

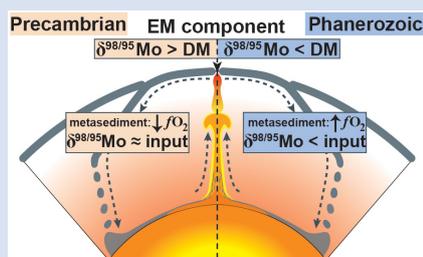
Molybdenum isotopes in plume-influenced MORBs reveal recycling of ancient anoxic sediments

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Abstract



Under modern oxidising Earth surface conditions, dehydrated subducted slabs show Mo isotope compositions as low as $\delta^{98/95}\text{Mo} = -1.5\text{‰}$, compared to the depleted mantle $\delta^{98/95}\text{Mo} = -0.2\text{‰}$. Such light Mo isotope compositions reflect the redox-dependent aqueous mobility of isotopically heavy Mo associated with slab dehydration. Here we analysed basaltic glasses from the South-Mid Atlantic Ridge, whose parental melts are influenced by the enriched Discovery and Shona mantle plumes. We report increasingly higher $\delta^{98/95}\text{Mo}$ of up to -0.1‰ from the most depleted samples towards those tapping more enriched mantle sources. $\delta^{98/95}\text{Mo}$ values correlate with radiogenic Sr and Nd isotopes, which indicates the recycling of Proterozoic sediments with a Mo isotopic composition that was not affected by subduction-related,

oxic dehydration. We propose that the Mo isotope signatures were retained during subduction and reflect anoxic conditions during deep sea sedimentation in the mid-Proterozoic. Finally, Mo isotope fractionation between different terrestrial reservoirs likely depends on the slab redox budget, and therefore on the timing of subduction with regard to Earth's surface oxygenation.

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Introduction

The quantification of element and isotope fractionation in subduction zones plays an important role in understanding (re)cycling mechanisms between the Earth's surface and its interior over geologic time scales. Element and isotope fractionation in this setting can be controlled by the prevailing redox conditions of the subducted material. As aerobic conditions prevail at the Earth's surface today, deep sea sediments and altered oceanic crust (AOC) are largely oxidised and influence the redox budget of the subducting slab (e.g., Evans, 2012). It is still unclear whether the redox budget of slabs is directly correlated with the oxygenation of Earth's atmosphere and oceans, and whether the redox state of the Earth's surface influences the behaviour of redox-sensitive elements in subduction zone settings through Earth's history.

A particularly suitable element to study the relationship between oxidised and reduced geochemical reservoirs is the redox-sensitive element Mo. The mobility of Mo from the subducted material is controlled by the redox state of slab-derived aqueous fluids and hydrous melts (Bali *et al.*, 2012; Skora *et al.*, 2017). Significant Mo mobilisation and isotope fractionation has been observed during subduction of oxidised lithologies, leaving behind a Mo depleted and isotopically light residual slab (e.g., Freymuth *et al.*, 2015; König *et al.*, 2016; Chen *et al.*, 2019; Ahmad *et al.*, 2021). Under reducing conditions, only limited Mo mobility is expected to occur in subducted lithologies

(Bali *et al.*, 2012; Skora *et al.*, 2017) thus preserving pre-subducted Mo signatures of the surface. This redox dependent mobilisation of Mo during subduction metamorphism potentially allows reconstructing the redox budget of ancient subduction zones through Mo isotope compositions of mantle-derived material enriched by ancient recycled crustal components.

This study investigates Mo isotope systematics in a well characterised basaltic sample suite from the South Mid-Atlantic ridge (S-MAR) that shows evidence for interaction with the enriched Shona and Discovery mantle plumes (Supplementary Information S-1, Fig. S-1). Previous studies on these samples suggested recycling of ancient oceanic crust and sediments in their mantle source with an age between 1 and 2 Ga based on radiogenic isotopes, and the absence of mass independent fractionation of S isotopes (Douglass *et al.*, 1999; Andres *et al.*, 2002; Labidi *et al.*, 2013). These basalts additionally feature increasingly heavier S and Se isotope compositions with indicators of mantle source enrichment, and are interpreted to reflect subduction recycling of reduced sediments from a redox stratified Proterozoic ocean (Labidi *et al.*, 2013; Yierpan *et al.*, 2020).

