

Authigenic molybdenum isotope signatures in marine sediments

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ABSTRACT

We present new Mo isotope data from the Mexican continental margin that, in conjunction with previous data, allow us to propose a mechanistic description of the Mo isotope system in marine sediments. We hypothesize that there are unique environmentally dependent Mo isotope signatures recorded in marine sediments that reflect the mechanisms responsible for authigenic Mo accumulation. Open-ocean anoxic sites, defined as having dissolved oxygen and sulfide concentrations near zero in the overlying water, exhibit a $\delta^{98/95}\text{Mo}$ isotope signature of $+1.6\text{‰}$. We believe this value reflects Mo sulfide formation via diagenetic processes within sediments. Quantitative formation of Mo sulfide within the sulfidic water column of euxinic environments results in sediment isotope values similar to the modern seawater value ($+2.3\text{‰}$), as typified by samples from the highly sulfidic Black Sea. In contrast to these reducing settings, manganese oxide-rich sediments have measured Mo isotope values that are more negative (relative to seawater) than any other sediment samples analyzed to date, similar to Fe-Mn crusts ($\sim -0.7\text{‰}$). Most measured Mo isotope compositions of marine sediments from open-ocean settings appear to reflect a mixture of lithogenic Mo (0.0‰) and the Mo signature of a specific authigenic Mo accumulation mechanism. We therefore suggest that Mo isotopes may record unique signatures that reflect the dominant chemical mechanism for Mo sequestration into sediments.

Keywords: molybdenum, isotopes, diagenesis, sediments.

INTRODUCTION

Molybdenum enrichments in reducing marine environments have been used in paleochemical reconstructions (e.g., Crusius et al., 1996), and the Mo isotope system has recently been utilized to the same end (Siebert et al., 2003; Arnold et al., 2004; Anbar, 2004). Studies have demonstrated significant natural variations in modern sediment Mo isotope compositions (Barling et al., 2001; Siebert et al., 2003; Siebert et al., 2006), but interpretation of these data is equivocal because not all mechanisms generating sediment isotope signatures have been constrained. We present new Mo isotope data from several marine anoxic sediments that, in conjunction with previous data, allow us to propose a possible mechanistic description of the Mo isotope system in marine sediments.

There are essentially three major reservoirs of Mo in the marine environment: seawater, lithogenic materials, and authigenically precipitated Mo. In modern seawater, Mo exists primarily as the soluble molybdate complex (MoO_4^{2-}). It has a conservative distribution with a concentration of $\sim 100 \text{ nM}$, and a residence time of $\sim 800 \text{ k.y.}$ (Morford and Emerson, 1999, and references therein). Although data remain limited ($n = 6$), isotopic analyses of modern seawater indicate a uniform Mo isotope composition of $\delta^{98}\text{Mo}_{\text{SW}} = +2.3\text{‰}$ (Fig. 1) (Siebert et al., 2003; Barling et al., 2001), which is consistent with seawater being a well-mixed reservoir (Anbar, 2004). Data are presented in delta notation as $\delta^{98}\text{Mo} = [({}^{98/95}\text{Mo}_{\text{SAMPLE}} / {}^{98/95}\text{Mo}_{\text{STANDARD}}) - 1] \times 1000$.

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Analyses of terrigenous materials (e.g., granites, clastic sediments) yield an average Mo isotope composition of $\sim 0.0\text{‰}$ ($n = 13$) (Siebert et al., 2003), and we take this value to be representative of the lithogenic background in marine sediments. Lithogenic Mo can be an important component of the total Mo measured in a sediment sample; thus measured sediment Mo isotope compositions require correction for the lithogenic Mo contribution. One of the potential strengths of Mo isotopes lies in the observation that, to date, only authigenic accumulations of Mo in marine sediments show significant isotopic variability, and it is this strength that we wish to exploit.

AUTHIGENIC MOLYBDENUM

Molybdenum is a trace metal that forms authigenic deposits under both oxic and reducing conditions. In oxic sediments, where aerobic respiration is the primary pathway for organic material decomposition, Mo is sequestered through adsorption onto Mn oxyhydroxides (Bertine and Turekian, 1973; Calvert and Pedersen, 1993). Authigenic Mo accumulated under oxic conditions has measured Mo isotope values more negative (relative to seawater) than any other samples analyzed to date (Fig. 1). Analyses of Fe-Mn crust surfaces produce an average ($n = 6$) value of $\delta^{98}\text{Mo} = -0.7 \pm 0.1\text{‰}$ (Barling et al., 2001; Siebert et al., 2003), which corresponds to an $\sim 3.0\text{‰}$ fractionation between modern seawater and the adsorbed Mo species (Fig. 1). This fractionation is in good agreement with experimental determinations of isotope fractionation during Mo adsorption (2.7‰) (Barling and Anbar, 2004). The exact speciation of adsorbed Mo is unknown, but recent quantum me-

