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Fully oxygenated water columns over continental shelves before the Great Oxidation Event

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Abstract

Late Archaean sedimentary rocks contain compelling geochemical evidence for episodic accumulation of dissolved oxygen in the oceans along continental margins before the Great Oxidation Event. However, the extent of this oxygenation remains poorly constrained. Here we present thallium and molybdenum isotope compositions for anoxic organic-rich shales of the 2.5 billion-year-old Mount McRae Shale from Western Australia, which previously yielded geochemical evidence of a transient oxygenation event. During this event, we observe an anti-correlation between thallium and molybdenum isotope data, including two shifts to higher molybdenum and lower thallium isotope compositions. Our data indicate pronounced burial of manganese oxides in sediments elsewhere in the ocean at these times, which requires that water columns above portions of the ocean floor were fully oxygenated: all the way from the air-sea interface to well below the sediment-water interface. Well-oxygenated continental shelves were likely the most important sites of manganese oxide burial and mass-balance modeling results suggest that fully oxygenated water columns were at least a regional-scale feature of early-Earth's oceans 2.5 billion years ago.

The extent of dissolved O₂ accumulation in Earth's oceans before the Great Oxidation Event remains poorly understood (GOE; ~2.4 to 2.3 Ga¹). Multiple lines of geochemical evidence indicate that O₂ was produced by cyanobacteria in the surface ocean well before

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accumulating in the atmosphere during and after the GOE²⁻⁸. Models indicate that cyanobacteria in the surface ocean were capable of promoting mild accumulation of dissolved O₂ (up to 25 μM⁹) in shallow waters under a predominately anoxic atmosphere, perhaps extending across large areas of the ocean¹⁰. However, it is difficult to test these models because existing geochemical proxies cannot easily be used to assess the breadth and depth of ocean oxygenation.

A case has been made for widespread oxygenation of shallow waters before the GOE in continental margin environments based on carbon isotopes in bulk rock and kerogen from 2.7 Ga carbonate sedimentary rocks². However, this prior work could not determine whether O₂ accumulation was restricted to surface waters or if it extended deeper in the water column, let alone whether oxygenation reached bottom-waters and sediments (i.e., a fully oxygenated water column).

A fully oxygenated water column at 2.6–2.5 Ga was inferred from black shales (upper Nauga Formation, Ghaap Group, South Africa) enriched in Re but not Mo relative to average crustal abundances³. This geochemical signature occurs when O₂ is present in pore waters at a depth of up to about one centimeter below the sediment-water interface, when Fe(III) becomes the dominant electron acceptor during organic matter oxidation and sulfide accumulation is low^{11,12} (Figure 1, panel A). However, this evidence was restricted to a single continental margin (Griqualand West Basin) and could not be extrapolated to the wider oceans.

If fully oxygenated water columns on continental margins were a widespread feature of pre-GOE oceans, then Mn oxide burial in sediments beneath these settings would also have been widespread. In the modern ocean, O₂ in marine bottom waters and sediments readily oxidizes dissolved Mn(II) and Mn(III) to insoluble Mn(IV)-bearing minerals that precipitate out of solution^{13,14}. In contrast, Mn oxides do not form under anoxic conditions, nor are they buried in anoxic marine sediments. Even if formed under O₂-rich conditions, Mn oxides undergo reductive dissolution shortly after being exposed to anoxic conditions within the water column or sediments¹³⁻¹⁵. Manganese oxides are highly unstable when O₂ is absent because in such conditions they are an efficient electron acceptor¹⁶. Therefore, appreciable Mn oxide burial today only occurs where water columns are fully oxygenated and O₂ persistently penetrates sediment pore waters¹⁴. In Earth's past, Mn oxides should have also been buried where O₂ penetrated deeply into marine sediments. This could have occurred under more oxidizing conditions than those identified by Kendall et al. (2010) in the Nauga Formation shales, where Re abundances are elevated but Mo abundances are negligible. Specifically, Mn oxide burial requires penetration of O₂ well beyond one centimeter below the sediment water interface and occurs before Fe(III) becomes the primary electron acceptor during organic carbon oxidation^{14,16} (e.g., Figure 1, Panel B).

Here, we pair Tl and Mo isotope data from the late Archaean (~2.5 Ga) black shales of the Mt. McRae Shale (Hamersley Basin, Western Australia) to track the extent of marine Mn oxide burial before the GOE. The isotopic cycling of both Tl and Mo in the ocean is directly linked to global Mn oxide burial fluxes^{17,18}. Therefore, their paired application is a powerful way to infer the extent of fully oxygenated water columns at a regional-to-global scale, in

contrast to other proxies (e.g., Re vs Mo enrichments and¹¹ sedimentary Fe speciation¹⁹) that focus only on redox conditions in the local water column.