Results

The $\delta^{98/95}\text{Mo}$ signatures of S-MAR basaltic glass samples range between -0.24‰ and -0.10‰ . These $\delta^{98/95}\text{Mo}$ values show

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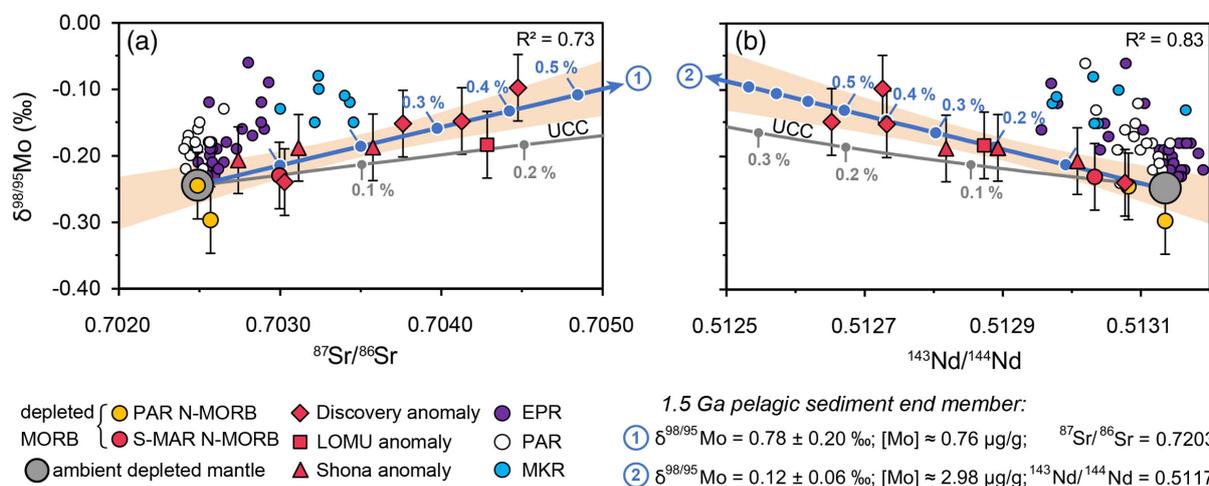


Figure 1 Covariation diagram of MORBs. (a) $\delta^{98/95}\text{Mo}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$; (b) $\delta^{98/95}\text{Mo}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$. Mixing of a 1.5 Ga old pelagic sediment end member (best fit parameters from linear regression) with the ambient depleted mantle (see Table S-2 for mixing parameters). Mixing with upper continental crust (UCC) is plotted for comparison. External reproducibility on each isotope value is considered for regression, and the shaded area indicates 95 % CI error envelope. PAR samples are excluded from regression. Error bars indicate 2 s.d. external reproducibility.

correlations with $^{87}\text{Sr}/^{86}\text{Sr}$ as well as $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and $\delta^{82/76}\text{Se}$ (Figs. 1, S-4a,b). The correlations indicate that Mo isotopes trace mantle source enrichment. The range in $\delta^{98/95}\text{Mo}$ of the samples is similar to that of MORBs (and seamounts) from the East Pacific Rise (EPR), the Pacific-Antarctic ridge (PAR), and the Mohs Knipovich ridge (MKR; Figs. 1, S-2). However, the samples from the S-MAR show a much larger variability in $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ and more systematic source enrichments (Figs. 1, S-2, S-4a,b).

Discussion

Origin of enriched mantle component. Combined element and isotope systematics of S-MAR samples strongly suggest that secondary mantle melting processes (such as sulfide melt segregation and fractional crystallisation), or seawater alteration, are unlikely the causes for the observed Mo isotope variations. This is because all these processes would have obliterated any correlation between Mo isotope composition and radiogenic isotopes (see Supplementary Information S-2 for further discussion). Low degree melting of mantle plume material has been suggested to affect geochemical signatures of investigated samples (le Roux *et al.*, 2002a), and might have affected their $\delta^{98/95}\text{Mo}$ (e.g., Chen *et al.*, 2022). We argue that this process did not result in a first order modification of the enriched source signatures of our samples. Their distinct radiogenic isotope compositions, their covariation with stable Se and S signatures, and trace element systematics are independent of partial melting variations, suggesting the plume source was enriched prior to low degree mantle melting (le Roux *et al.*, 2002a; Labidi *et al.*, 2013; Yierpan *et al.*, 2020). Moreover, the absence of a covariation of $\delta^{98/95}\text{Mo}$ and Pb isotopes (Fig. S-4c,d) does not support the influence of an ancient low degree melt (Chen *et al.*, 2022). Rather, a recycled sediment component can explain the Pb isotope signature of LOMU-affinity samples (cf. Douglass *et al.*, 1999; Andres *et al.*, 2002). In addition, mantle melting degrees of 2.5 % (le Roux *et al.*, 2002a) cannot explain the observed variations of $\delta^{98/95}\text{Mo}$ indicating that heavy Mo is likely a characteristic primary signature of the enriched plume material (see Supplementary Information S-2 for further details). Previous studies attributed this source enrichment to the influence of a recycled component, such as delaminated subcontinental lithospheric mantle, lower continental crust, or subducted sediment

