Supplementary Information

The Mt. McRae Shale in drill core ABDP9

The core sampled in this study was drilled in the Pilbara Craton of Western Australia during the summer of 2004 as a part of the Archean Biosphere Drilling Project (ABDP)[34,35]. Drilling took place at 21º59'29.5" S, 117 º25'13.6"E, and the hole azimuth was 186º with a dip of 89º. One-half of the core is housed and curated at the School of Earth and Space Exploration at Arizona State University (ASU). The archived half is housed at the Geological Survey of Western Australia's Perth Core Library.

Sedimentary rocks preserved in the ABDP9 core have experienced only mild regional metamorphism (prehnite-pumpellyite facies; <300ºC) and minimal deformation (gentle folding dips <5º) since original deposition[57]. Geochemical signatures preserved in these rocks are thought to be primary, with no indication of a secondary and metasomatic origin[6,34,39]. Both the upper and lower shale members were deposited below wave base in a marine environment[35,58]. Black shales from the upper shale member previously yielded depositional ages of 2495 ± 14 Ma (145.22-148.32 m depth) and 2495 ± 20 Ma (128.71-129.85 m) using Re-Os geochronometry[34,39]. The lower Mt. McRae Shale in ABDP9 (189.65 – 173 m) contains pyritic black shales, with carbonate/marl interbeds. The first ~2m of the upper Mt. McRae Shale (153.3 – 125.5 m) contains interbedded black shale and siderite. This is followed by ~19m of black shales with frequent pyrite laminae and abundant pyrite nodules, with a few short occurrences of carbonate. Massive pyrite nodules occur in black shales from 134 – 131m. Above this, and until the end of the analyzed section, black shales without massive pyrite nodules again dominate. To best estimate primary depositional chemistry, and not post-depositional diagenetic effects, we avoided pyrite nodules and laminae when possible.

Tl concentration data

Measured $Tl_{authigenic}$ abundances are invariant in the lower shale member (avg. = 1.3 µg/g ± 0.2 SE) and increase at the same depths as whole-rock Mo concentrations in the upper member (Supplementary Figure 2). Peak values (6 µg/g), however, are sustained over a greater range of depths (~145 to 135 m compared to ~147 to 143 m for Mo).

Tl concentration trends mirror those of S from previous work[35], highlighting the slight affinity Tl possesses for sulfides[17,59] (Supplementary Figure 1). This trend is different from that