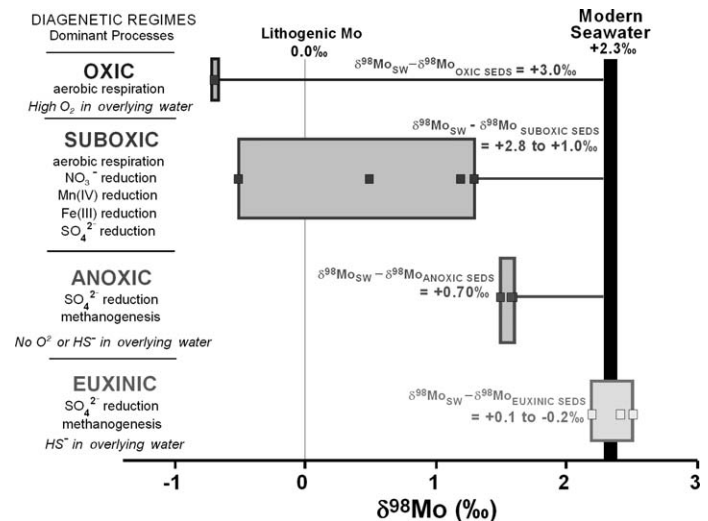


Figure 1. Measured Mo isotope compositions of various marine sediments and the presumed dominant electron transport processes for each environment. Oxic sediment Mo isotope data are from Fe-Mn crust surfaces (Barling et al., 2001; Siebert et al., 2003). Suboxic sediment Mo isotope data are average site compositions from California margin sites of Siebert et al. (2006). Anoxic sediment Mo isotope data are average site compositions from three Mexican margin sites of this study. Euxinic sediment Mo isotope data are deep Black Sea sediments from Barling et al. (2001) and Arnold et al. (2004). All data are shown without lithogenic Mo correction.

chemical calculations consistent with natural observed fractionations suggest MoO₃ is a potential candidate (Tossell, 2005).

Under reducing conditions, where anaerobic processes dominate electron transport, Mo is sequestered into sediments via Mo sulfide formation. Pore-fluid studies of Zheng et al. (2000) argue for two separate thresholds of Mo sulfide formation: coprecipitation of Mo-Fe-S phases at dissolved sulfide concentrations of ~0.1 μM, and Mo-S precipitation without Fe at sulfide concentrations of ~100 μM or more. Authigenic precipitation of Mo at ~0.1 μM sulfide likely corresponds to the initial formation of thiomolybdate intermediate complexes (MoO_xS_{4-x}²⁻), which can be scavenged by sulfidized organic and Fe-S phases (Helz et al., 1996).

At high dissolved sulfide concentrations a “geochemical switch” is proposed where the dominant dissolved Mo phase transitions from soluble molybdate to less soluble tetrathiomolybdate (MoS₄²⁻) (Helz et al., 1996). This presumably corresponds to the ~100 μM sulfide threshold proposed by Zheng et al. (2000), where Mo depletion in pore waters was observed in the absence of Fe-S precipitation. It is assumed that in euxinic settings with high dissolved sulfide concentrations, the “geochemical switch” threshold will be met, and the dominant dissolved species may be MoS₄²⁻ rather than MoO₄²⁻ (Helz et al., 1996). Previous work has proposed that because the conversion of MoO₄²⁻ to MoS₄²⁻ in euxinic waters is quantitative, any transient fractionation between species will not be recorded in the underlying sediments, as evidenced by sediments from the euxinic Black Sea with Mo isotope compositions analytically indistinguishable from the modern seawater value (δ⁹⁸Mo = +2.4‰) (Barling et al., 2001; Arnold et al., 2004) (Fig. 1). Though restricted euxinic basins are rare in the modern ocean, they were more widespread on ancient Earth, and represent an important Mo isotopic end-member composition as the most reducing authigenic Mo deposits in the marine environment (e.g., Arnold et al., 2004).