Pairing Tl and Mo isotopes to track paleoredox conditions

The use of Tl isotopes as a paleoredox proxy is relatively new^{17,20,21}, but builds on extensive prior study of Tl isotope systematics. The Tl isotope composition of modern seawater [reported in epsilon notation: $\epsilon^{205}\text{Tl}$, where $\epsilon^{205}\text{Tl} = ({}^{205}/{}^{203}\text{Tl}_{\text{sample}}/{}^{205}/{}^{203}\text{Tl}_{\text{NIST-997}} - 1) \cdot 10^4$] is homogenous and lighter than that of bulk continental crust ($\epsilon^{205}\text{Tl}_{\text{seawater}} = -6.0 \pm 0.3$ ^[18,22], compared to $\epsilon^{205}\text{Tl}_{\text{bulk-crust}} = -2.1 \pm 0.3$ ^[23]). The light $\epsilon^{205}\text{Tl}$ in modern seawater is a result of preferential removal of isotopically heavy Tl from seawater by Mn oxides in well-oxygenated marine sediments²⁴. Importantly, the contemporaneous seawater $\epsilon^{205}\text{Tl}$ signature is captured and preserved in sediments from anoxic and sulfidic (i.e. euxinic) basins¹⁸. Therefore, Tl isotope studies of sedimentary rocks deposited under euxinic conditions provide a means to track ancient seawater $\epsilon^{205}\text{Tl}$ signatures, which should vary in response to changes in Mn oxide burial fluxes. In support of this application, two recent studies used Tl isotope compositions in Mesozoic shales deposited in locally euxinic conditions to track changes in Mn oxide burial fluxes before, during, and after Oceanic Anoxic Events, documenting episodes of significant marine deoxygenation^{20,21}.

Molybdenum isotopes are a more established proxy also shown to be sensitive to marine Mn oxide burial²⁵. The modern seawater Mo isotope composition [reported in delta notation: $\delta^{98}\text{Mo}$, where $\delta^{98}\text{Mo} = (({}^{98}/{}^{95}\text{Mo}_{\text{sample}}/{}^{98}/{}^{95}\text{Mo}_{\text{NIST-SRM-3134}} - 1) \cdot 10^3) + 0.25\%$ ^[26]] is heavier than that of bulk continental crust ($\delta^{98}\text{Mo}_{\text{seawater}} = 2.34 \pm 0.10\%$ ^[26], compared to $\delta^{98}\text{Mo}_{\text{bulk-crust}} = 0.47 \pm 0.12\%$ ^[27]). This heavy seawater $\delta^{98}\text{Mo}$ composition is due largely to preferential removal of lighter-mass Mo isotopes by adsorption to Mn oxides in well-oxygenated marine sediments²⁵. Similar to Tl, this heavy seawater $\delta^{98}\text{Mo}$ value is captured in strongly euxinic settings where Mo removal from bottom waters is nearly quantitative²⁸.

It is advantageous to measure Tl isotopes in addition to Mo isotopes because Mo isotope interpretation is complicated by alternative fractionation pathways that do not affect Tl isotopes. For example, processes that occur during continental weathering²⁹ and riverine transport³⁰ can remove isotopically light Mo (but see reference 31), but do not cause measurable Tl isotope fractionation²³. Weakly sulfidic marine sediments also incorporate lighter-mass Mo isotopes²⁸ but impart no known isotopic effect on Tl¹⁸. Iron oxides can remove isotopically light Mo and drive seawater to heavy $\delta^{98}\text{Mo}$ values³², but are unlikely to fractionate Tl isotopes because Fe oxides lack the ability to oxidize Tl(I) to Tl(III), which is what drives isotopic fractionation during sorption to Mn oxides^{24,33}. This study is the first to pair both proxies in the same sample set.

Anti-correlation of Mo and Tl isotopes in the Mt. McRae Shale

We focus on the 2.5 Ga Mt. McRae Shale from Western Australia in drill core ABDP9 because black shales from the upper part of this formation host convincing evidence for a widespread oxygenation episode predating the GOE^{5,6,34-40}. These rocks are an ideal archive for tracking fluctuations in seawater Tl and Mo isotope compositions at 2.5 Ga

because they were deposited in locally euxinic conditions³⁷ that favor preservation of seawater $\delta^{98}\text{Mo}$ and $\epsilon^{205}\text{Tl}$ values (Figure 1; see supplement for more information about the Mt. McRae Shale).

Molybdenum isotope signatures much heavier than those in igneous crustal rocks were previously found in the Mt. McRae Shale (and in coeval shales from South Africa⁴¹) but could not be definitively ascribed to Mn oxide burial elsewhere in the ocean³⁸. If Mn oxides were being buried at this time, $\epsilon^{205}\text{Tl}$ should also be fractionated relative to bulk continental crust. An anti-correlation between $\epsilon^{205}\text{Tl}$ and $\delta^{98}\text{Mo}$ is expected because fractionation incurred during Mn oxide adsorption is in opposing directions for the two isotope systems^{17,18}.

We find that $\epsilon^{205}\text{Tl}$ is systematically lighter during two distinct intervals of the euxinic upper shale (US) member in the Mt. McRae Shale: 153.30–144.36 m (US1) and 134.17–126.15 m (US3) (average $\epsilon^{205}\text{Tl} = -2.65$) (Figure 2). $\delta^{98}\text{Mo}$ exhibits heavier values in these same intervals (average $\delta^{98}\text{Mo} = 1.37\text{‰}$), revealing the predicted anti-correlation with $\epsilon^{205}\text{Tl}$. Compared to these intervals, Tl and Mo isotope compositions for 144.26–135.58 m (US2) are heavier (average $\epsilon^{205}\text{Tl} = -2.39$, p -value = 0.05, two-tailed unpaired t-test) and lighter (average $\delta^{98}\text{Mo} = 1.23\text{‰}$, p -value $\ll 0.05$), respectively. A cross-plot of shale samples with both isotope measurements from the US reveals a statistically significant anti-correlation (p -value = 0.01). In contrast to the euxinic US, isotope compositions are invariant in the non-euxinic lower shale member (170–190 m core depth, see supplement for discussion of this interval, and interpretation of concentration data).

