sedimentary metal enrichments to a mass balance model that includes spatially variant metal burial rates. We find that the metal enrichment record implies a Proterozoic deep ocean characterized by pervasive anoxia relative to the Phanerozoic (at least ~30–40% of modern seafloor area) but a relatively small extent of euxinic (anoxic and sulfidic) seafloor (less than ~1–10% of modern seafloor area). Our model suggests that the oceanic Mo reservoir is extremely sensitive to perturbations in the extent of sulfidic seafloor and that the record of Mo and chromium enrichments through time is consistent with the possibility of a Mo–N colimited marine biosphere during many periods of Earth's history.

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The chemical composition of the oceans has changed dramatically with the oxidation of Earth's surface (1), and this process has profoundly influenced and been influenced by the evolutionary and ecological history of life (2). The early Earth was characterized by a reducing ocean-atmosphere system, whereas the Phanerozoic Eon (< 0.543 Ga) is known for a stably oxygenated biosphere conducive to the radiation of large, metabolically demanding animal body plans and the development of complex ecosystems (3). Although a rise in atmospheric O<sub>2</sub> is constrained to have occurred near the Archean–Proterozoic boundary (~2.4 Ga), the redox characteristics of surface environments during Earth's middle age (1.8–0.543 Ga) are less well known. The ocean was historically envisaged to have become ventilated at ~1.8 Ga based on the disappearance of economic iron deposits (banded iron formations; 2), but over the past decade it has been commonly assumed that the mid-Proterozoic Earth was home to a globally euxinic ocean, a model derived from theory (4) and supported by evidence for at least local sulfidic conditions in Proterozoic marine systems (5–8). However, the record of sedimentary molybdenum (Mo) enrichment through Earth's history has been interpreted to suggest that euxinia on a global scale was unlikely (9).

More recently, it has been proposed that the deep ocean remained anoxic until the close of the Proterozoic, but that euxinia was limited to marginal settings with high organic matter loading (10–13). In anoxic settings with low dissolved sulfide levels, ferrous iron will accumulate—thus these anoxic but nonsulfidic settings have been termed “ferruginous” (10). This model has also found

support in at least local evidence for ferruginous marine conditions during the mid-Proterozoic (12, 13). However, it has been notoriously difficult to estimate the extent of this redox state on a global scale, even in the much more recent ocean—largely because most of the ancient deep seafloor has been subducted.

In principle, trace metal enrichments in anoxic shales can record information about seafloor redox on a global scale. Following the establishment of pervasive oxidative weathering after the initial rise of atmospheric oxygen at ~2.4 Ga (14), the concentration of many redox-sensitive elements in the ocean has been primarily controlled by marine redox conditions. For example, in today's well-oxygenated oceans, Mo is the most abundant transition metal in seawater (~107 nM; ref. 15), despite its very low crustal abundance (~1–2 ppm; ref. 16). Under sulfidic marine conditions the burial fluxes of Mo exceed those in oxygenated settings by several orders of magnitude (17). Hence, it follows that when sulfidic conditions are more widespread than today, global seawater concentrations of Mo will be much lower. Because the enrichment of Mo in sulfidic shales scales with dissolved seawater Mo concentrations (18), Mo enrichments in marine shales (independently elucidated as being deposited under euxinic conditions with a strong connection to the open ocean) can be used to track the global extent of sulfidic conditions (9). Substantial Mo enrichment in an ancient euxinic marine shale, such as occurs in modern euxinic marine sediments, implies that sulfidic bottom waters represent a very small extent of the global seafloor.

In principle, a similar approach can be used with other metals such as Cr, which, importantly, will also be reduced and buried in sediments under anoxic conditions but without the requirement of free sulfide. Chromium is readily immobilized as (Fe,Cr)(OH)<sub>3</sub> under ferruginous conditions (19, 20) and will be reduced and rendered insoluble by reaction with a wide range of other reductants under sulfidic or even denitrifying conditions (21–23). Thus, comparing Mo enrichments in independently constrained euxinic shales and Cr enrichments in independently constrained anoxic shales can offer a unique and complementary perspective on the global redox landscape of the ocean.

A better understanding of the marine Mo cycle in Proterozoic oceans may also illuminate key controlling factors in biological evolution and ecosystem development during the emergence of eukaryotic life. The biogeochemical cycles of marine trace elements form a crucial link between the inorganic chemistry of seawater and the biological modulation of atmospheric composition. The availability of iron, for example, has been invoked as a primary control on local carbon export fluxes and atmospheric

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$p\text{CO}_2$  on glacial–interglacial timescales (24, 25). However, the leverage exerted by Fe on recent oceanic carbon fixation is most fundamentally driven by the sparing solubility of Fe in an ocean that is well-ventilated by an oxygen-rich atmosphere. By analogy, on a more reducing Earth surface Mo is likely to be a key colimiting trace nutrient given its importance in biological nitrogen fixation, assimilatory/dissimilatory nitrate reduction, and a number of other metabolically significant electron transfer processes (26–28).

To move forward in our understanding of Proterozoic redox evolution, we present a unique view of Cr and Mo enrichments in anoxic shales and a complementary modeling approach to interpret these data. From this vantage point, we present evidence that anoxic conditions were a globally important feature in the mid-Proterozoic ocean. In our analysis, we take anoxic environments to include those that are euxinic (anoxic and  $\text{H}_2\text{S}$ -rich), ferruginous (anoxic and  $\text{Fe}^{2+}$ -rich), and  $\text{NO}_3^-$ -buffered (i.e., anoxic but with low concentrations of both  $\text{H}_2\text{S}$  and  $\text{Fe}^{2+}$ ). We note, however, that the latter environments are likely to be spatially and temporally limited given the relatively low concentration (and thus redox buffering capacity) of  $\text{NO}_3^-$  in seawater, particularly during the Proterozoic (29).

Despite evidence for pervasive marine anoxia during the Proterozoic, we highlight that euxinia covered only a small portion of the seafloor. On this basis, we present a framework for linking Mo enrichments to seawater Mo concentrations that points toward Mo–N colimitation in the Proterozoic ocean. Therefore, despite a more limited extent of euxinia than previously envisaged, life in the Proterozoic ocean was heavily influenced by a prevalence of sulfide in the water column that far exceeded the small amounts of euxinia that characterize the modern ocean.

### Mid-Proterozoic Geochemical Record

We present a record of Cr and Mo enrichments in anoxic and euxinic black shales through time (Fig. 1). Samples for this study ( $n > 3,000$ ) come from our analytical efforts and a literature survey (Fig. S1 and Table S1). Our own data include results from over 300 Precambrian samples and modern anoxic systems. Samples were filtered for basic lithology (fine-grained siliciclastics) using a combination of basic sedimentary petrology and major-element thresholds. We relied on well-established paleoproxies rooted in Fe–S systematics to infer the redox state of the water column overlying the site of shale deposition. Importantly, these paleoredox proxies are calibrated to delineate anoxic settings (where Cr will be reduced and buried) and euxinic settings (where both Cr and Mo will be reduced/sulfidized and buried). The Fe–S paleoproxies have recently been reviewed in detail (30, 31), and full information on sample filters is provided in *SI Discussion*. We emphasize the noncircularity of our approach to

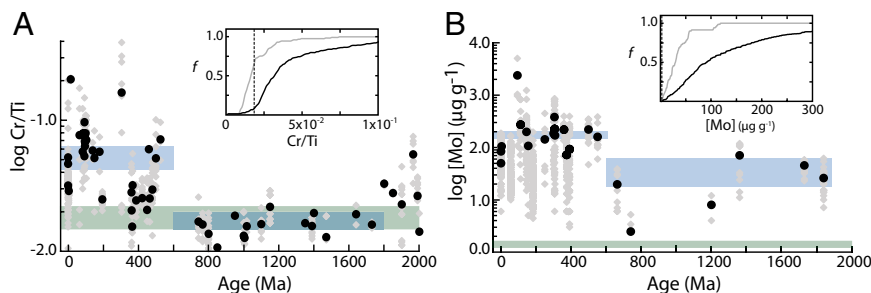
analyzing the shale record—specifically, we constrained local paleoredox to have been anoxic or euxinic with no appeal to sedimentary trace metal enrichments as fingerprints of those conditions. This approach allows us to use the metal enrichments themselves as proxies for broader ocean redox state and its control on the ocean-wide inventories of those metals.

There are significant Mo enrichments in mid-Proterozoic (~1.8–0.6 Ga) euxinic shales (Fig. 1B). However, these enrichments are significantly lower than those observed in late Proterozoic and Phanerozoic euxinic equivalents (9). Proterozoic enrichments range from less than 10 to greater than 100 ppm, compared with concentrations on the order of ~1–2 ppm in average upper crust (16). The total mean for temporally binned mid-Proterozoic euxinic shale data (2.0–0.74 Gya) is 40.5 ppm ( $\pm 22.5$  at the 95% confidence level) compared with the Phanerozoic where the total mean is 170.2 ppm ( $\pm 33.4$  ppm at the 95% confidence level).