($\pm\text{AOC}$) (Douglass *et al.*, 1999; Andres *et al.*, 2002; le Roux *et al.*, 2002b). In line with previous investigations showing covariations between other redox-sensitive stable Se-S isotope systematics and radiogenic isotopes (Labidi *et al.*, 2013; Yierpan *et al.*, 2020), we suggest that a sediment contribution to the S-MAR mantle source is the most likely scenario for the observed heavy Mo isotope enrichment in our samples (see Supplementary Information S-3 for further discussion). This sedimentary source was previously inferred to have a mid-Proterozoic age (1 to 2 Ga; Douglass *et al.*, 1999; Andres *et al.*, 2002; Labidi *et al.*, 2013; Yierpan *et al.*, 2020).

Mobility of Mo during subduction: the role of $f\text{O}_2$.

Recycled Proterozoic sediments that enriched the S-MAR mantle source with isotopically heavy Mo are in stark contrast to inferred, isotopically light Mo in dehydration residues of subducted Phanerozoic metasediments (Ahmad *et al.*, 2021). The trend towards higher observed (co-) variations of $\delta^{98/95}\text{Mo}$ with increasing degrees of mantle source enrichment within the S-MAR suite therefore implies recycling of a sedimentary $\delta^{98/95}\text{Mo}$ or even a total Mo budget unaffected by dehydration and melting during subduction. This may be reconciled with experimental studies showing immobility of Mo in low $f\text{O}_2$ -bearing slab fluids and hydrous slab melts (Bali *et al.*, 2012; Skora *et al.*, 2017; Chowdhury *et al.*, 2022). These experiments were conducted at subduction zone P - T and at reducing conditions, and showed that Mo^{4+} is immobile in fluids in the presence of rutile (Bali *et al.*, 2012) and mobilisation of Mo is inefficient in melts due to increased partitioning of Mo^{4+} relative to Mo^{6+} into the residual phases such as sulfides or rutile (Skora *et al.*, 2017; Chowdhury *et al.*, 2022). These findings are also consistent with subduction of organic matter (OM)-rich black shales in the Lesser Antilles Arc, where lavas south of Martinique exhibit high $\delta^{98/95}\text{Mo}$ along with lower Mo/Ce (Freymuth *et al.*, 2016; Gaschnig *et al.*, 2017), suggesting the minute contribution of unfractionated slab-derived Mo to the mantle sources relative to melts originating from more oxidising sediments. Therefore, significant loss of heavy Mo during subduction metamorphism did not occur in the enriched mantle source component. This would have resulted in a preferential loss of more incompatible (isotopically heavy) Mo^{6+} during melting and dehydration (e.g., Chen *et al.*, 2019; McCoy-West *et al.*, 2019) and would shift $\delta^{98/95}\text{Mo}$ of the residual subducted material towards lighter values. The interpretation is in line with the $f\text{O}_2$ -sensitive stable

Table 1 Average Mo isotope composition of MORBs from the S-MAR and PAR together with radiogenic isotope data (Douglass *et al.*, 1999) and Se isotope compositions (Yierpan *et al.*, 2020). Individual measurements are listed in Table S-1.