Fully oxygenated regional water columns on continental shelves

Light $\epsilon^{205}\text{Tl}$ and heavy $\delta^{98}\text{Mo}$ in US1 and US3 provide strong evidence for the formation and subsequent burial of Mn oxides elsewhere in the ocean at these times. To drive the observed isotopic trends, water columns needed to have been fully oxygenated over portions of the ocean floor. Most likely, Mn oxide burial at 2.5 Ga occurred in shallow oxygenated shelf environments where O_2 produced within the surface ocean by cyanobacteria was capable of being continuously transferred to underlying waters and marine sediments (e.g., the environment illustrated in Figure 1).

Alternative local basin controls or processes in the sedimentary environment where the Mt. McRae Shale was deposited cannot explain the observed isotope trends in the upper shale member. In a modern euxinic basin that is not well-connected to the open ocean (i.e., the Black Sea), Tl isotopes in the local water column and underlying sediments are heavier than the open-ocean signature¹⁸. If the Hamersley Basin was also not well-connected to the open-ocean, then $\epsilon^{205}\text{Tl}$ of the Mt. McRae Shale may have been higher than the open-ocean signature. This would require even lighter seawater $\epsilon^{205}\text{Tl}$ compositions during deposition of US1 and US3, which would then imply an even greater extent of sediment Mn oxide burial elsewhere in the oceans. Furthermore, in modern euxinic settings where Mo is not quantitatively transferred from seawater to sediments, sedimentary $\delta^{98}\text{Mo}$ compositions are always lighter than the coeval seawater signature²⁸. Hence, if Mo removal from euxinic bottom waters in the Hamersley Basin was not quantitative, then seawater $\delta^{98}\text{Mo}$ would be

even heavier than observed in the Mt. McRae Shale, again implying even more significant sediment Mn oxide burial elsewhere in the ocean.

In theory, the observed Tl and Mo isotope shifts might be alternatively explained by “shuttling” of Tl and Mo bound to oxide minerals formed in oxic surface waters to underlying anoxic waters and/or sediments on Late Archaean continental margins, where these elements could then be captured in euxinic sediments. If so, fully oxygenated water columns would not be required to explain the antithetic shifts in Tl and Mo isotopes recorded in the Mt. McRae Shale. However, this notion is not supported by observations in the modern Cariaco Basin, a modern analog environment where Mn oxides are formed in oxygenated surface waters and subsequently transported to euxinic bottom waters and sediments deeper in the basin⁴². An oxide shuttle should cause $\epsilon^{205}\text{Tl}$ in euxinic sediments to be heavier than in surface oxic seawater²⁴. This is not observed, however. Rather, euxinic sediment $\epsilon^{205}\text{Tl}$ in the Cariaco Basin is indistinguishable from overlying seawater (average $\epsilon^{205}\text{Tl}_{\text{euxinic}} = -5.1 \pm 1.3$; 2SD vs. $\epsilon^{205}\text{Tl}_{\text{seawater}} = -5.5 \pm 0.7$; 2SD)¹⁸. One possible explanation for this lack of Tl isotope is that Tl released by Mn oxide dissolution in sulfidic deep waters is first re-mixed and re-homogenized with the dissolved Tl pool prior to Tl capture in pyrite. Regardless, since anoxic sediments in the modern Cariaco Basin *do not* preserve the Tl isotope effects of oxide adsorption¹⁸ even though oxide minerals are shown to be delivered at least transiently to these sediments⁴², a Mn oxide shuttle in redox-stratified marine basins probably had a minimal impact on the Late Archaean seawater Tl isotope mass-balance.

Although there are proposed pathways of Mn oxide formation that do not require O₂, they would not be likely to cause the observed isotopic effects in the upper shale member. Oxidation of reduced Mn in the upper water column by hypothesized Mn-oxidizing phototrophs⁴³ or by UV light⁴⁴ cannot account for burial at the seafloor because underlying anoxic waters and sediments would recycle Mn back into solution [as Mn(II)]^{13,14}. The high abundance of Fe(II) in deep ferruginous waters of the Archaean oceans¹, for example, would readily promote reduction of Mn oxides in anoxic waters. If the water column or sediment pore waters were anoxic, even seasonally¹⁵, reductive dissolution of Mn oxides would release sorbed Tl and Mo. Additionally, invoking an O₂-free explanation to explain the observed isotopic trends requires neglecting the many independent lines of evidence for a “whiff” of O₂ at 2.5 Ga^{5,6,34–40}.