In strong contrast with the Mo record, there are no discernible Cr enrichments in mid-Proterozoic anoxic shales. We report Cr enrichments by normalizing to Ti content, as detrital inputs of Cr to marine sediments can be substantial and are greatly in excess of those for Mo. The total mean for Cr/Ti values for mid-Proterozoic anoxic shales is  $1.69 \times 10^{-2}$  (ppm/ppm), and the 95% confidence interval ( $1.45 \times 10^{-2}$  to  $1.93 \times 10^{-2}$ ) is indistinguishable from post-Archean average upper crust (32–34) (Fig. 1A). There is a marked increase in Cr/Ti ratios after the late Proterozoic, with Phanerozoic shales showing Cr/Ti values indicating enrichments of tens to hundreds of ppm. This pattern is mirrored in the sharp rise in Mo enrichments through the same interval.

We hypothesize that the enrichment trends for both metals reflect the progressive expansion of marine anoxia between 2.0 and 1.8 Ga and persistent oceanic Cr drawdown during the mid-Proterozoic. Because of the different conditions required for the reduction, immobilization, and accumulation in sediments for Cr (anoxic) and Mo (euxinic), we suggest that a relatively small proportion of oceanic anoxia was represented by euxinic conditions, which allowed a moderate although muted seawater Mo reservoir to coexist with a strongly depleted Cr reservoir. We note also that the much greater density of Cr data once the datasets have been filtered for local redox suggests qualitatively that anoxic shales were much more common than euxinic shales during the Proterozoic.

In contrast, the Phanerozoic record is generally characterized by elevated enrichments of both elements, suggesting that for most of the Phanerozoic both anoxic and euxinic conditions were less spatially and/or temporally widespread. Comparatively short-lived Phanerozoic oceanic anoxic events (OAEs), such as those famously expressed in the Mesozoic, are a notable exception. We suggest that combining enrichment records for elements that respond to



**Fig. 1.** Sedimentary Cr (A) and Mo (B) enrichments in anoxic and euxinic black shales through time. Because of the relatively high Cr content of typical detrital material, Cr enrichments are expressed as Cr/Ti ratios. Gray diamonds represent all filtered data, whereas black circles represent temporally binned averages. Blue boxes show the total mean ( $\pm 95\%$  confidence interval) of temporally binned averages for the mid-Proterozoic and Phanerozoic (*SI Discussion*). (Insets) Cumulative frequency distribution of enrichments for the mid-Proterozoic (gray curve) and the Phanerozoic (black curve). Green boxes show the composition of average post-Archean upper crust (31–33) used to approximate the detrital input. Note the log scale.

the presence of free  $\text{HS}^-$  in anoxic marine environments (Mo, Zn, etc.) with elements that respond to anoxia more generally (Cr, Re, V, etc.) may allow us to place more detailed constraints on the fabric of seafloor redox and bioinorganic feedbacks throughout Earth's history. We can then expand this approach by interpreting such data within a global mass balance framework.

### Interpreting the Enrichment Record: Model for Global Mass Balance and Burial in Marine Sediments

Our quantitative model begins with a conventional mass balance formulation (35), in which the ocean is treated as a single well-mixed reservoir (Fig. S2)—a reasonable assumption given the relatively long residence times of the elements of interest (*SI Discussion*). The globally averaged concentration of a metal in the ocean evolves as

$$\frac{d}{dt} \int_v [\text{Me}] dv = F_{in} - F_{out},$$

where  $[\text{Me}]$  represents the seawater concentration of a given metal, integrated over ocean volume  $v$ . The terms  $F_{in}$  and  $F_{out}$  represent input and output fluxes, respectively. In both cases, input fluxes associated with riverine delivery and/or seawater-basalt interaction are grouped into a single input term ( $F_{in}$ ; *SI Discussion* and Fig. S3), whereas output fluxes ( $F_{out}$ ) are broken into burial terms specific to each metal cycle (Fig. S2 and Tables S2–S6). Riverine input dominates the overall input flux for both metals (*SI Discussion*), and this flux is unlikely to have varied significantly (relative to variations in the removal fluxes) after Earth's initial oxygenation. Sink fluxes (burial in sediments) are a function of the characteristic burial rate and areal extent of a given sink environment ( $i$ ):

$$F_i = k \int_{A_i} b_i^{\text{ini}} dA_i,$$

where  $A_i$  represents the seafloor area of each sink environment (oxic, ferruginous, sulfidic, etc.), and  $b_i^{\text{ini}}$  represents the globally averaged initial burial rate characteristic of that environment. In this equation,  $k$  is a reaction coefficient that relates the burial flux to the seawater concentration. For a strictly first-order model,  $k = [\text{Me}]_t / [\text{Me}]_M$ , where  $[\text{Me}]_t$  is the mean oceanic concentration of a given metal at time  $t$ , and  $[\text{Me}]_M$  is the modern seawater concentration. As previously noted (36), this kind of first-order mass balance approach to specifying removal fluxes is a specific variant of the more generalized case:

$$F_i = k^\alpha \int_{A_i} b_i^{\text{ini}} dA_i,$$

where  $\alpha = 1.0$ .

Combining the above terms yields an expression for each removal flux:

$$F_i = A_i b_i^{\text{ini}} \left[ \frac{[\text{Me}]_t}{[\text{Me}]_M} \right]^\alpha.$$

Following previous approaches, we first assume that  $\alpha = 1.0$  (i.e., first-order mass balance). This approach is grounded in the notion that the burial rate of a metal in a given sink environment will scale in a roughly linear fashion with the ambient seawater reservoir size (18, 35). After substitution and rearrangement of the above equations, we arrive at a generalized mass balance equation for both metals:

$$\frac{d}{dt} \int_v [\text{Me}] dv = F_{in} - \sum A_i b_i^{\text{ini}} \frac{[\text{Me}]_t}{[\text{Me}]_M}.$$

Because we are mainly interested in broad ( $\sim 10^6$  y) shifts in deep ocean redox, we assume steady-state conditions for both metal systems. Assuming steady state (i.e.,  $d[\text{Me}]/dt = 0$ ) yields an expression for the average oceanic concentration of a given metal:

$$[\text{Me}]_t = [\text{Me}]_M \frac{F_{in}}{\sum A_i b_i^{\text{ini}}}.$$

An important component of our model is the specification of spatially variant metal burial rates. Most past treatments of oceanic metal mass balance suffer from the physically unrealistic assumption that the metal burial rates characteristic of modern environments, typically encountered in restricted or marginal settings such as the Black Sea and Cariaco Basin, where overall sediment and carbon fluxes are high, can be scaled to very large regions of the abyssal seafloor where bulk sediment delivery and organic carbon fluxes are typically much lower (37, 38). We have attempted to avoid the same oversimplification by coupling an algorithm that addresses carbon flux to the seafloor as a function of depth (39) to a polynomial function fitted to bathymetric data (40) and by tuning an imposed burial ratio parameter ( $R_{\text{Me}/\text{C}}$ ) to reproduce the modern globally averaged burial rate for each metal (*SI Discussion* and Fig. S4).

The essential assumption here is that a given region of the seafloor will have a characteristic “burial capacity” for Mo and Cr, regulated to first order by carbon flux to the sediment, and that this capacity will only be realized if the environment is anoxic (in the case of Cr) or euxinic (in the case of Mo). From a mechanistic perspective, this approach builds from clear evidence that the burial in sediments of many redox sensitive metals in anoxic settings scales strongly with carbon flux to the sediments (18, 41, 42). We hold that this approach allows for a more realistic depiction of perturbations to seawater metal inventories as a function of seafloor redox dynamics by smoothly decreasing globally averaged burial rates as larger regions of the seafloor become anoxic (Cr) or sulfidic (Mo).

### Interpreting the Enrichment Record: Model Results

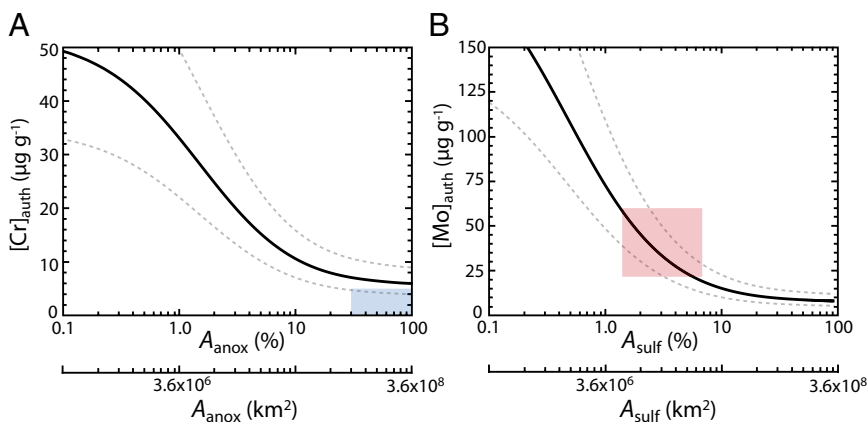
Our approach assumes, by definition, that the burial rate of a given metal in an authigenically active environment (i.e., environments that remove Cr and/or Mo from seawater and sequester them within the sediment column) scales with the ambient concentration in seawater:

$$b_i = b_i^{\text{ini}} \left[ \frac{[\text{Me}]_t}{[\text{Me}]_M} \right]^\alpha.$$

The seawater reservoir is controlled largely by how this relationship is expressed on a global scale, but this relationship will also apply to individual settings or regions of the seafloor. As a result, we can envision a generalized authigenically active setting and estimate sedimentary metal enrichments as a function of seawater concentration, in turn controlled by the relative areas of different redox environments on a global scale.