A fractionation between MoO₄²⁻ and Mo sulfide is suggested by the findings of McManus et al. (2002), who calculate a 0.7‰ fractionation as dissolved Mo is removed into sediments in Santa Monica Basin. We propose that this isotopic signature would most likely be preserved in open-ocean anoxic sediments (defined here as those areas having dissolved oxygen and sulfide concentrations near zero in the overlying bottom water) where thiomolybdates (MoO_xS_{4-x}²⁻) are formed through diagenetic processes within the sediments. In this study, we have analyzed Mo isotope compositions from a suite of modern anoxic sediments to determine if such a fractionation exists.

RESULTS

We selected three sites on the Mexican continental margin for Mo isotope analysis. Each site has low bottom-water oxygen concentrations (Table 1), and presumably no dissolved sulfide present. The Soledad and San Blas sites are located within depositional basins, while the Mazatlan site is from the open continental margin. The Soledad Basin is 545 m deep with an approximate sill depth of 250 m (van Geen et al., 2003; Silverberg et al., 2004). The San Blas Basin is 430 m deep with an approximate sill depth of 300 m (Berelson et al., 2005). The Mazatlan station is at a depth of ~440 m and is located near the sites previously discussed in Ganeshram et al. (1999) and Hartnett and Devol (2003).

The two basin sites have higher sedimentation rates than the open margin Mazatlan site, yielding authigenic Mo accumulation rates of 2.19 and 5.29 nmol/cm²/yr compared to 1.28 nmol/cm²/yr on the open margin (Table 1). At the Soledad site, it has been shown that a significant portion of organic carbon degradation can be attributed to sulfate reduction (Berelson et al., 2005), and it is reasonable to assume that

TABLE 1. MOLYBDENUM ISOTOPE COMPOSITIONS OF VARIOUS MARINE DEPOSITIONAL ENVIRONMENTS

SITE	Lat. (°N)	Long. (°W)	δ ⁹⁸ Mo (‰)	# of samples averaged	Avg. Mo Conc (ppm)	Avg. Mo:Al (g/g)	Avg. % Mo _{LITH}	δ ⁹⁸ Mo (Lith. Corr.) (‰)	Sed. rate (mg/cm ² yr)	Mo _{AUTH} accumulation rate (nmol/cm ² yr)	Carbon oxidation rate (mmol/cm ² yr)	Bottom water oxygen (μM)	References
Oxic													
Fe-Mn Crusts				8									Barling et al. (2001); Siebert et al. (2003)
Suboxic													Siebert et al. (2006)
San Clemente	32.6	118.1	-0.7 ± 0.1	8	6.5	1.07E-04	41	-0.8	15	0.04	0.04	65	
Tanner Basin	33	119.7	-0.5 ± 0.4	8	4.6	1.42E-04	8	+0.5	12	0.62	0.04	27	
Santa Monica	33.7	118.8	+0.5 ± 0.3	11	5.5	8.33E-05	14	+1.4	16	0.73	0.07	9	
San Pedro	33.6	118.5	+1.2 ± 0.3	9	4.4	6.37E-05	20	+1.6	29	0.86	0.07	3	
Anoxic													this study
Mazatlan	22.7	106.5	+1.6 ± 0.1	11	14	3.14E-04	4	+1.6	9	1.28	0.04	0.2	
San Blas	21.3	106	+1.6 ± 0.1	7	10.7	1.50E-04	8	+1.7	21	2.19	0.05	0	
Soledad	25.2	112.7	+1.5 ± 0.1	11	12.2	3.14E-04	4	+1.6	50	5.29	0.06	0	Arnold et al. (2004); Nægler et al. (2005)
Restricted Basins													
Cariaco Basin			+1.8 ± 0.1	4									Arnold et al. (2004); Nægler et al. (2005)
Black Sea Margin			+1.7 ± 0.2	6									Barling et al. (2001); Arnold et al. (2004)
Euxinic													
Black Sea			+2.4 ± 0.2	3									Barling et al. (2001); Arnold et al. (2004)