Paleo-seawater $\epsilon^{205}\text{Tl}$ and $\delta^{98}\text{Mo}$ can be estimated directly from the Mt. McRae Shale data and used to reconstruct ocean redox conditions. Measured $\epsilon^{205}\text{Tl}$ values serve as a direct estimate for the coeval seawater signature (as low as -3.57 ± 0.48) because euxinic sediments capture the overlying seawater Tl isotope value¹⁸. The $\delta^{98}\text{Mo}$ recorded in euxinic marine sediments is always equal to or lighter than seawater²⁸, and thus represent a lower limit for the coeval seawater signature (as heavy as $1.56 \pm 0.10\text{‰}$). It is possible, indeed likely, that the Tl and Mo isotope compositions of seawater fluctuated during deposition of the US member of the Mt. McRae Shale. Deposition of this interval is estimated to have occurred over ~11 million years³⁴ and the “whiff” of O₂ was likely a transient episode of even shorter duration³⁹. To estimate ocean redox conditions during peak Mn oxide burial, we use the lightest $\epsilon^{205}\text{Tl}$ and heaviest $\delta^{98}\text{Mo}$ from the US member. During peak Mn oxide

burial, retention of heavier-mass Tl and lighter-mass Mo isotopes would have been maximized, resulting in the lightest $\epsilon^{205}\text{Tl}$ and heaviest $\delta^{98}\text{Mo}$ seawater signatures. Unsurprisingly, the lightest $\epsilon^{205}\text{Tl}$ (-3.57 ± 0.48 epsilon units at 148.75 m) and heaviest $\delta^{98}\text{Mo}$ ($1.56 \pm 0.10\text{‰}$ at 145.74 m) occur during US1, an interval that hosts multiple lines of geochemical evidence for an oxygenation episode^{5,6,34,37–39}.

Using the estimated seawater $\epsilon^{205}\text{Tl}$ and $\delta^{98}\text{Mo}$, ocean redox conditions can be inferred using isotope mass-balance equations as follows:

$$\epsilon^{205}\text{Tl}_{\text{Inputs}} = \epsilon^{205}\text{Tl}_{\text{AOC}}(f_{\text{AOC}}) + \epsilon^{205}\text{Tl}_{\text{oxic}}(f_{\text{Tl-oxic}}) + \epsilon^{205}\text{Tl}_{\text{other}}(f_{\text{other}})$$

and

$$\delta^{98}\text{Mo}_{\text{Inputs}} = \delta^{98}\text{Mo}_{\text{euxinic}}(f_{\text{euxinic}}) + \delta^{98}\text{Mo}_{\text{SAD}}(f_{\text{SAD}}) + \delta^{98}\text{Mo}_{\text{oxic}}(f_{\text{Mo-oxic}})$$

where $\epsilon^{205}\text{Tl}_x$ and $\delta^{98}\text{Mo}_x$ represent the isotopic composition of average oceanic inputs and outputs, and f_x denotes the relative removal flux for each output. For Tl, we designate low-T alteration of oceanic crust (f_{AOC}), well-oxygenated Mn oxide-rich sediments ($f_{\text{Tl-oxic}}$), and “other” (f_{other}) as the three dominant marine outputs. The “other” output signifies Tl removal with no associated isotopic fractionation (e.g., euxinic basins¹⁸). For Mo, similar to recent work, we use euxinic sediments (f_{euxinic}), sediments that are sulfidic at depth (f_{SAD} ; where sulfide is limited to sediment pore waters), and well-oxygenated Mn oxide-rich sediments ($f_{\text{Mo-oxic}}$) as the three outputs⁴⁵ (see supplementary material for more detailed information about modeling, including key assumptions).

The mass-balance model results indicate that well-oxygenated Mn oxide-rich sediments were an important sink for both Tl ($f_{\text{Tl-oxic}} = 6\text{--}21\%$) and Mo ($f_{\text{Mo-oxic}} = 20\text{--}34\%$) at 2.5 Ga. Together, these results suggest that fully oxygenated shelf environments were a common feature on continental margins, at least regionally at 2.5 Ga.

We make no attempt here to convert these fluxes into the areal extent of seafloor because the flux per areal unit into these marine outputs was likely much different in the Archean compared to today. Burial rates of Tl and Mo in modern oxic marine environments that bury Mn oxides are very low, much lower than their burial rates into other modern marine outputs (e.g., burial of Tl during low-T alteration of oceanic crust⁴⁶ and burial of Mo under strong euxinic conditions⁴⁵). For this reason, seafloor area calculations using modern Tl and Mo burial rates and our ancient seawater isotope signature estimates would require the majority of the seafloor at 2.5 Ga to have been oxic. Expansive oxic conditions before the GOE is unlikely because many independent lines of evidence support a predominately anoxic global ocean at this time¹. Most likely, burial rates of Tl and Mo in 2.5 Ga oxic environments were much higher than today. For example, dissolved Mn concentrations in Archean seawater may have been four orders of magnitude higher than today⁴⁷, providing a strong potential for high Mn oxide burial rates in oxic environments, and therefore a stronger potential for Tl and Mo adsorption. Furthermore, the burial rate of Mo (and potentially also of Tl) into euxinic environments could have been much lower than today because sulfate concentrations in Archean oceans were very low⁴⁸. Euxinic conditions in a low-sulfate ocean could have been much weaker than today, lowering the potential for sedimentary retention of Mo. In

summary, a smaller area of 2.5 Ga seafloor burying Mn oxides could conceivably drive a more pronounced seawater Tl and Mo isotope signature effect than today but is difficult to estimate precisely.