The results of such an exercise are shown in Fig. 2. Here, we have used as our starting point burial rates and overall sediment mass accumulation rates from one of the best-characterized perennially euxinic basins on the modern Earth, the Cariaco Basin in Venezuela. Our purpose here is to depict a generalized setting accumulating Cr and Mo within sediments that has a relatively open connection to the seawater metal reservoir(s), and for that reason we have chosen the Cariaco Basin over the highly

**Fig. 2.** Estimated authigenic sedimentary enrichments ( $[X]_{\text{auth}}$ ) for Cr (A) and Mo (B) in a generalized anoxic or euxinic setting, respectively, as a function of anoxic and sulfidic seafloor area ( $A_{\text{anox}}$ ,  $A_{\text{sulf}}$ ). Black curves represent a bulk mass accumulation rate of  $1.0 \times 10^{-2} \text{ g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$ , whereas gray dotted curves represent a factor of 1.5 above and below this value (SI Discussion; Fig. S5). The blue box in A represents the approximate area of seafloor anoxia required to drop below an enrichment threshold of  $5 \mu\text{g} \cdot \text{g}^{-1}$ , a conservative value for our purposes given the negligible enrichments recorded by mid-Proterozoic anoxic shales. The red box in B shows the approximate sulfidic seafloor area consistent with the range of mid-Proterozoic Mo enrichments, and is scaled relative to the y axis according to the 95% confidence interval of temporally binned averages shown in Fig. 1. Seafloor areas are shown as a percentage relative to modern seafloor area (%) and in terms of raw area ( $\text{km}^2$ ).



restricted Black Sea, which shows clear local reservoir effects for Mo (18). In essence, we pose the question, “How would an anoxic or euxinic continental margin or epicontinental environment, such as that represented in the marine black shale record, respond to a particular perturbation to seafloor redox state?” We can then scale this relationship to spatially varying organic carbon burial and bulk sedimentation to inform metal uptake away from the continental margin.

A striking pattern emerges when we consider the magnitude of enrichment that can be achieved in an authigenically active environment under different oceanic redox conditions (Fig. 2). If our model is correct, the negligible sedimentary Cr enrichments characteristic of the entire mid-Proterozoic would require extremely pervasive anoxic conditions. Our approach (which is likely conservative; SI Discussion) suggests that at least  $\sim 30\text{--}40\%$  of the seafloor must have underlain anoxic deep waters to drive Cr enrichments to crustal values for sustained periods. We stress that this is a minimum estimate, and that our results are also fully consistent with virtually complete seafloor anoxia.

The Mo enrichment record, however, tells a very different story. Enrichments in euxinic environments during the mid-Proterozoic are muted relative to the Phanerozoic, a pattern that emerges as a consequence of more widespread sulfidic deposition relative to most of the Phanerozoic and is reinforced when Mo enrichments are normalized to total organic carbon (TOC; ref. 9). However, Mo enrichments in Proterozoic euxinic environments that are mostly well above crustal values are inconsistent with pervasive, ocean-scale euxinia (Fig. 2B). Instead, our model results point to roughly  $\sim 1\text{--}10\%$  of the seafloor as having been euxinic during the mid-Proterozoic, although there is likely to have been dynamic expansion/contraction of the area of euxinic seafloor area within and occasionally beyond this range—as related, for example, to spatiotemporal patterns of primary production along ocean margins. A similar range of euxinic seafloor is implied for some brief periods of the Phanerozoic (43, 44), but the record of appreciable Cr enrichment during this latter phase of Earth history indicates much more spatially and temporally restricted anoxia overall.

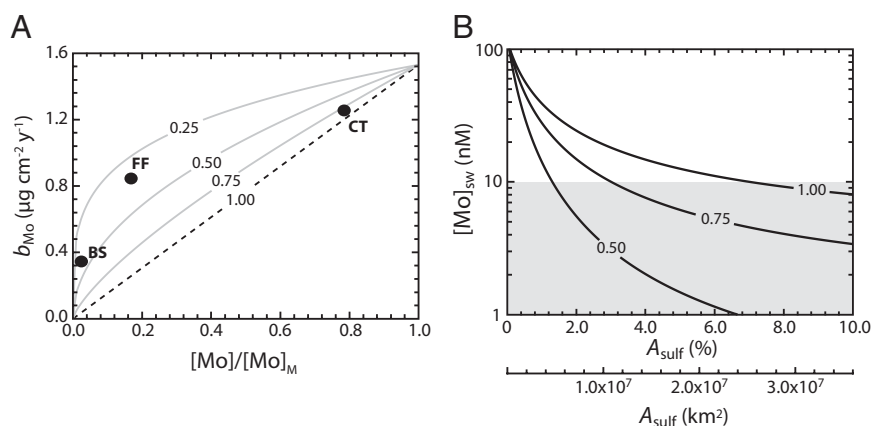
### Marine Euxinia: Global Effects of Regional Ocean Chemistry

The record of Cr and Mo enrichment, when interpreted in light of our model results, necessitates that euxinia covered a relatively small fraction of overall seafloor area during the mid-Proterozoic despite pervasive anoxic conditions on a global scale. Such a result adds to growing evidence that Proterozoic deep ocean chemistry was dominated by anoxic but nonsulfidic (ferruginous) conditions (10, 12, 13), in contrast with most modern anoxic marine settings that tend toward euxinia. Nevertheless, euxinia in the mid-Proterozoic ocean was likely orders of magnitude more widespread than

today’s estimate of  $\sim 0.1\%$  of the seafloor, and the deleterious impacts on nutrient availability could have been enough to significantly alter global biogeochemical processes. In effect, the sensitivity of the oceanic Mo reservoir to small perturbations in the extent of sulfidic seafloor suggests that a strong distinction should be made between a sulfidic ocean in an oceanographic sense, in which a large proportion of oceanic volume and basin- or global-scale areas of the seafloor (much more than our estimate of  $\sim 1\text{--}10\%$ ) are characterized by sulfidic waters, and an ocean that is sulfidic from a nutrient or biological perspective. From a biological perspective, trace nutrient colimitation of marine primary producers will be strongly controlled by the extent of euxinic conditions despite euxinia not being persistent throughout most of the ocean. These conditions are, of course, not mutually exclusive—a globally sulfidic ocean will almost certainly result in trace element colimitation. However, the distinction is important as it highlights the leverage that relatively small regions of the ocean can exert on the biogeochemical cycling of certain biolimiting trace elements (9, 26).

To further explore this concept, we use the model to estimate globally averaged seawater  $[Mo]$  under variable scaling between the ambient seawater concentration and burial rate within sediments. The most common approach, as discussed above, is to assume strictly first-order (i.e., linear) scaling ( $\alpha = 1.0$ ). Although data are somewhat limited and it is difficult to establish precisely what the form of this relationship should be, data from the most well-characterized perennially euxinic settings on the modern Earth suggest that this relationship may in fact be nonlinear (Fig. 3A). The effect of this parameter on steady-state globally averaged seawater  $[Mo]$  is shown in Fig. 3B. Because lowering the value for  $\alpha$  allows for a higher burial rate (and thus removal flux from the ocean) at a given value for seawater  $[Mo]$ , the concentration is ultimately drawn down to much lower steady-state values for a given perturbation.

Although the term  $\alpha$  regulates the scaling between ambient  $[Mo]$  and Mo burial rate on a global scale in an integrated sense across diverse redox settings, it will also do so within individual authigenically active environments. Importantly, this means that the sedimentary enrichments predicted by the model for a given extent of euxinic seafloor do not vary as a function of  $\alpha$ . Changes in this parameter are reflected by the steady-state concentration of Mo in seawater (the same applies for Cr). It is clear from this exercise (Fig. 3) that even relatively small areas of the seafloor overlain by euxinic water masses (a fraction of modern continental shelf area) are sufficient to draw the ocean’s average Mo concentration to  $\sim 10 \text{ nM}$  (an order of magnitude below that seen in the modern ocean), even with strictly linear scaling between ambient  $[Mo]$  and burial flux.