of Mo most likely because of the redox-sensitivity of Mo not shared by Tl. Increases in the rate of oxidative weathering will enhance dissolution of continental molybdenite (MoS_2) and pyrite, and thus delivery of Mo to the ocean[60]. Tl is only a trace constituent in continental minerals[46], and thus it is unlikely that the delivery rate of Tl to the ocean would be greatly affected under increased oxidative weathering. Instead, the rate of Tl delivery to the ocean would be more sensitive to changes in subaerial volcanism, the primary oceanic Tl source today[46]. Similarly, changes in global marine redox can have a profound effect on the dissolved marine Mo reservoir, but are unlikely to affect the dissolved marine Tl reservoir to the same extent. Changes in the area of sulfidic seafloor – the strongest marine sink of Mo – are largely responsible for driving variations in the size of the global marine Mo reservoir[61]. Sulfidic environments are not a strong sink for Tl in the ocean[18], where removal from seawater is instead dominated by low-temperature hydrothermal alteration of oceanic crust and during adsorption to Mn oxides[46].
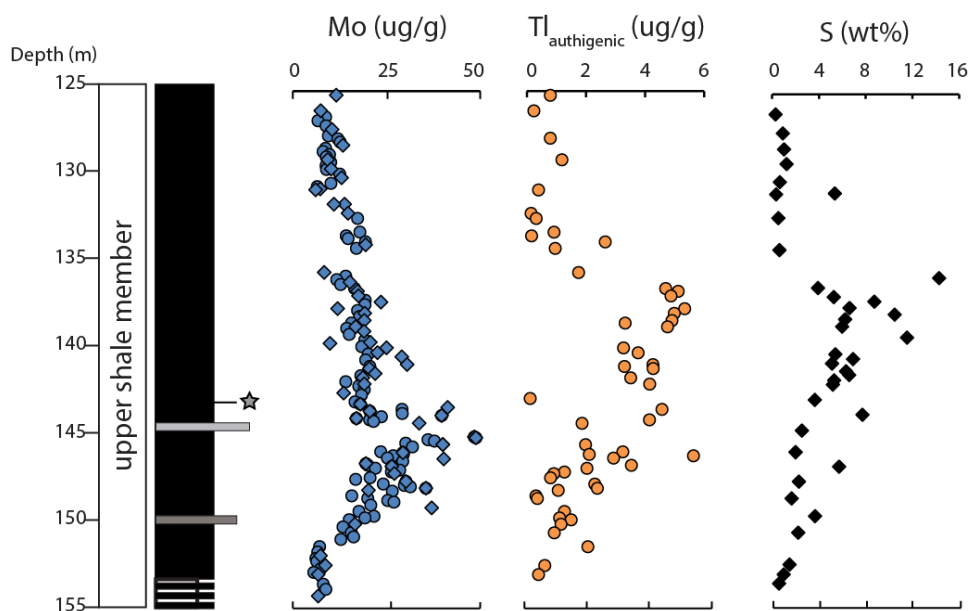
Supplementary Figure 1. **Mo and Tl concentration data from this study from the upper Mt. McRae Shale member, plotted alongside data from previous work.** Concentration measurements from this study are signified by circles. Data from previous work[34,35] are plotted as diamonds. See Figure 1 of the main text for a lithological key.

Mo concentration data

Measured Mo abundances in the upper Mt. McRae Shale mirror the trends from previous lower-resolution work in the same core and are perhaps the most substantial evidence for a "whiff" of oxygen at 2.5 Ga[34] (Supplementary Figure 1). Concentrations rise gradually from ~150 to 145 m, where they reach a peak value of 50 µg/g.

Whole-rock sample digestion liberates Mo from the two primary sources of Mo in shales: authigenic incorporation and detrital minerals, both of which have unique δ^{98}Mo values. Therefore, there is a potential for whole-rock δ^{98}Mo to be diluted by the detrital value (~0.35 – 0.60‰[27]) if the sample contains an appreciable amount of detrital-sourced Mo. The following equation can be used to calculate authigenic δ^{98}Mo (δ^{98}Mo$_{auth}$) by correcting for detrital dilution:

$$\delta^{98}Mo_{auth} = (\delta^{98}Mo_{sample} - \delta^{98}Mo_{detrital} * Mo/X_{detrital} * [X]_{sample} \div [Mo]_{sample}) \div (1 - Mo/X_{detrital} * [X]_{sample} \div [Mo]_{sample})$$

where δ^{98}Mo$_{detrital}$ is the Mo isotope composition of continental detritus and Mo/X$_{detrital}$ is the ratio of Mo (in µg/g) to a non-redox sensitive element (X). By normalizing to a non-redox sensitive element, we assume any surplus in the Mo/X ratio of our samples relative to continental Mo/X is due to enrichment from authigenic Mo. Here, we use aluminum (Al) as our non-redox sensitive element and assume a Mo/Al$_{detrital}$ of 0.13 (Al being in wt%[62]). Results are presented in Supplementary Figure 2 and show that calculated δ^{98}Mo$_{auth}$ closely matches whole-rock values throughout the upper Mt. McRae Shale member regardless of the assumed δ^{98}Mo$_{detrital}$ value.