Our findings provide a new perspective on marine oxygenation at 2.5 Ga, on the eve of the GOE. Multiple lines of geochemical evidence provide strong support for O₂ in shallow waters of the Hamersley Basin at 2.5 Ga^{5,6,34} and the adjoining Griqualand West Basin^{4,41} (which may have bordered the same ocean basin⁴⁹). However, because Mn oxide burial requires fully oxygenated water columns at 2.5 Ga, our multi-isotope data supports more oxygenated continental shelves over a greater area than previously recognized using other geochemical datasets. Specifically, the inferred seawater $\epsilon^{205}\text{Tl}$ and $\delta^{98}\text{Mo}$ requires fully oxygenated water columns in shelf environments within the Hamersley Basin and adjoining basins(s), and potentially even large portions of the continental margins worldwide. Our results highlight the significant and expanding role of cyanobacteria as engineers of the Archean biosphere, particularly in the runup to the Great Oxidation Event.

Methods:

Tl isotopes

Tl sample preparation and purification were performed in the NIRVANA Laboratory at Woods Hole Oceanographic Institution (WHOI), as well as in Dr. Jeremy Owens' Laboratory at Florida State University (FSU) within the National High Magnetic Field Laboratory (NHMFL). Powdered samples from ABDP9 were leached using a method from previous literature^{17,20}, which has been shown to effectively separate authigenic Tl (i.e. Tl bound to pyrite) from detrital Tl. Each fraction was subsequently digested following procedures discussed in that literature. Ion exchange chromatography was completed using previously described techniques^{51,52}. Similar to recent work²⁰, samples were only subjected to one column pass because Tl concentrations were high and thus very little sample mass was processed.

Tl isotopic analyses were conducted at the WHOI Plasma Mass Spectrometry Facility and at the NHMFL in Tallahassee. At both locations a Thermo Neptune MC-ICPMS was used with an Aridus II desolvating nebulizer sample introduction system. Measurements were made in low-resolution mode utilizing sample-standard bracketing relative to NIST 997 Tl in epsilon notation. External normalization to NIST SRM 981 Pb was utilized to monitor instrumental mass bias, similar to previous studies^{51,52}. Since a known quantity of NIST SRM 981 Pb was added to each sample, Tl concentrations could be calculated during MC-ICPMS analysis using the measured ²⁰⁵Tl/²⁰⁸Pb ratios. Tl isotope values are reported in epsilon notation relative to NIST 997 Tl metal. One USGS shale SCO-1 standard was leached, purified, and analyzed with each sample set to monitor accuracy and showed good reproducibility ($\epsilon^{205}\text{Tl}_{\text{authigenic}} = -2.80 \pm 0.13$, 2SD, n = 8) compared to a recent study: $(-2.92 \pm 0.11)^{(20)}$.

Mo isotopes

All Mo sample digestion, isotope purification, and analysis were completed at the W.M. Keck Foundation Laboratory for Environmental Biogeochemistry at Arizona State University. Quarter cores were cut from ABDP9, powdered, ashed, digested, and concentrations were analyzed using the same techniques employed in previous work³⁴. Enough sample was then taken from the same digested stock solutions to provide 125 ng Mo that was spiked with an optimal amount of calibrated synthetic Mo isotope double-spike (⁹⁷Mo and ¹⁰⁰Mo) before purification via ion exchange chromatography, again utilizing methods from previous studies^{53,54}. The double spike is used for chromatography and instrumental mass fractionation correction.