**Fig. 3.** Effects of deviating from a strictly first-order model. (A) Mo burial rates as a function of ambient dissolved Mo concentration (shown as a proportion of modern seawater  $[\text{Mo}]/[\text{Mo}]_M$ ) for a range of  $\alpha$ -values between 1.0 (strict first-order) and 0.25. Curves are calculated assuming a modern globally averaged euxinic burial rate of  $1.53 \mu\text{g cm}^{-2} \text{y}^{-1}$ . Black circles represent values for well-characterized perennially euxinic marine basins on the modern Earth [Black Sea (BS), Framvaren Fjord (FF), and the Cariaco Trench (CT)]. (B) Steady-state globally averaged seawater Mo concentrations as a function of sulfidic seafloor area ( $A_{sulf}$ ) for different values of  $\alpha$ . The shaded box depicts values below 10 nM.

Further work is needed to better pinpoint the levels of seawater Mo that should be considered biologically limiting, but available evidence is consistent with biolimiting concentrations in mid-Proterozoic oceans. Culturing experiments with modern strains of diazotrophic (nitrogen-fixing) cyanobacteria generally indicate that rates of nitrogen fixation and overall growth become impacted by Mo availability once concentrations fall to within the  $\sim 1$ – $10$ -nM range (45–49). Some strains seem to show resilience to Mo scarcity until concentrations fall below  $\sim 5$  nM (48), but in general there seems to be a sharp change in overall growth rates, cell-specific nitrogen fixation rates, and stoichiometric growth status within the 1–10-nM range. Even small changes in relative rates of diazotrophy, if expressed globally and on protracted timescales, can be expected to have large effects on carbon, nitrogen, and oxygen cycling as well as ecosystem structure in the surface ocean.

Although Mo enrichments in anoxic shales deposited during the mid-Proterozoic do not approach those characteristic of Phanerozoic settings, enrichment levels are nonetheless maintained well above crustal values. Thus, Mo enrichments in mid-Proterozoic euxinic marine settings seem poised within a very sensitive region of parameter space. We stress that such a relationship implies some kind of stabilizing feedback controlled by Mo–N colimitation (e.g., ref. 9). In this scenario, widespread euxinic conditions would deplete the Mo reservoir, thereby limiting primary productivity and carbon export flux. This in turn would reduce the amount of biomass oxidized via microbial sulfate reduction (which produces  $\text{HS}^-$ ), limiting sulfide accumulation in marine settings. The ultimate result would be for Mo concentrations to rebound (a negative feedback; ref. 9). However, it would be difficult to transition from a Mo–N colimited system to a strongly oxidizing, Mo-replete ocean. Such a shift would need to be driven ultimately by a long-term increase in sedimentary burial of organic matter, but this burial would lead to a corresponding increase in Mo burial fluxes pushing the system back to Mo–N colimitation. The link between primary production and Mo removal from the ocean would again be the microbial production of hydrogen sulfide needed for efficient Mo burial. The response time of Mo in a Mo-depleted ocean is likely to be short enough (relative to the residence time of oxygen in the ocean/atmosphere system) to induce a rapid and efficient stabilizing feedback on redox conditions. Iron will be orders of magnitude more soluble under any form of anoxia (euxinic or ferruginous) than it is in the modern ocean. In this light, in a reducing ocean, the coupled C–S–Fe–Mo biogeochemical cycles form an attractor—driving the marine system toward persistent trace metal–macronutrient colimitation. This relationship is similar, in essence, to the control exerted by limited Fe solubility in an oxidizing and well-ventilated ocean, but we expect that the

stabilizing feedbacks and sensitivity responses will be very different between the two systems.

### Conclusions

Exploration of the Cr and Mo enrichment record in anoxic marine shales during the last  $\sim 2.0$  Ga within a mass balance framework reveals that the mid-Proterozoic ocean was characterized by pervasive anoxic conditions, as manifested by negligible Cr enrichments in anoxic shales, but limited euxinia, as reflected in nontrivial Mo enrichments in euxinic shales that are nonetheless quite muted relative to most Phanerozoic equivalents. The Phanerozoic ocean appears to have been marked by more circumscribed anoxia on the whole, with anoxic shales typically showing substantial Cr enrichments. As a result, a potentially much larger relative fraction of this anoxia may have been represented by euxinic conditions, in particular during Cretaceous OAEs and periods of anomalously widespread anoxia during the Paleozoic (44). It remains to be explored if these episodes represent a fundamentally different mode of anoxic marine conditions or whether they can be viewed as temporary reversions to mid-Proterozoic conditions.

In addition, our model points toward a view in which the chemistry of small and dynamic regions of the seafloor exerts fundamental control on biological carbon and oxygen cycling through bioinorganic feedbacks related to trace element availability (9, 26), in much the same way that carbon cycling and export in large regions of the modern well-ventilated ocean are controlled by the availability of Fe. Moving forward, it will be important to explore in detail, and with a wide range of organisms, the thresholds at which diazotrophs are strongly impacted by Mo availability. It will also be important to develop explicit ecological models aimed at delineating the constraints and feedbacks associated with Mo–N colimited planktonic ecosystems. For example, elevated growth rates and doubling times due to greater overall Fe availability (as the solubility of Fe in any anoxic state will be orders of magnitude above that seen in oxic systems) may be able to compensate for lower cell-specific rates of nitrogen fixation within the context of ecosystem nitrogen supply. Further, although there is some understanding of the Mo requirements for assimilatory nitrate uptake (e.g., ref. 50), little is known regarding the effects of Mo availability on dissimilatory nitrate reductase. Finally, it is clear that some diazotrophs show biochemical idiosyncrasies aimed at dealing with Mo scarcity (49), and recent work on the exquisite adaptation of some diazotrophic organisms to Fe limitation in the modern oceans (51) begs for a more thorough exploration of the biochemistry of Mo-limited diazotrophy.

In any case, our results provide strong independent evidence for an emerging first-order model of Proterozoic ocean redox structure. In this model, the surface ocean is well-ventilated

through air–sea gas exchange and local biological O<sub>2</sub> production, but the deep ocean is anoxic largely as a result of equilibration with atmospheric pO<sub>2</sub> at least 1–2 orders of magnitude below the modern value in regions of deep-water formation (4). The increased mobility and transport of dissolved Fe(II) under reducing conditions, combined with spatially heterogeneous carbon fluxes through marine systems (as constrained by the intensity of vertical exchange through upwelling and eddy diffusion), yielded an ocean that was pervasively anoxic (i.e., redox-buffered by Fe<sup>2+</sup> or NO<sub>3</sub><sup>-</sup>) with localized regions of euxinia in marginal settings (12, 13). We note that although our model is, in principle, somewhat sensitive to variations in the sourcing of Cr to the ocean (*SI Discussion*), it is also supported by data from other elements whose sourcing to the ocean should only be weakly dependent on atmospheric pO<sub>2</sub> (52). This emerging model provides a backdrop for the early evolution and ecological expansion of eukaryotic organisms (26, 53) and the biogeochemical

feedbacks controlled by the progressive restructuring of primary producing communities (54). Finally, the sensitivity of the oceanic Mo reservoir to perturbation, combined with the relative uniformity of the Mo enrichment record in Proterozoic euxinic shales, implies that this redox structure may have been stable on long timescales as a function of Mo–N colimitation in the surface ocean. This hypothesis can be tested through the generation of more Proterozoic shale data, whereas further modeling might constrain how robust such a feedback could be and what conditions would have been required to overcome it during the later Proterozoic oxygenation of the deep ocean and subsequent evolution of macroscopic life.

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# Supporting Information

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## SI Discussion

**Metal Enrichment Database and Filtering Protocols.** Through our own analytical efforts and a literature survey, we have assembled a database of molybdenum (Mo) and chromium (Cr) concentrations for over 3,000 samples. Data sources are shown in [Table S1](#). Samples were initially filtered to represent solely fine-grained siliciclastic sediments, using basic petrographic observation and major element thresholds. Samples were required to contain weight percent (wt %) levels of iron (Fe) and aluminum (Al). Samples containing less than 1.0 wt % total organic carbon were also removed.

The information contained within a particular degree of authigenic enrichment of Cr or Mo depends on local depositional redox. Thus, samples were further filtered such that Cr data were only analyzed from anoxic shales, and Mo data were only analyzed from euxinic shales. Anoxic shales were delineated as having  $Fe_T/Al > 0.5$  (1) and/or  $Fe_{HR}/Fe_T > 0.38$  (2–4), where  $Fe_{HR}$  designates “highly reactive” Fe (Fe that is reactive to dissolved  $H_2S$  on syngenetic or diagenetic timescales; ref. 5) and  $Fe_T$  represents total Fe. Euxinic settings were delineated by combining the above thresholds for anoxia with either  $Fe_{PY}/Fe_{HR} > 0.7$  (4, 6) or with elevated values for degree of pyritization (DOP  $> 0.6$ ; ref. 7), defined as (8)

$$DOP = \frac{Fe_{PY}}{Fe_{PY} + Fe_{HCL}}$$

where  $Fe_{HCL}$  is Fe soluble in a 1-min boiling concentrated HCl leach and  $Fe_{PY}$  denotes pyrite Fe. Because elevated DOP has also been shown to require enhanced Fe mobility and transport (1, 7), and because it is an extremely robust analytical measurement, DOP  $> 0.8$  supersedes all other redox filters in the designation of euxinia. In some cases, total sulfur content is used to calculate  $DOP_T$ , according to

$$DOP_T = \frac{Fe_S}{Fe_S + Fe_T}$$

where  $Fe_S$  denotes the inferred amount of sulfur-bound Fe assuming that total sulfur represents pyrite sulfur (9). Modern systems (such as the Black Sea and Cariaco Basin) were additionally filtered by site location, for extreme siliciclastic dilution, and the presence of bioturbation, and units with fewer than ten filtered samples were not included in overall statistical calculations.