Sample	Type	$\delta^{98/95}\text{Mo}$ (‰) ^A	<i>n</i>	$\delta^{82/76}\text{Se}$ (‰) ^B	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$
	<i>Southern Mid-Atlantic ridge</i>					
EW9309 40D-1g	Depleted N-MORB	-0.231	3	-0.18	0.702997	0.513033
EW9309 33D-1g	Discovery influenced MORB (North)	-0.098	3	-0.03	0.704475	0.512726
EW9309 28D-1g	Discovery influenced MORB (North)	-0.239	2	-0.14	0.703028	0.513077
EW9309 2D-1g	Discovery influenced MORB (South)	-0.148	2	-0.08	0.704127	0.512652
EW9309 4D-3g	Discovery influenced MORB (South)	-0.152	3	-0.04	0.703762	0.512732
EW9309 9D-3g	LOMU MORB	-0.183	2	-0.03	0.704284	0.512873
EW9309 15D-1g	Shona influenced MORB	-0.207	2	-0.13	0.702741	0.513008
EW9309 21D-1g	Shona influenced MORB	-0.188	2	-0.12	0.703115	0.512818
EW9309 22D-3g	Shona influenced MORB	-0.187	2	-0.08	0.703576	0.512893
	<i>Pacific-Antarctic ridge</i>					
PAC2 DR3 3-1	Depleted N-MORB	-0.245	3	-0.15	0.702488	0.513082
PAC1 CV-02g	Depleted N-MORB	-0.297	3	-0.23	0.702568	0.513135

^A The external reproducibility (2 s.d.) is 0.05 ‰ (see Supplementary Information S-4).

^B The external reproducibility (2 s.d.) is 0.08 ‰, except for EW9309 2D-1g and EW9309 9D-3g, for which it is 0.04 ‰ (Yierpan *et al.*, 2020).

isotope systematics of S and Se (Table 1), which indicate negligible mobilisation and isotope fractionation during subduction (Labidi *et al.*, 2013; Yierpan *et al.*, 2020). It is noteworthy that in some cases, that do not apply here, sediments may also buffer subduction zone fluids towards oxidising conditions, such as Fe- and Mn-rich (meta)sediments that show a high metamorphic f_{O_2} (Ague *et al.*, 2022 and references therein). Yet, our S-MAR data can be attributed to an immobile behaviour of Mo with unchanged $\delta^{98/95}\text{Mo}$ under reducing conditions, which is in sharp contrast with the mobility of Mo under oxidising conditions where prograde subduction metamorphism can cause Mo mobilisation and alter the primary slab Mo isotope signature.

Recycled sediments from an anoxic deep ocean. The $\delta^{98/95}\text{Mo}$ - $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{143}\text{Nd}/^{144}\text{Nd}$ covariations (Fig. 1) in the S-MAR data combined with the previously established model of the linear $\delta^{34}\text{S}$ - $\delta^{82}\text{Se}$ - $^{87}\text{Sr}/^{86}\text{Sr}$ -($^{143}\text{Nd}/^{144}\text{Nd}$) relationship (Labidi *et al.*, 2013; Yierpan *et al.*, 2020) allows extrapolation of $\delta^{98/95}\text{Mo}$ and [Mo] to constrain the nature of the recycled sediment. Extrapolation of the linear regression to a model composition of 1.5 Ga old sediment ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7203$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.5117$; Fig. 1, see Table S-2 for details) yields two vastly different end member Mo signatures with $\delta^{98/95}\text{Mo}$ of 0.78 ± 0.20 ‰ and 0.12 ± 0.06 ‰, and [Mo] of ~ 0.76 $\mu\text{g/g}$ and 2.98 $\mu\text{g/g}$, respectively (see blue mixing lines in Fig. 1). This indicates that the linear extrapolation might not sufficiently constrain the Mo composition of the recycled sediment source. Considering the present day $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ model composition of 1.5 Ga old subducted sediment, the isotopic variations of the samples represents only a small fraction of the mixing space between the ambient depleted mantle and recycled sediment. Therefore, for given radiogenic Nd and Sr signatures of the sedimentary component, different $\delta^{98/95}\text{Mo}$ and [Mo] combinations can potentially result in a minimum least squares error between the mixing model and the S-MAR data. As both variables cannot be independently constrained, a misfit function (Supplementary Information S-5) was applied to calculate the sedimentary $\delta^{98/95}\text{Mo}$ and [Mo] that represent the measured $\delta^{98/95}\text{Mo}$ - $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{143}\text{Nd}/^{144}\text{Nd}$ covariation best (Fig. 2).