Isotope ratio measurements were performed on a Thermo Neptune multi-collector ICPMS (MC-ICPMS) in low-resolution mode with an Elemental Scientific Inc. Apex inlet system and using sample-standard bracketing^{38,55}. All measurements were made using the Johnson Matthey Specpure Mo plasma standard (Lot #802309E; RochMo2) as the bracketing standard, and then re-calculated relative to the new international NIST SRM 3134 standard = + 0.25‰⁽²⁶⁾. Samples and standards were analyzed at a concentration of 25 µg/g Mo, which yielded about three volts of signal on mass 98. Samples were analyzed in triplicate (at least), with the average 2SD sample reproducibility being 0.06‰, and the maximum being 0.11‰. Over the 12-month period of Mo isotope analysis for this study, USGS rock reference material SDO-1 was simultaneously processed with each batch of samples to monitor accuracy and showed good reproducibility ($\delta^{98}\text{Mo} = 1.00 \pm 0.09\text{‰}$ 2SD compared to $1.05 \pm 0.14\text{‰}$ from a previous study⁵⁶), as did various analytical replicates (Table 1). Lastly, for each analytical run, a series of standards with varying spike-sample ratios was measured. All samples were within the validated spike-sample range for accurate and precise $\delta^{98}\text{Mo}$ values.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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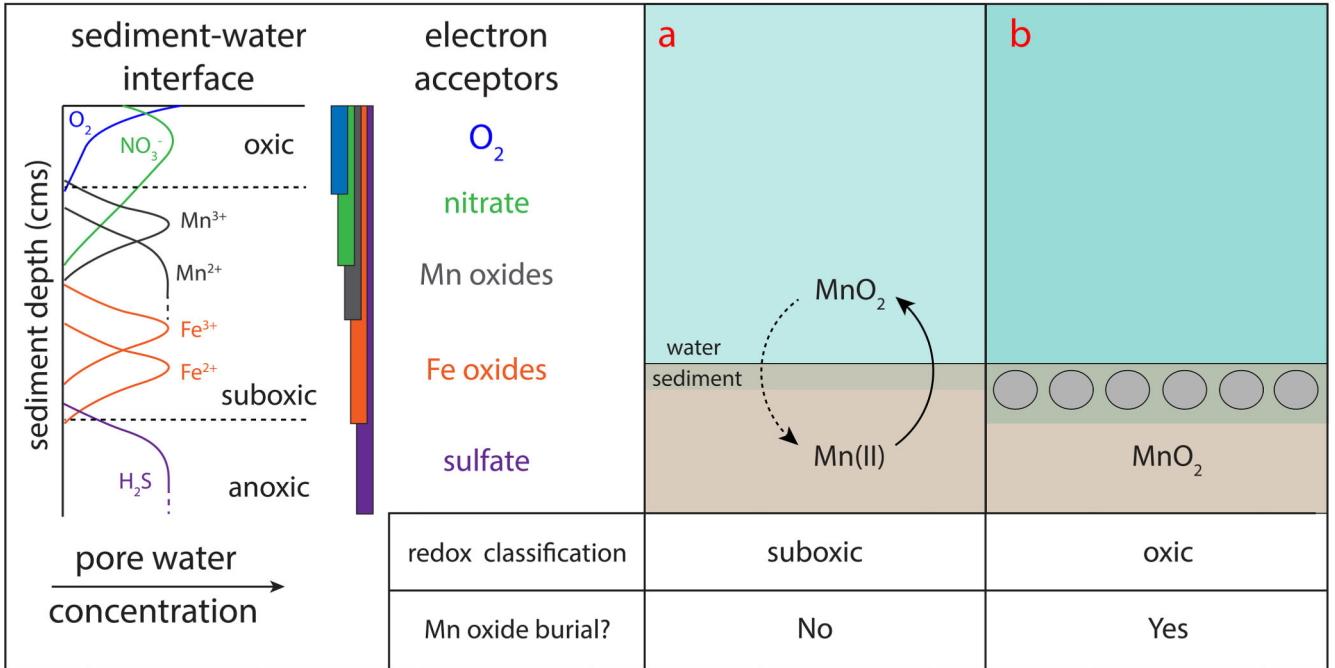
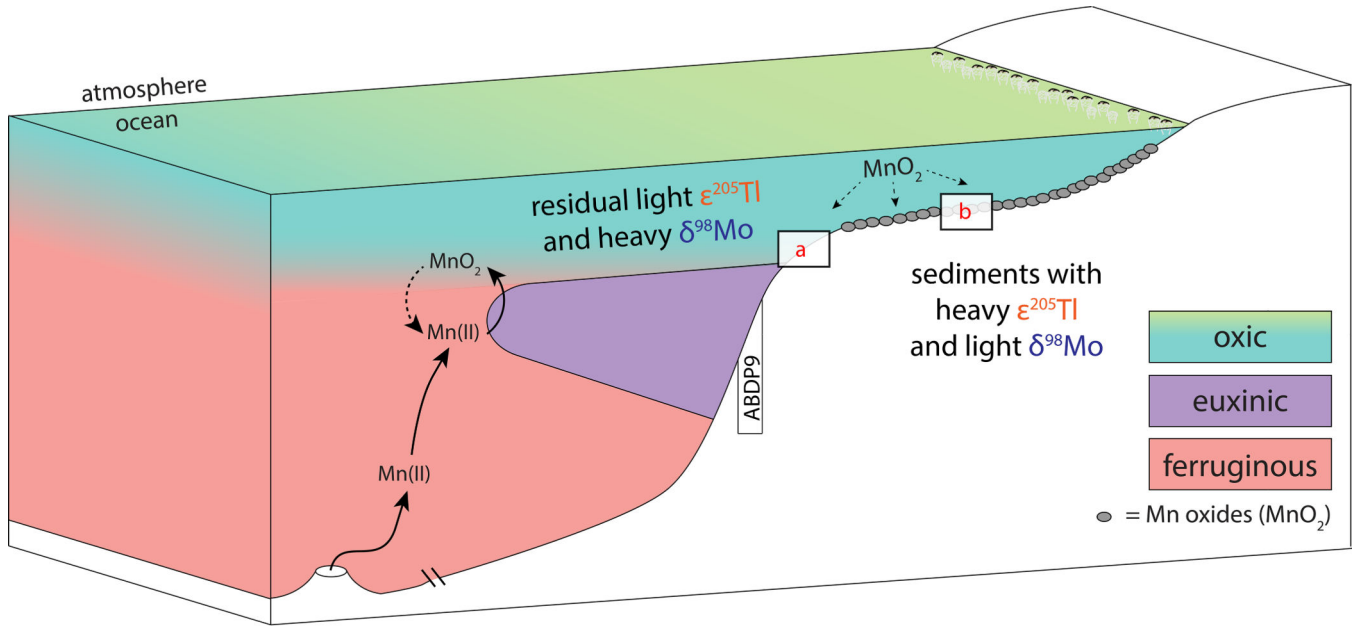


Figure 1. Illustration of a possible well-oxygenated marine margin before the GOE. Evidence exists for sufficient O_2 accumulation in an ancient water column between 2.6 and 2.5 Ga to weakly oxygenate underlying sediments³ (“suboxic”; Panel A). However, O_2 penetration into these sediments was not sufficient to promote Mn oxide burial^{11,12}. If settings capable of burying Mn oxides were present in ancient oceans (“oxic”; Panel B) over a large seafloor area, then seawater Tl and Mo isotope compositions would have decreased and increased, respectively. The Mt. McRae Shale was deposited under locally euxinic conditions³⁷ and should therefore have captured these changes in seawater isotope signatures^{18,28}. Sedimentary redox structure is modified from previous work⁵⁰.