Our focus here is on the contrast in enrichment records between the mid-Proterozoic and the Phanerozoic. However, as noted in the main text, there appear to be substantial Cr enrichments in late Paleoproterozoic anoxic shales. Recent work has suggested an increase and subsequent decrease in Earth surface oxidation during the Paleoproterozoic (10, 11), and we suggest in the main text that the Cr enrichment pattern is possibly related to this, with the subsequent drawdown of Cr enrichments representing the progressive expansion of anoxic marine environments. Shown in Fig. S1 is the full enrichment record, including Archean and Paleoproterozoic data. The Mo enrichment record in euxinic shales (Fig. S1B) is similar to previous work (12), showing minimal enrichment during the Archean and appreciable although muted enrichments (relative to the Phanerozoic) during most of the Proterozoic. The Cr enrichment record shows some very high enrichments during the Archean and Paleoproterozoic (Fig. S1A). Some of this trend is almost certainly because Archean upper crust was more mafic in composition, and much of these enrichments could be linked to

very Cr-rich source terrains. The Paleoproterozoic enrichments, on the other hand, may well be authigenic enrichments. Future isotopic and petrographic work is required to distinguish between these two models.

**Modern Mo Mass Balance.** We begin by assuming steady state, wherein a single input flux ( $F_{in}$ ) is balanced by removal via authigenic burial into three main sedimentary sinks: an oxic sink ( $F_{ox}$ ), a reducing sediment sink ( $F_{red}$ ), and a sulfidic sink ( $F_{sulf}$ ). Our balanced modern Mo budget is shown in Fig. S2 and [Table S2](#), and individual removal terms are discussed below. The weathering flux of Mo on the modern Earth is dominated by the mobilization of Mo from sulfide mineral phases or organics in sedimentary and igneous rocks and transport as dissolved  $MoO_4^{2-}$ , and we set as  $F_{in}$  a recently obtained modern riverine flux of dissolved  $MoO_4^{2-}$  to the ocean (13). This flux is somewhat larger than those conventionally used, but is derived from the most extensive riverine database generated to date, representing 38 rivers across 5 continents and including 11 of 19 large-scale drainage areas. However, regardless of our choice of estimate for the riverine Mo flux, sensitivity analysis (Fig. S3) indicates that our conclusions are weakly sensitive to the assumed value of the input flux over a wide range. We neglect hydrothermal fluxes of Mo to/from the ocean, as these are either poorly established or likely to be quantitatively small (see below).

Oxic settings are defined as those in which Mn is permanently removed from the ocean as an oxide phase (with associated adsorbed Mo). In many oxic deep-sea settings, dissolved  $O_2$  penetrates to the sediment–basalt interface (14, 15) and this Mn (and Mo) will effectively be buried permanently. In other settings, dissimilatory microbial Mn reduction deeper in the sediment column can remobilize Mn (and, presumably, associated Mo). However, when  $O_2$  penetration depths are large (multiple centimeters or more) upward-diffusing Mn will be quantitatively oxidized at a steady-state oxidation front (16–18), effectively removing Mn and Mo from the ocean on a timescale characteristic of tectonic recycling of seafloor sediments (on the order of  $\sim 10^8$  y). Morford and Emerson (19) suggest that once  $O_2$  penetration falls below  $\sim 1$  cm, Mn and Mo will be recycled and released from shallow sediments. We therefore characterize oxic seafloor as being the areal extent of sediments in which  $O_2$  penetration exceeds 1 cm. This is estimated using global diagenetic models (20, 21) to be  $\sim 3 \times 10^8$  km<sup>2</sup>, or roughly 84% of modern seafloor area. We stress that there are fairly large regions of the seafloor that are essentially Mo neutral (see below), such that the total seafloor area for the entire budget need not sum to 100%. This area is then combined with a burial rate of  $2.75 \times 10^{-3}$   $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ , estimated by compiling Mo burial rates in oxic settings (22) and by combining Mn burial rates in oxic pelagic sediments (23) with a characteristic Mo/Mn ratio of  $2 \times 10^{-3}$  (24). The combined sink is shown in [Table S2](#).

Sulfidic settings are defined as environments in which dissolved  $H_2S$  accumulates at or above the sediment–water interface. This includes traditional euxinic settings (Black Sea, Cariaco Basin), but is also meant to include small areas of the seafloor below regions of intense upwelling (Peru margin, Namibian shelf), where dissolved  $H_2S$  is present at high levels essentially at the sediment–water interface and occasionally breaches into the water column (25, 26). Our sulfidic sink is calculated by combining estimates of seafloor area, authigenic enrichment, and bulk mass accumulation rate (MAR) for modern sulfidic settings (2, 27–39). The globally averaged sulfidic burial calculated

through such an approach will be biased low—given that the modern extent of euxinic seafloor, on an areal basis, is dominated by the Black Sea, and this setting is characterized by low burial rates due to restricted exchange over the Bosphorus sill and an evolved Mo reservoir (36). As a result, the global sulfidic burial rates implemented in the model are referenced to a modern globally averaged sulfidic burial rate that neglects the influence of the Black Sea. This is done in an effort to represent the burial capacity of marine settings with unfettered access to the seawater Mo reservoir (12).

The final sink is reducing sediments. This sink represents environments that have been referred to by the rather ambiguous term “suboxic.” We follow ref. 12 in designating these environments as those in which dissolved  $\text{H}_2\text{S}$  accumulation is restricted to pore waters, but further point out that reducing sediments in which  $\text{O}_2$  penetration is less than  $\sim 1$  cm and  $\text{H}_2\text{S}$  accumulation occurs more deeply in the sediments do not effectively bury Mo (19). From a mechanistic perspective, these reducing sediment environments are typically associated with relatively low bottom-water  $\text{O}_2$ , but the effectiveness of Mo sequestration in these settings is most likely a more complex function of Mn flux to sediments (and, thus, bottom-water  $\text{O}_2$ ), sedimentation rate, and labile organic carbon flux to the sediment–water interface. In any case, we use a somewhat moderate burial rate for reducing sediments of  $0.27 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$  (37, 40–43), and use the remaining parameters of the budget to solve for the seafloor area represented by this sink (Table S2). Although we present a revised approach for estimating the global Mo removal fluxes, our result is similar to previous estimates based on consideration of bulk burial rates (12) and isotope mass balance (40).

**Modern Cr Mass Balance.** As for Mo, we begin by assuming steady state, with a single input flux ( $F_{\text{in}}$ ) balanced by three authigenic burial fluxes: an oxic sink ( $F_{\text{ox}}$ ), a reducing sediment sink ( $F_{\text{red}}$ ), and an anoxic sink ( $F_{\text{anox}}$ ). In our modeling analysis, we take anoxic environments to include those that are euxinic (anoxic and  $\text{H}_2\text{S}$ -rich), ferruginous (anoxic and  $\text{Fe}^{2+}$ -rich), and  $\text{NO}_3^-$ -buffered (i.e., anoxic but with low concentrations of both  $\text{H}_2\text{S}$  and  $\text{Fe}^{2+}$ ). We note, however, that the latter environments are likely to be spatially and temporally limited, given the relatively low concentration (and thus redox buffering capacity) of  $\text{NO}_3^-$  in seawater. Potential hydrothermal fluxes to/from the ocean are neglected in our treatment of the modern Cr cycle, as currently available data suggest that these fluxes are quantitatively insignificant (see below). The Cr mass balance is rather poorly constrained—compared with that for Mo. However, we suggest that although our mass balance is likely to be revised as better estimates of fluxes and reservoirs become available, this is very unlikely to change our fundamental conclusions.