Isotope trends in the lower Mt. McRae Shale

In contrast to the upper member, deposition of the lower Mt. McRae Shale took place under primarily non-euxinic conditions (i.e. Fe$_{HR}$/Fe$_T$ < 0.70[37]) and makes it difficult to extrapolate seawater trends from sedimentary isotope compositions. Measured δ^{98}Mo are heavier than bulk continental crust (avg. δ^{98}Mo = 0.97‰[38]; see Figure 2 of the Main Text) but may still fall short of the coeval seawater signature because deposition under non-euxinic conditions results in a sedimentary δ^{98}Mo value lighter than seawater[28]. The actual seawater value is impossible to estimate, but the mere fact that it must have been heavier than continental crust implies some mechanism was removing isotopically light Mo (either adsorption to Mn oxides[25], oxidation during riverine and continental weathering[29,30], Fe oxides[32], and/or weakly sulfidic sediments[28]).

The ε^{205}Tl in the lower Mt. McRae Shale are near crustal (~ -2 epsilon units[23]; see Figure 2 of the Main Text) and may indicate little to no fractionation of Tl by Mn oxides in the ocean. Little is known about Tl removal under ferruginous conditions, however, and thus any interpretation of the near-crustal Tl isotope values in the lower Mt. McRae Shale is highly speculative.
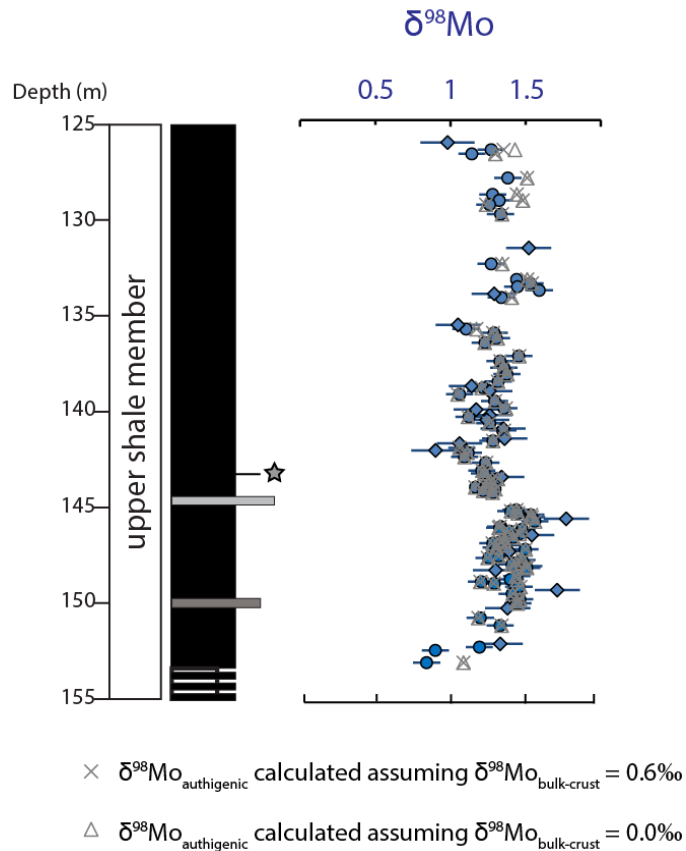
Supplementary Figure 2. Measured bulk-rock δ^{98}Mo plotted alongside calculated authigenic δ^{98}Mo estimates. The dominant Mo isotope trend observed in the upper Mt. McRae Shale is preserved even after correction for detrital dilution using extreme endmembers for the possible detrital Mo isotope value. This includes a very light detrital δ^{98}Mo composition, similar to estimates of bulk-Earth (~ 0.0‰[70]), and a heavy δ^{98}Mo similar to that used as an upper estimate for bulk continental crust (0.6‰[27]). See Fig. 1 of the main text for a lithological key. All error bars represent the 2SD reproducibility of that sample or the external long-term reproducibility of natural reference materials, whichever is greater.