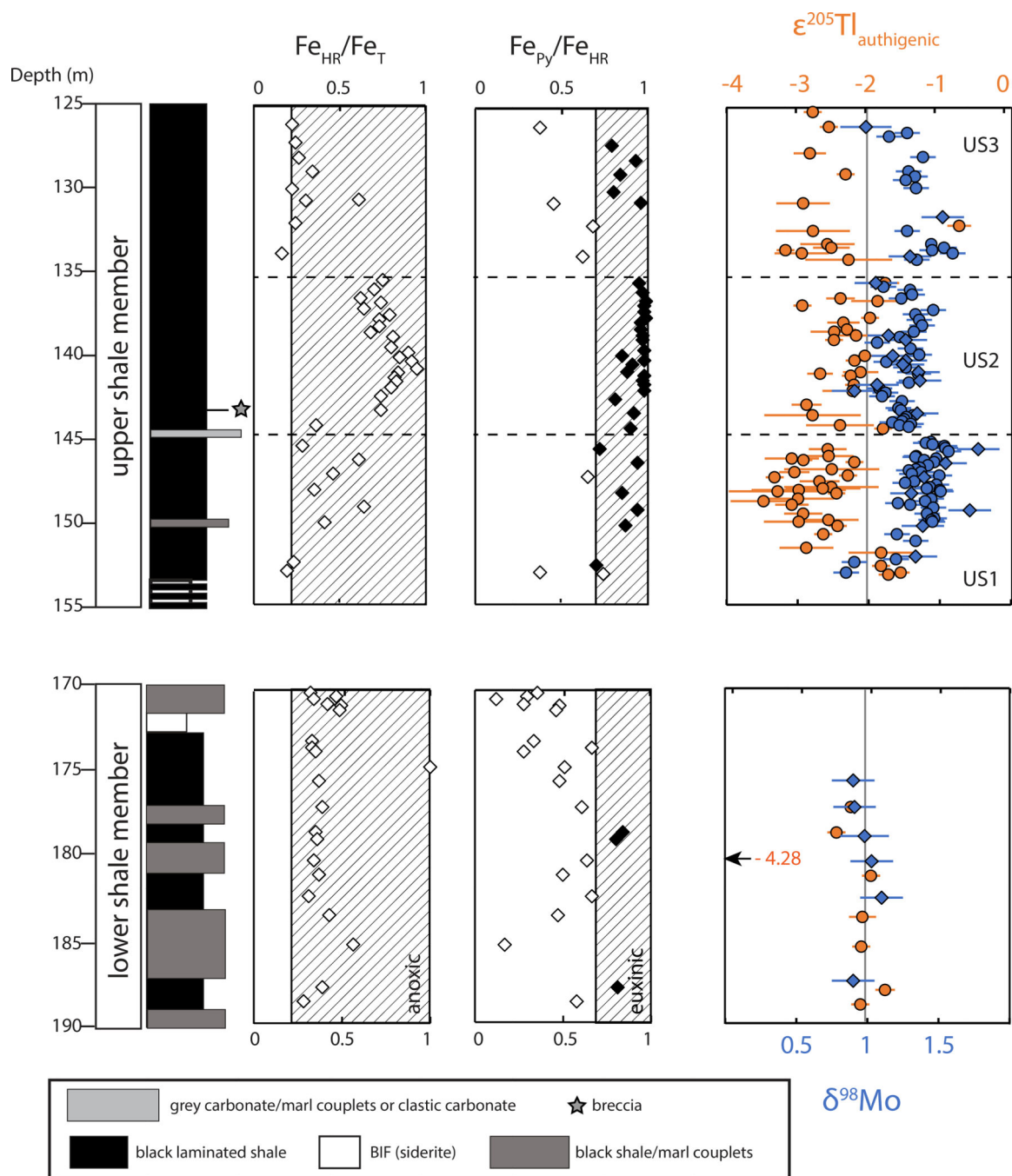


Figure 2. Geochemical profiles in organic-rich shales from the Mt. McRae Shale (orange = $\epsilon^{205}\text{Tl}$, blue = $\delta^{98}\text{Mo}$).

Hatched boxes represent values indicative of anoxic ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.22$) and euxinic ($\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}} > 0.7$) deposition¹⁹. Data that exceed both criteria are in black. Diamonds reflect data from previous work^{37,38} and circles are data from this study. The grey vertical line in the isotope plot represents average isotope compositions from the lower shale member, with the exception of one anomalous Tl isotope value ($\epsilon^{205}\text{Tl} = -4.28 \pm 0.13$ at 180.33 m). All error bars represent the 2SD reproducibility of that sample or the external long-term reproducibility of natural reference materials, whichever is greater.