Least squares errors for variable $\delta^{98/95}\text{Mo}$ and [Mo] values for a given 1.5 Ga old sediment with $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ end member values (blue field in Fig. 2) show a similar pattern for both radiogenic isotope systems, which indicates that a mid-Proterozoic pelagic sediment is likely to be a valid end member. Best fits with minimum errors overlap with the lower 1σ of Proterozoic OM-rich sediment data from the literature (Ye *et al.*, 2021; Table S-2) and can also be achieved with a recycled sediment contribution close to that of the UCC (~ 0.05 to 0.15 ‰; Willbold and Elliott, 2017 and references therein) with slightly higher $\delta^{98/95}\text{Mo}$ and/or [Mo] values. This points towards a minor authigenic Mo enrichment from seawater or a residual enrichment of Mo (e.g., Kendall *et al.*, 2017) and implies that $\delta^{98/95}\text{Mo}$ has not been affected by oxic conditions during slab dehydration due to subduction of reducing lithologies (Fig. 2).

These findings support the notion that the deep ocean remained anoxic until the beginning of the Phanerozoic (e.g., Poulton and Canfield, 2011; Stolper and Keller, 2018). The extent of the biological pump in the Proterozoic ocean, where primary productivity in the oxygenated surface ocean was dominated by cyanobacteria, was lower compared to modern oceans and higher primary surface productivity was restricted to marine environments close to continents (Laakso and Schrag, 2019). This limited the OM flux to the Proterozoic deep ocean and therefore authigenic Mo accumulation from seawater. However, deep ocean anoxic conditions increased OM preservation and burial efficiency (Burdige, 2007). Furthermore, under anoxic conditions with an overall low concentration of dissolved SO_4^{2-} and MoO_4^{2-} , neither a significant Mo enrichment from seawater into the sediment nor a significant Mo mobilisation during fluid alteration is expected (Lyons *et al.*, 2014). The overall lower OM input to the deep ocean and smaller oceanic Mo reservoir can therefore explain the small authigenic heavy Mo contribution to the recycled mid-Proterozoic deep sea sediment (Fig. 2). With respect to the much shorter ocean residence time of Mo relative to the average lifetime of an oceanic crust, the S-MAR enriched end member is likely representative for overall reducing conditions during subduction and an average

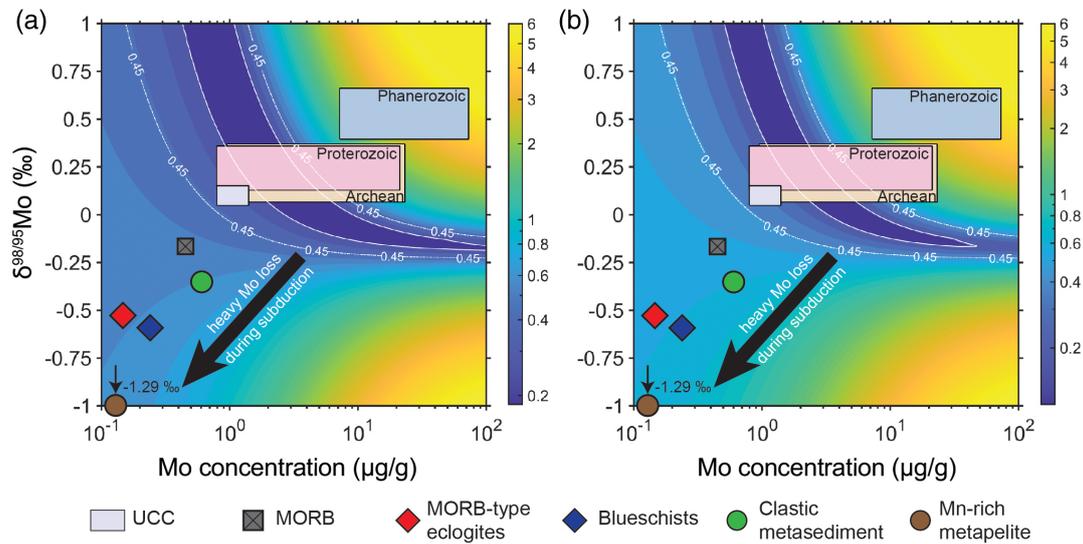


Figure 2 Least squares error ($\Delta^{98/95}\text{Mo}$ in ‰; up to 6 ‰) between calculated mixing lines and analysed samples. Variables are the $\delta^{98/95}\text{Mo}$ and $[\text{Mo}]$ values derived from (a) the $\delta^{98/95}\text{Mo}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ and (b) the $\delta^{98/95}\text{Mo}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ relationship (Fig. 1). Literature values for potential (concentration averaged) recycled lithologies, and anoxic sediments sorted by age intervals are shown for comparison. See Table S-2 and Supplementary Information S-5 for references, mixing parameters, and further details.

subducted sedimentary Mo signature, which provides a context of deep ocean redox conditions.