Isotope mass-balance modeling

Thallium

The following Tl isotope mass-balance equation was used in this study:

$$\varepsilon^{205}Tl_{Inputs} = \varepsilon^{205}Tl_{AOC}(f_{AOC}) + \varepsilon^{205}Tl_{oxic}(f_{Tl-oxic}) + \varepsilon^{205}Tl_{other}(f_{other})$$

where $\varepsilon^{205}Tl_X$ represents the isotopic composition of average oceanic inputs and the dominant marine outputs, and f_{Tl-X} their relative removal flux. We designate low-T alteration of oceanic crust (AOC), oxic sediments (oxic), and "other" as three dominant outputs, where "other" signifies Tl removal with no associated isotopic fractionation. $\varepsilon^{205}Tl$ of each output can be calculated if a seawater $\varepsilon^{205}Tl$ estimate is made, and the isotopic offset of that output is assumed: $\varepsilon^{205}Tl_{output} = \varepsilon^{205}Tl_{seawater} - \Delta^{205}Tl_{solution-output}$.

Low-T alteration of oceanic crust preferentially removes isotopically light Tl from solution[21], with the most recent estimate for $\Delta^{205}Tl_{seawater-AOC}$ being 0 to 2.5[20]. Importantly, the lower estimate (i.e. zero-fractionation) would signify complete uptake of seawater Tl into AOC and is likely unrealistic. Here, as in the most recent estimate[46], we utilize the larger offset of 2.5 epsilon units.

Mn oxides impart the greatest magnitude of Tl isotope offset from solution, preferentially retaining heavier-mass isotopes[24]. The most recent estimate for $\Delta^{205}Tl_{seawater-MnOx}$ is -13.5 to -19[20]. Here, we utilize the larger offset of -19 epsilon units so as to satisfy mass-balance.

The Tl isotope composition of oceanic inputs is shown to not differ within analytical uncertainty from bulk Earth and continental crust[23] and is therefore assigned a $\varepsilon^{205}Tl$ of -2.

Our Tl isotope mass-balance differs from previous work in that it departs from the typical two-sink model that applies to modern oceans [only AOC and MnOx[20,63]] by adding a third, non-fractionating sink. Euxinic settings minimally fractionate Tl isotopes and are not thought to be a dominant Tl removal mechanism from seawater today[18]. However, this may not have been the case in Earth's past. Moreover, in the absence of a strong Mn oxide sink, Tl isotope fractionation in the marine environment would be taking place primarily at the flanks of mid-ocean ridges during low-T alteration of basalt, which continues until hydrothermal circulation is arrested by a sufficient sediment blanket. This means the bulk of the seafloor would not be fractionating Tl isotopes, and must, due to its sheer size, be viewed as a contributor to the seawater $\varepsilon^{205}Tl$.

Sensitivity calculations for Tl isotope mass-balance show that, regardless of the fractionation factors used, Mn oxide-rich oxic sediments are required to drive the measured light $\varepsilon^{205}Tl$ compositions (Supplementary Table 1). The minimum $f_{Tl-oxic}$ is always non-zero, but the maximum can vary between 0.06 and 0.28.

Supplementary Table 1.
Results of sensitivity calculations for Tl isotope mass-balance

$\Delta^{205}Tl_{SW-MnOx}$	$\Delta^{205}Tl_{SW-AOC}$	$\varepsilon^{205}Tl_{SW}$	min $f_{Tl-oxic}$	max $f_{Tl-oxic}$	
-19	0	-3.57 ± 0.48	0.06	0.11	
-13.5	0	-3.57 ± 0.48	0.08	0.15	
-19	**2.5**	-3.57 ± 0.48	**0.06**	**0.21**	***this study**
-13.5	2.5	-3.57 ± 0.48	0.08	0.28	

Molybdenum

The following Mo isotope mass-balance equation was used in this study:

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

where, similar to Tl, $\delta^{98}Mo_X$ represents the isotopic composition of average oceanic inputs and the dominant marine outputs, and f_{Mo-X} their relative removal flux. We designate euxinic sediments, Mn oxide-rich oxic sediments (oxic), and sediments that are sulfidic at depth (SAD; where sulfide is limited to sediment pore waters) as the three dominant outputs. These are the three marine sinks used in recent Mo isotope mass-balance calculations[45,64]. Estimates for our $\delta^{98}Mo_X$ values are calculated similar to those for Tl and are identical to these references (i.e. refs 45 and 64).