Our input flux is calculated following the method of ref. 13. In brief, we compiled a database of dissolved [Cr] values and annual discharge rates for rivers (Table S3), and used this to calculate discharge-weighted dissolved [Cr] values for individual large-scale drainage regions according to the available data. The Cr flux from each large-scale drainage region was then computed by combining the discharge-weighted [Cr] value with the total discharge flux from each region. These regional fluxes were combined and used to estimate a global discharge-weighted dissolved [Cr] value of 14.82 nM. This value was then combined with an estimated global exorheic flux of  $3.9 \times 10^4 \text{ km}^3\cdot\text{y}^{-1}$  (44), yielding an estimate of the discharge-weighted flux of dissolved Cr to the modern ocean. Although dissolved Cr data are less common than dissolved major ion data for rivers, the large-scale drainage regions in our database account for  $\sim 70\%$  of the overall exorheic flux to the oceans. Assuming minimal estuarine removal (45, 46), and combining this estimate with an average seawater concentration of 4 nM (47) and an ocean volume of  $1.37 \times 10^{21}$  L, this yields a residence time for Cr in the modern ocean of  $\sim 9,500$  y

(i.e., over a factor of 9 greater than characteristic timescales of ocean mixing). To our knowledge, estimates of this sort are few, but ours is well in line with previous attempts (e.g., ref. 48). As for Mo, sensitivity analysis (Fig. S3) indicates that our conclusions are not likely to be fundamentally altered unless input fluxes to the ocean become extremely low.

Dissolved Cr(VI) species should become adsorbed onto the surface of metal- and Al-oxide phases (49–51). We therefore expect some nontrivial burial flux of Cr in oxic settings, although we note that sorption to Al-oxide phases decreases sharply when approaching circumneutral pH (52). The Cr content of pelagic red clays, although often elevated above crustal values with respect to Cr/Ti ratios, is rather variable. We use in our budget a relatively low oxic Cr burial rate of  $1.0 \times 10^{-3} \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ , of the same order as our much better constrained Mo burial flux. This corresponds to a sediment with a Cr/Ti ratio of  $1.87 \times 10^{-2}$ , consistent with typical values from pelagic red clays (53–55), accumulating at a burial rate of  $1.0 \times 10^{-3} \text{ g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ . Because the burial of Cr in oxic settings should depend on the efficiency of metal oxide burial, this burial rate is then combined with the same areal extent of oxic seafloor (defined by sediment  $\text{O}_2$  penetration depth) discussed above.

The anoxic sink for Cr is defined in a similar manner to the sulfidic sink for Mo, a natural result of the fact that on the modern Earth the relative mobility and transport of S and Fe are such that anoxic settings tend to become euxinic (anoxic and sulfidic). We use Cr/Ti ratios from the Cariaco Basin (34, 56, 57) to obtain a modern anoxic burial rate of  $\sim 0.5 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ , and scale this to the seafloor area of anoxic environments as discussed above for the modern Mo budget. This burial rate is roughly of the same order as that for Mo in euxinic settings, although we acknowledge that these estimates will improve with further generation and analysis of Cr data in anoxic marine systems. However, Cr will be reduced and immobilized as Cr(III) via a wide range of reductants—dissolved  $\text{H}_2\text{S}$  is not necessary (58–60). Indeed, Cr(VI) reduction to Cr(III) has been shown to take place in the open-water column of the eastern tropical Pacific, coincident with the onset of microbial denitrification (61). This provides a crucial distinction with the behavior of Mo, in that effective Mo capture requires the additional presence of free dissolved sulfide, and forms the centerpiece of our analysis. The reducing sediment sink is again solved for using the other parameters of the budget. We assume an authigenic burial rate of  $0.15 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$ , derived from combining Cr/Ti ratios in the Gulf of California (62) with the requisite bulk MAR (63). This aspect of the budget is not well constrained, but we consider it unlikely that such settings will authigenically bury Cr at rates much higher than this. In other words, we use what we consider to be a relatively high burial rate to avoid underestimating the magnitude of this sink relative to the anoxic sink, rendering this portion of the budget conservative for the conclusions presented here. Parameters for our modern balanced Cr budget are shown in Fig. S2 and Table S4.

**Hydrothermal Cycling of Mo and Cr.** The systematics of Mo and Cr in hydrothermal systems and the effects of hydrothermal processes on the Earth surface cycles of Mo and Cr have not been explored in detail, but we can place some basic constraints on the possible effects of high- and low-temperature seawater–basalt interaction on the mass balances of Mo and Cr in the ocean. The water flux through a high-temperature hydrothermal system ( $F_{(ht)}$ ; in  $\text{kg}\cdot\text{y}^{-1}$ ) can be estimated as (64)

$$F_{(ht)} = \frac{Q_{(ht)}}{\Delta T_{(ht)} c_p},$$

where  $Q_{(ht)}$  is the hydrothermal heat flux,  $\Delta T_{(ht)}$  is the seawater temperature anomaly, and  $c_p$  is the specific heat of seawater (at



seafloor pressure and vent fluid temperature). We can combine this with a concentration anomaly for a given metal ( $\Delta[\text{Me}] = [\text{Me}]_{\text{SW}} - [\text{Me}]_{\text{fluid}}$ ) to estimate a high-temperature hydrothermal flux to/from seawater ( $F_{\text{hyd}}$ ) as

$$F_{\text{(ht)}} = \frac{Q_{\text{(ht)}}}{\Delta T_{\text{(ht)}} c_p} \Delta[\text{Me}],$$

Results of this calculation for both Mo and Cr are shown in Table S5. These calculations suggest that high-temperature seawater–basalt interaction represents a removal flux of both Mo and Cr that is very small relative to the riverine flux of either element. We note that such estimates are inherently imprecise, given uncertainties in the magnitude of on-axis heat flow (ref. 64 and references therein) and analytical difficulties associated with obtaining unadulterated fluid chemistry. In the case of high-temperature fluids, it is most likely that these concentrations have been perturbed by mixing with seawater Cr and/or Mo, which would cause us to underestimate the magnitude of these sink terms. However, this should have a negligible effect on our result, given that reported concentration anomalies indicate near-complete removal of both elements during high-temperature seawater–basalt interaction (Table S5). Assuming complete removal of seawater Mo from the circulating fluid (i.e.,  $\Delta[\text{Mo}] = 107 \text{ nM}$ ) would increase our estimated high-temperature removal flux from 0.85 to 0.91% of the total input flux. Making the same assumption for Cr (i.e.,  $\Delta[\text{Cr}] = 4 \text{ nM}$ ), would have a trivial effect on the estimated high-temperature removal flux.

Low-temperature, off-axis hydrothermal systems are a much more difficult problem to address. Pristine vent fluid composition is not well constrained for many settings, but, more importantly, the global water flux through such systems is very poorly constrained. Given that the temperature anomaly is probably small, a much larger water flux would be necessary to dissipate the requisite heat flow. As a result, even a very small concentration anomaly may result in a significant flux to/from seawater on a global scale. Magnesium ( $\text{Mg}^{2+}$ ) substitutes readily for calcium ( $\text{Ca}^{2+}$ ) during seafloor basalt alteration (65), and is removed from seawater during hydrothermal fluid evolution at both high and low temperature (66–68). Using the above method of calculation, the high-temperature removal flux of  $\text{Mg}^{2+}$  from seawater can be estimated as  $\sim 1.3 \times 10^{12} \text{ mol}\cdot\text{y}^{-1}$ . By combining the global discharge rate used above with a global average riverine  $\text{Mg}^{2+}$  concentration of  $128 \mu\text{mol}\cdot\text{kg}^{-1}$  (69), we derive a global riverine  $\text{Mg}^{2+}$  flux of  $\sim 5.0 \times 10^{12} \text{ mol}\cdot\text{y}^{-1}$ . If we assume that the balance between the riverine flux and removal during high-temperature seawater–basalt interaction is made up by low-temperature flow, we can use the  $\text{Mg}^{2+}$  concentration anomaly ( $\Delta[\text{Mg}^{2+}] = [\text{Mg}^{2+}]_{\text{SW}} - [\text{Mg}^{2+}]_{\text{fluid}}$ ) of well-constrained diffuse flow systems such as that along the Juan de Fuca Ridge to calculate an approximate water flux through such systems of  $9.5 \times 10^{13} \text{ kg}\cdot\text{y}^{-1}$ .

Combining this estimated water flux with available chemical anomalies for Mo and Cr allows us to place rough limits on the magnitude of the low-temperature fluxes of these elements to seawater (Table S6). These may be upper limits given available constraints, as the calculations assume no other removal fluxes of  $\text{Mg}^{2+}$  from seawater [i.e., uptake during carbonate burial or clay mineral alteration during “reverse weathering” reactions (70)]. We suggest that although low-temperature fluxes are likely to be somewhat larger than those that occur during on-axis fluid flow, they are still a relatively small fraction of the corresponding riverine fluxes. Given the framework outlined above, it is highly unlikely that the flux of either element will exceed  $\sim 10\%$  of their respective riverine inputs. Furthermore, as stated above, sensitivity analysis indicates that our results are not strongly affected by reasonable changes in Cr and/or Mo input fluxes (Fig. S2).