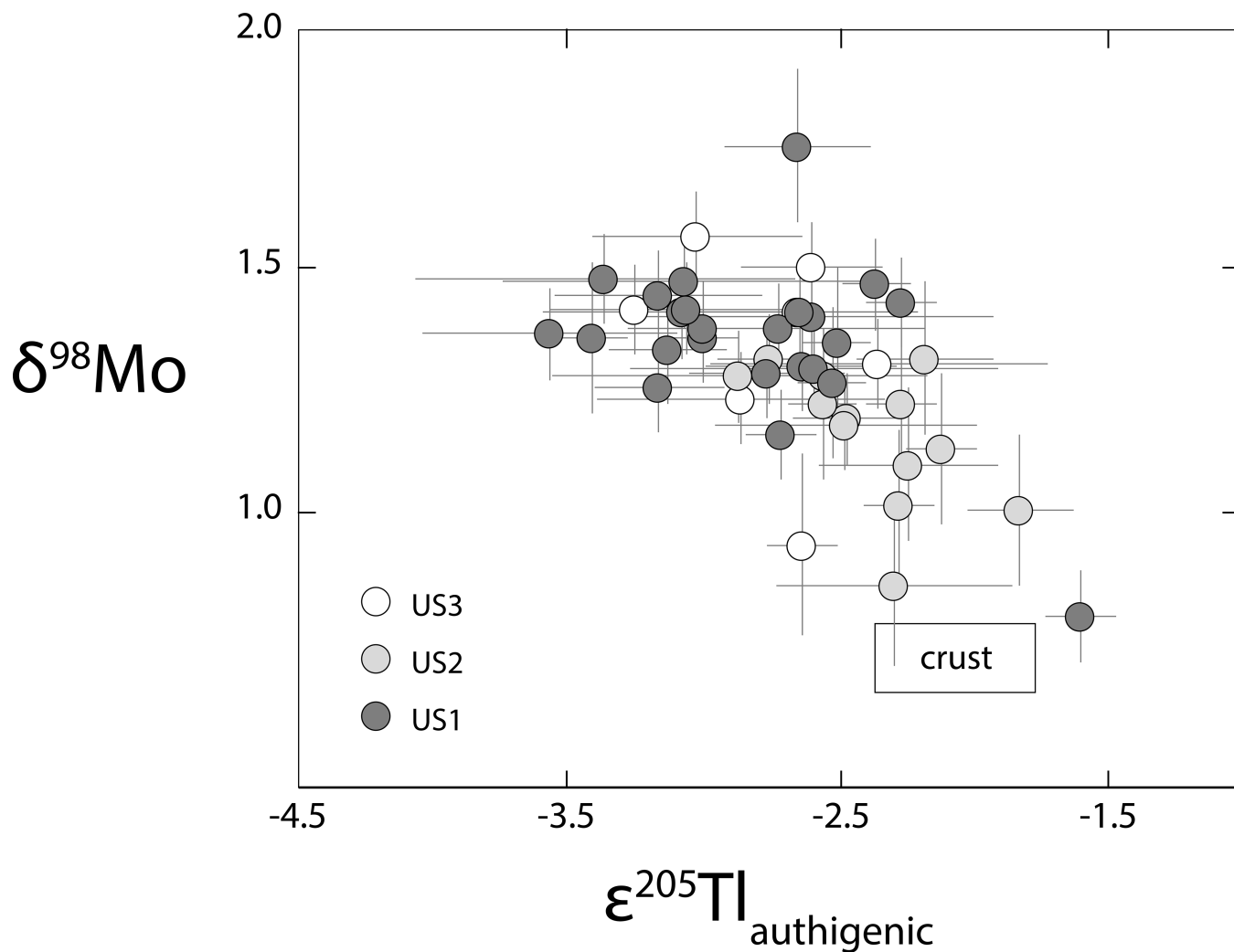


Figure 3. Mo and Tl isotope cross-plot from the upper shale member. The anti-correlation trend in this plot, which is also apparent in Figure 1, is statistically significant (p -value = 0.01). The brown box indicates current estimates for the isotope compositions of bulk continental crust^{23,27}. All error bars represent the 2SD reproducibility of that sample or the external long-term reproducibility of natural reference materials, whichever is greater.

Table 1.Standard solution $\delta^{98}\text{Mo}$ values from this study vs. previous work

Standard	<i>This study</i> ^a	<i>n</i>	<i>Normalized to NIST + 0.25%</i> ^b	<i>Goldberg et al. (2013)</i>
Roch-Mo2	Bracketing std.		-0.09‰	-0.09 ± 0.05‰
ICL-Mo	0.16 ± 0.03‰	38	0.07 ± 0.03‰	0.09 ± 0.05‰
Kyoto-Mo	-0.04 ± 0.05‰	39	-0.13 ± 0.05‰	-0.12 ± 0.06‰
NIST SRM 3134	0.33 ± 0.06‰	45	0.24 ± 0.06‰	0.25‰ (reporting std.)
SDO-1	1.12 ± 0.05‰	45	1.03 ± 0.05‰	1.05 ± 0.14‰

^a Measured relative to Roch-Mo2^b Normalized using $\delta^{98}\text{Mo}_{\text{Roch-Mo2}} = -0.09\text{‰}$ relative to $\delta^{98}\text{Mo}_{\text{NIST}+0.25\text{‰}}$ ⁵⁶

* all reported errors are 2SD of the standard reproducibility