Implications for the sedimentary Mo subduction cycle.

Due to the anoxic conditions in the Proterozoic deep ocean, oxidised species of major and minor elements like Fe, S and Mn, were absent in deep sea sediments, thus lowering their redox budget/oxidising capacity compared to present day marine lithologies (e.g., Evans, 2012; Ague et al., 2022). This may also explain the preserved $\delta^{98/95}\text{Mo}$ of a reduced Proterozoic sediment component recycled into the S-MAR mantle source, in contrast to Neoproterozoic, deep mantle recycling of low $\delta^{98/95}\text{Mo}$ into mantle plume sources (see also Ma et al., 2022). This is in line with Samoan OIBs, where $\delta^{98/95}\text{Mo}$ signatures

are interpreted as a mixture of isotopically heavy terrigenous sediments ($\delta^{98/95}\text{Mo} \approx \text{UCC}$) and isotopically light dehydrated mafic oceanic crust, which reflect the influence of a distinct pool of mid-Proterozoic recycled ocean crust (Gaschnig et al., 2021). Altogether, this indicates that changing Earth surface redox conditions have influenced the $f\text{O}_2$ conditions during subduction and the mobility of sedimentary Mo (and by analogy that of other redox sensitive elements) and hence, the Mo isotope budget between different Earth (silicate) reservoirs. This emphasises the time- and condition-related variations in Mo mobility during subduction on our planet (Fig. 3). We therefore conclude that the Mo isotope signature of plume-influenced volcanic rocks can be used to reconcile the redox conditions during

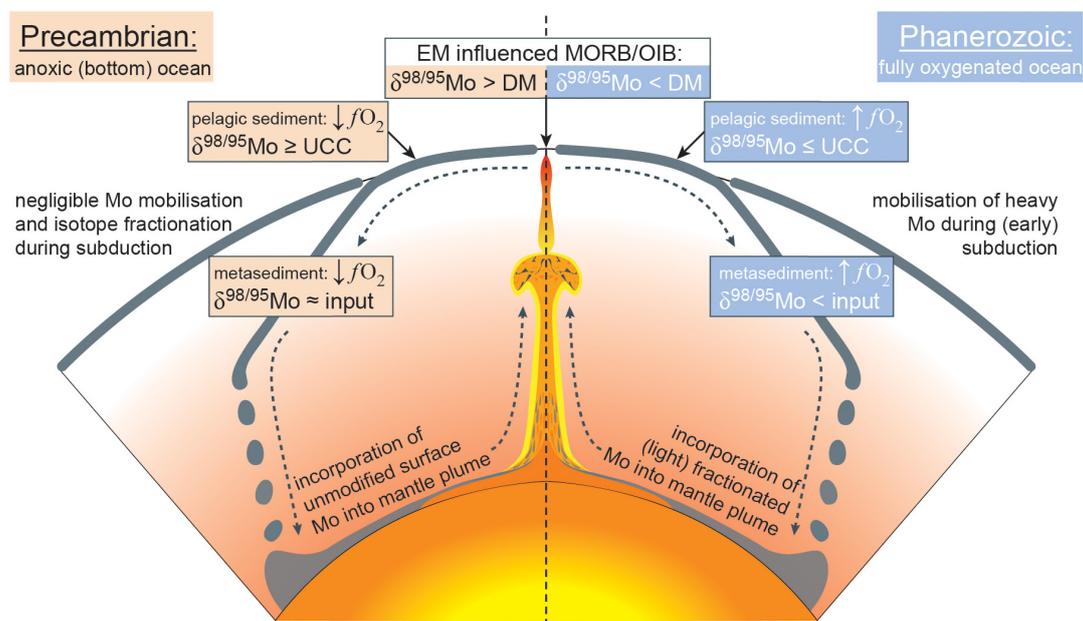


Figure 3 Illustration of the subducted sedimentary Mo cycle during the Precambrian (left) and Phanerozoic (right). Deep sea sediments carry variable redox budgets influencing Mo mobility and hence isotope fractionation during subduction over Earth’s history (see text). UCC, upper continental crust; DM, depleted mantle; EM, enriched mantle.

ancient surface deposition of deep sea sediments (cf. Gaschnig *et al.*, 2021) as well as during subduction-related prograde metamorphism and the inception of modern subduction.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2236>.



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