**Offshore Scaling of Metal Burial Rates in the Model.** Our modeling approach essentially involves balancing the modern steady-state cycles of both Cr and Mo and applying a continuous range of perturbations to this balanced cycle to explore the new steady state attained under different oceanic redox regimes. In doing so, we begin with a conventional first-order mass balance formulation. This class of model, often used to explore the dynamics of various chemical tracers in the ocean and their isotope systems, makes the implicit assumption that the burial fluxes characteristic of some particular environment (typically organic-rich continental margin sediments or marginal restricted basins) can be universally applied to extremely large regions of the seafloor. In other words, it is assumed that a burial rate characteristic of, say, the Peru margin can be applied to the abyssal realm of the ocean. This is almost certainly physically unrealistic, as open ocean settings are characterized by much lower bulk sediment fluxes, and, in particular, organic carbon fluxes (71–74). As a result, if a particular region of the abyssal ocean becomes authigenically active for some chemical constituent of seawater, it can be expected that the removal rates of that constituent into the sediment column will be much lower than those seen in more marginal settings. The net result will be a system that is overly sensitive to perturbation, as burial fluxes in large regions of the deep sea will be overestimated. This dilemma, inherent in conventional first-order mass balance analysis, has been noted by some previous work (75, 76) but has not been explored in detail. This problem is particularly acute for redox-sensitive transition metals, such as Mo and Cr, given that the organic matter flux is typically thought to be directly involved in metal sequestration (e.g., ref. 36).

We have attempted to alleviate this problem by adding a “pseudospacial” dimension to the conventional one-box ocean mass balance approach. We take an algorithm used in global diagenetic models (77) for organic carbon flux to the seafloor as a function of depth, which is then coupled to a polynomial function fitted to bathymetric data for the modern ocean (78). We then use a burial flux ratio ( $R_{\text{Me/C}}$ , where Me refers to Mo or Cr) for each element, a tuned parameter resulting in a relationship that encodes a decrease in local (and globally averaged) metal burial rates as larger regions of the seafloor become authigenically active. Values for  $R_{\text{Me/C}}$  are tuned to reproduce the modern condition (i.e., the modern globally averaged burial rates at  $\sim 0.1\%$  seafloor anoxia; Fig. S4). The essential concept here is that a given region of the seafloor has a characteristic burial capacity for either Cr or Mo, regulated to first order by the relative carbon flux through the water column and to the sediments, and that this burial capacity will only be reached when a region of the ocean achieves the requisite redox characteristics for each metal.

We stress that because the metal burial rates are derived by using a tunable ratio, this pattern is not explicitly dependent on the absolute value of the carbon flux to the seafloor at a given depth—rather, it hinges on the observation that carbon fluxes to the seafloor will decrease as one moves out into the deep sea, with the first-order topology depicted in Fig. S3. This is important, as dramatically different redox structures within the ocean, extreme differences in the composition of primary producing communities, mineral ballasting, etc., might be expected to result in significant differences in the absolute value of the carbon flux to the seafloor within different regions of the ocean. However, we consider it unlikely that the basic pattern of an offshore decrease in carbon fluxes has changed much throughout Earth’s history on a global scale. In addition, although the basic bathymetry of the ocean has doubtless changed throughout Earth’s history, we consider the modern depth–area curve to represent a reasonable first approximation. This approach must ultimately be refined if used in efforts to delineate more subtle changes in ocean redox, or if applied to periods during which continental

configuration and/or bathymetry are better constrained, but we contend that it provides a much more realistic depiction of the sensitivity of Cr and Mo mass balance to perturbation than previous model treatments. Further work should focus on the development and implementation of more spatially explicit approaches for dealing with the effects of seafloor redox perturbation on biogeochemical cycling and isotope systematics, for example coupling efficient models of benthic diagenesis that can be forced by gridded domains (79) to Earth system models of intermediate complexity (e.g., GENIE; ref. 80).

**Prescribed Perturbations in the Model and the Role of Reducing Sediments.** As discussed above, our model analysis involves balancing the modern steady-state cycles of Cr and Mo, applying a continuous range of perturbations to seafloor redox state, and establishing the ultimate steady-state conditions and local burial rates attained by the model system. Because our model includes a representation of offshore decreases in authigenic burial rates, essentially a spatial component, we must make some explicit assumptions about the basic seafloor environments in which perturbations begin and expand.

We assume first that ~5% of the shallow seafloor remains essentially authigenically neutral unless it becomes absolutely necessary to encroach upon this area (i.e., above 95% seafloor anoxia or euxinia). This assumption is meant to encompass coastal sediments deposited within the well-oxygenated mixed layer of the ocean. In addition, we assume that if atmospheric oxygen levels are low enough such that large portions of the oceanic mixed layer are anoxic, then the vast majority of the ocean will almost certainly be anoxic as well, effectively rendering the exercise moot and making our conclusions with respect to anoxia rather self-evident without changing our conclusions with respect to euxinia. Perturbations are then applied by expanding a given redox state (anoxic or euxinic) from the shallow shelf out into the deep sea. An important corollary of this approach is that during a given perturbation the first environments to become authigenically active are characterized by the highest metal burial rates. We view this as generally justifiable on mechanistic grounds, as elevated carbon fluxes through the water column and water column oxidant depletion are most commonly seen along ocean margins.

However, it is important to entertain the possibility that the nature of perturbations to seafloor redox may not be the same for Cr and Mo. For example, given that deep-sea anoxia during the mid-Proterozoic was most likely caused by gas-exchange constraints expressed in deep-water formation regions (81), rather than local reductant (i.e., carbon) input, it may be argued that large regions of the deep sea would first become anoxic and authigenically active for Cr, whereas euxinic environments driven by the combined effects of more reducing source waters and local carbon flux would be limited to marginal environments. In effect, this would result in less efficient Cr removal and similar Mo removal compared with the results presented here, which would in turn require a larger area of marine anoxia for a given Cr reservoir change. Thus, to remain conservative we prescribe that perturbations to both models begin and expand from settings where metal accumulation rates are highest. The reverse scenario, in which euxinia develops first in the abyssal realm of the ocean but anoxia is confined to the shelves, is difficult to imagine simply because of regional variability in carbon flux.

Another important assumption that is made in our modeling exercise is that the seafloor area of reducing sediments is fixed at a constant value (~1.9% for the Mo model and ~4.9% for the Cr model). However, it is reasonable to expect that if the ocean becomes less oxygenated on a global scale there should be a first-order expansion of reducing sediment environments. With respect to our basic conclusions, it is clear that this is a much larger concern for Cr than for Mo. Expanding the reducing sediment sink in the Mo model would only serve to decrease the extent of

euxinic seafloor inferred for a given calculated enrichment. In other words, our interpretation that the mid-Proterozoic Mo enrichment record in euxinic shales implies relatively limited euxinic seafloor is rendered conservative by neglecting the expansion of reducing sediments in the model, and our conclusion that euxinia represents a small relative fraction of overall anoxia will remain unchanged. In the case of Cr, it might be argued that expansion of the reducing sediment sink together with expanding anoxia could result in our model significantly overestimating the amount of anoxic seafloor necessary to drive shifts in the seawater Cr reservoir. We consider this a problem that is somewhat scale-dependent, and that it is unlikely to change our fundamental conclusions for two reasons. First, in our model experiments we have artificially enhanced the impact of the reducing sediment sink, by choosing a relatively high Cr burial rate and by specifying that this burial rate applies to ~5% of the seafloor in addition to the expansion of anoxia in shelf environments. When we consider that the offshore scaling of metal burial rates (Fig. S4) should equally well apply to reducing sediment environments, this essentially amounts to “double counting” ~5% of the seafloor as being both reducing sediments and anoxic, with the highest metal burial rates specified for both. Alternatively, we can envision this as representing the exclusive expansion of anoxia in marginal settings, whereas ~5% of the seafloor offshore is covered by reducing sediments with unrealistically high burial rates. In either case, alternative approaches would need to either expand the reducing sediment sink at the expense of anoxic environments on the shelf, or expand it within the deep sea where metal burial capacity decreases sharply (Fig. S4). Both approaches would yield a comparable (and in some cases smaller) overall removal flux into reducing sediment environments.

Lastly, it is unlikely for very large regions of the seafloor to be characterized by this type of chemical environment at steady-state timescales. Such systems can be driven by sharp redox gradients, as often occurs in modern continental margin settings, but these environments require a rather unique combination of extremely high organic matter (i.e., reductant) loading and a degree of bottom-water ventilation such that the system does not become truly anoxic. Such sharp redox gradients will be difficult to maintain across large regions of the deep sea as a result of generally attenuated local organic carbon flux to offshore sediments. Alternatively, such a system can be driven by oxidant limitation. However, it is difficult to imagine this kind of system persisting on an extremely large scale, as it is poorly redox-buffered—small changes to circulation or carbon flux will result in the development of either true anoxia or increased bottom water O<sub>2</sub> such that the environment becomes effectively oxic with respect to metal burial.

**Using the Model to Calculate Authigenic Metal Enrichments.** From a qualitative perspective, it is difficult to avoid the conclusion that the coupled enrichment records require much more pervasive anoxia than that implied by equivalent Phanerozoic settings, but also that the relative fraction of anoxia represented by sulfidic deposition was not large. Our attempt to place more quantitative constraints on this conceptual interpretation involves using the scaling between seawater reservoir size and metal burial rates (inherent in a first-order mass balance model) to estimate sedimentary enrichments by assuming a bulk MAR in a hypothetical siliciclastic-dominated continental margin setting.