Mn oxides present in well oxygenated marine sediments are the strongest Mo isotope fractionation mechanism found to date, and multiple estimates agree on a $\Delta^{98}Mo_{solution-MnOx}$ of ~3.0‰[25]. For this study, we use a $\delta^{98}Mo_{oxic}$ value of $\delta^{98}Mo_{seawater} - 3.0‰$ (e.g. using the seawater $\delta^{98}Mo$ estimate from data in this study: 1.56‰ – 3.0‰ = -1.46‰, where 1.56‰ represents a minimum value for seawater $\delta^{98}Mo$ based on the highest $\delta^{98}Mo$ measured for the Mt. McRae Shale in this study).

For $\delta^{98}Mo_{euxinic}$, we use an isotopic offset from seawater of 0.5‰ so as to lump together weakly and strongly euxinic environments, both of which are strong sinks for Mo[64] (i.e. where H_2S is present in the water column and pore waters). Hence, $\delta^{98}Mo_{euxinic}$ would be equal to 1.06‰ if seawater $\delta^{98}Mo$ was 1.56‰.

For $\delta^{98}Mo_{SAD}$, we use an isotopic offset from seawater of 0.7‰ because this is the value most often observed in modern settings where H_2S is limited to sediment pore waters [65-68]. A substantial amount of Mo is removed from the ocean today into these environments[61]. Applying this isotopic offset would result in a $\delta^{98}Mo_{SAD}$ composition of 0.86‰ if seawater $\delta^{98}Mo$ was 1.56‰.

For our Mo isotope mass-balance calculation $\delta^{98}Mo_{Inputs}$ is assumed to be 0.3‰, within the range of currents estimates for the continental crust (modern continental crust $\delta^{98}Mo = 0.48 \pm 0.12‰^{[27]}$) and molybdenite ($\delta^{98}Mo_{molybdenite} = 0.29 \pm 1.04‰^{[69]}$), which is the predominant Mo host in the continental crust. A recent study shows that, while Mo isotope fractionation can occur during transport of Mo to the ocean[29,30], the vast majority of this Mo comes to the ocean unfractionated[31]. As such, the isotopic composition of Mo delivered to the ocean should replicate that of the upper continental crust.

The results of sensitivity calculations for Mo isotope mass-balance are reported below (Supplementary Table 2). These calculations were performed to test the influence of changing two modeling parameters: 1) a $\delta^{98}Mo_{Inputs}$ value equal to 0.7‰, which was until recently[31] thought to be the modern value[30]. And 2) a $\delta^{98}Mo_{euxinic}$ composition equal to that of seawater, which does happen in some basins today[28]. Again, regardless of the changes, Mn oxide-rich oxic sediments are required to drive the measured Tl isotope compositions. The minimum $f_{Mo-oxic}$ is always non-zero, but the maximum can vary between 0.18 and 0.45.

Supplementary Table 2.
Results of sensitivity calculations for Mo isotope mass-balance

$\delta^{98}Mo_{IN}$ (‰)	$\Delta^{98}Mo_{SW-euxinic}$	$\delta^{98}Mo_{SW}$ (‰)	min $f_{Mo-oxic}$	max $f_{Mo-oxic}$	
0.7	0.5‰	1.56 ± 0.10	0.03	0.18	
0.7	0.0‰	1.56 ± 0.10	0.03	0.32	
0.3	**0.5‰**	1.56 ± 0.10	**0.20**	**0.34**	***this study**
0.3	0.0‰	1.56 ± 0.10	0.20	0.45	

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