These two parameters (authigenic metal burial rate and bulk sediment MAR) should not be arbitrarily decoupled. This is true arithmetically, as metal burial rates in modern settings are in fact derived from bulk MARs. It is also expected on mechanistic grounds, as higher bulk MARs result in more rapid delivery of reactive mineral surfaces and organic carbon, and more rapid and efficient burial of authigenically sequestered elements. Indeed, there is good evidence from a range of modern (82) and ancient (83) settings that metal burial rates will scale in a general sense

with bulk sediment MARs—in other words, metal enrichments will not simply scale linearly with changes in MAR. This issue is similar to that discussed above, in that an arbitrary decoupling of metal burial rates from bulk MARs is akin to applying a metal burial rate from a continental margin setting to the abyssal realm of the ocean, an approach we consider physically unrealistic.

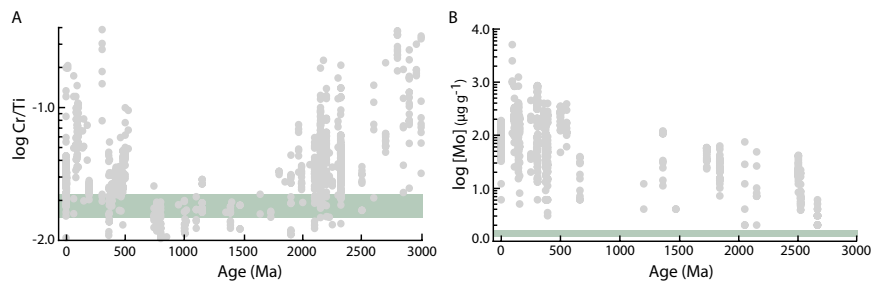
Because this scaling between metal burial rate and bulk MAR is a somewhat broad relationship, we use well-constrained recent Cariaco Basin sediment data as a guide. We separate the range of Cr and Mo burial rates and bulk MAR values constrained for the Cariaco Basin over the last ~20,000 y, and sequentially combine them to explore the effect of a reasonable decoupling between these two parameters (Fig. S5). In an effort to render our estimates conservative, we choose combinations of metal burial rate

and bulk MAR that result in relatively low enrichments for Cr and relatively high enrichments for Mo, and these are presented in the main text (Fig. S5).

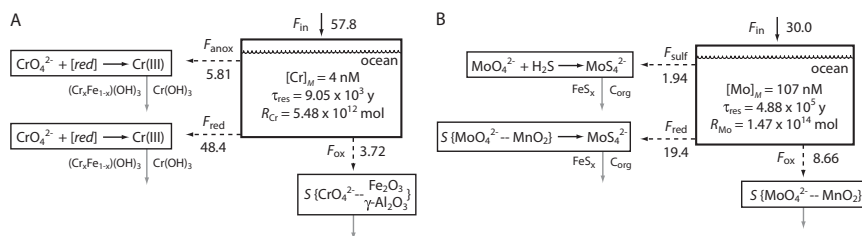
No single combination of parameters will be adequate to describe the entire shale record, but we view this broad range as sufficient to encompass the vast majority of environments represented in our database. It is apparent from this exercise that a very strong decoupling between metal burial rate and bulk MAR values, which we consider unrealistic, is necessary to invalidate our basic conclusions. Furthermore, this condition would need to pertain to every mid-Proterozoic anoxic shale in our database over ~1.5 Ga, whereas fortuitously being alleviated during the early Phanerozoic, a combination of circumstances that that would be improbable.

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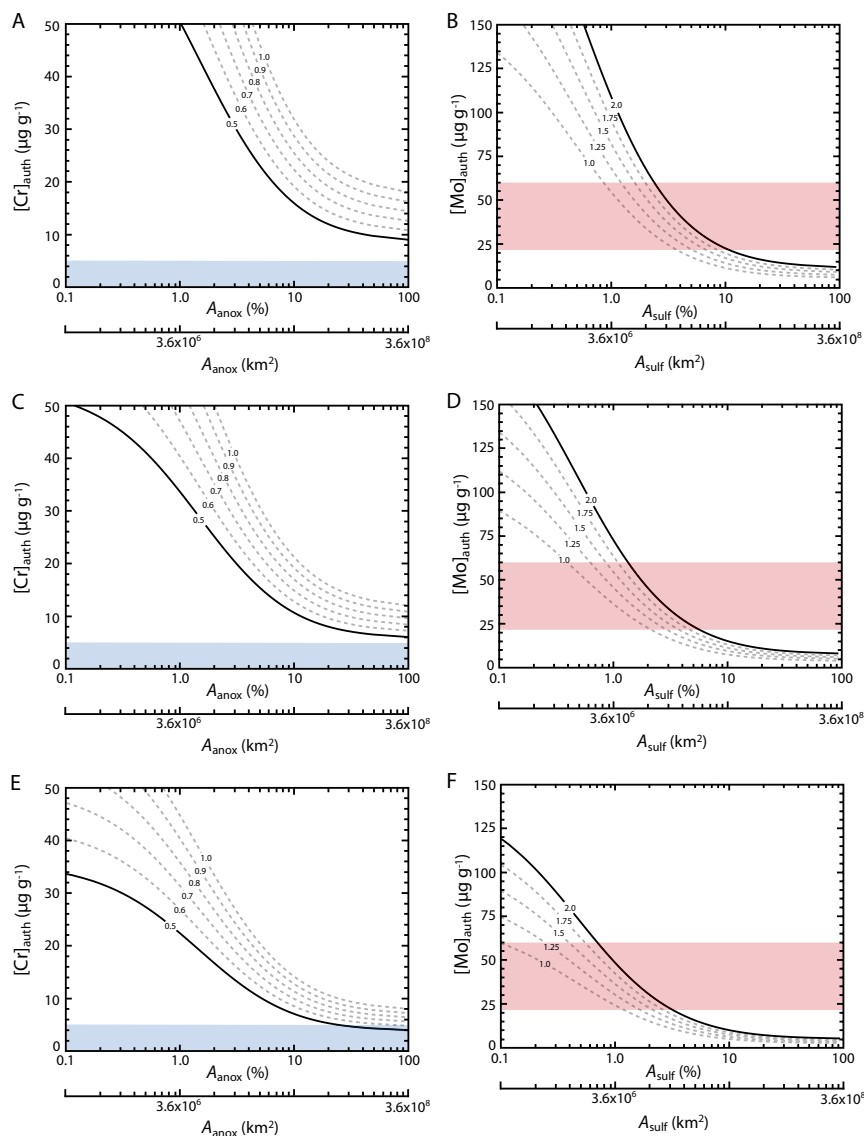


**Fig. S1.** Complete database for Cr (A) and Mo (B) enrichments through time, filtered according to protocols discussed in the text. Shaded boxes denote the range of upper modern crustal concentrations.



**Fig. S2.** Schematic of the global Cr (A) and Mo (B) mass balance models, showing the modern balanced state. Average modern seawater concentrations ( $[Cr]_M$  and  $[Mo]_M$ ), reservoir sizes ( $R_{Cr}$  and  $R_{Mo}$ ), and residence times ( $\tau_{res}$ ) are shown. Dominant authigenic removal processes are depicted schematically for each sink [oxic (ox), anoxic (anox), reducing (red), and sulfidic (sulf) sinks].  $C_{org}$  represents organic carbon, whereas terms shown as  $S\{x-y\}$  denote sorption processes. Hydrothermal fluxes are neglected in our treatment here (see *SI Discussion* for further details). Fluxes are in  $10^7 \text{ mol} \cdot \text{y}^{-1}$ .





**Fig. S5.** Range of metal burial rates and bulk sediment MAR explored in the model. *A*, *C*, and *E* depict estimated authigenic Cr enrichments as a function of anoxic seafloor area at a range of plausible metal burial rates and bulk sediment MAR. The blue box represents our conservative threshold for Cr enrichment as constrained by the shale record. *B*, *D*, and *F* depict estimated authigenic Mo enrichments as a function of sulfidic (euxinic) seafloor area at a range of plausible metal burial rates and bulk sediment MAR. The red box represents the 95% confidence interval around the overall mean for the mid-Proterozoic shale enrichment record. Each panel represents a different bulk MAR (increasing from top to bottom, and depicting a range of a factor of 1.5 around  $1.0 \times 10^{-2} \text{ g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$ , the approximate value for deep sediments of the modern Cariaco Basin) and the contours are labeled by authigenic metal burial rate (in  $\mu\text{g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$ ). The solid black curves are those depicted in the main text.

## Other Supporting Information Files

[Table S1 \(DOCX\)](#)

[Table S2 \(DOCX\)](#)

[Table S3 \(DOCX\)](#)

[Table S4 \(DOCX\)](#)

[Table S5 \(DOCX\)](#)

[Table S6 \(DOCX\)](#)