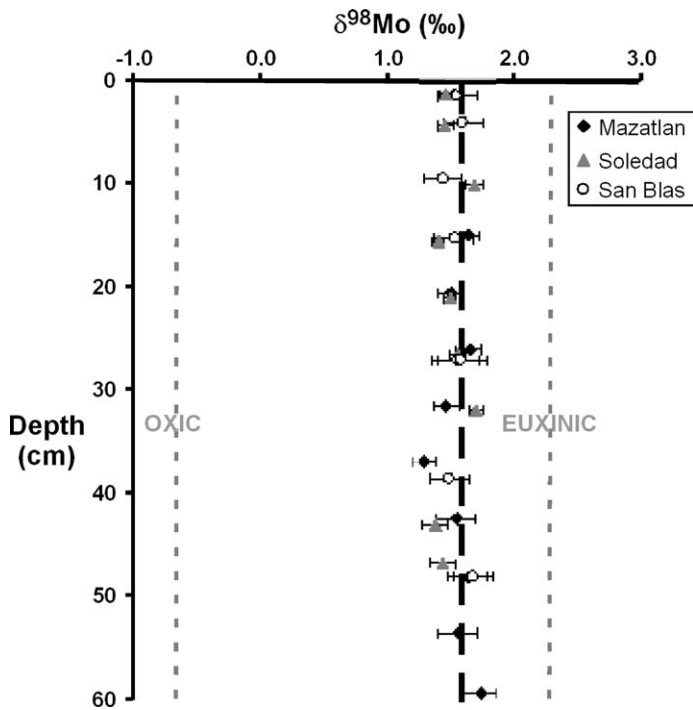


Figure 2. All $\delta^{98}\text{Mo}$ data (without lithogenic correction) from down-core profiles of the three anoxic Mexican margin sites in this study; errors shown are 2σ . The average Mo isotope composition of all measured samples is $\delta^{98}\text{Mo} = +1.6 \pm 0.1\text{‰}$ (1σ , $n = 29$) (Table 1).

sulfate reduction and methanogenesis are dominant processes regulating electron transport at all three sites in this study.

Mo isotope analyses of sediments from all three anoxic sites demonstrate a strikingly invariant average Mo isotope composition of $\delta^{98}\text{Mo} = +1.6 \pm 0.1\text{‰}$ (1σ , $n = 29$) (Table 1; Fig. 2). A mathematical correction was applied to all Mo isotope compositions after analysis, to account for lithogenic Mo (Table 1). This correction was applied based on the mass balance assumption that the total Mo isotope composition measured is a mixture of the lithogenic Mo (0.0‰) present and the authigenic Mo signature: $\delta^{98}\text{Mo}_{\text{SEDS}}X_{\text{SEDS}} = \delta^{98}\text{Mo}_{\text{LITH}}X_{\text{LITH}} + \delta^{98}\text{Mo}_{\text{AUTH}}X_{\text{AUTH}}$. For all sites in this study, the lithogenic Mo component was $\leq 8\%$ of the total Mo concentration, resulting in a very small isotopic correction (Table 1). The data from these anoxic sites indicate that Mo isotopes record a fractionation of 0.7‰ between seawater and Mo sulfides diagenetically produced within the sediments (Fig. 1), which is consistent with the Mo isotope fractionation calculated by McManus et al. (2002).

DISCUSSION

The anoxic Mo isotope signature determined in this study, when combined with existing sediment Mo isotope data, allows us to construct a model for the behavior of Mo isotopes in authigenic marine deposits (Fig. 3). This model proposes that there are unique environmentally dependent Mo isotope signatures recorded in marine sediments, each reflecting the primary mechanisms responsible for authigenic Mo accumulation. Adsorption of an oxic Mo phase (presumably MoO_3) in Mn-rich sediments produces an adsorbed Mo isotope signature more negative than any other sediments measured to date, being as much as 3‰ lighter than the modern seawater value (e.g., Barling et al., 2001):

$$\delta^{98}\text{Mo}(\text{MoO}_4^{2-}\text{-aq}) - \delta^{98}\text{Mo}(\text{MoO}_3\text{s}) \approx 3.0\text{‰}. \quad (1)$$

We further propose that transformation of pore-water MoO_4^{2-} to

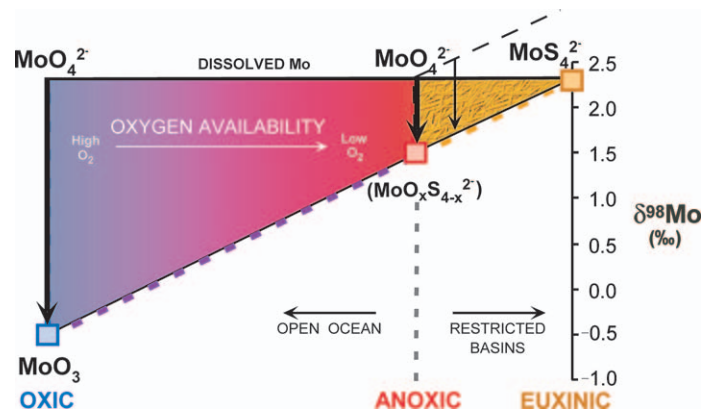


Figure 3. Schematic of the authigenic Mo isotope system in marine sediments depicting the measured oxic ($\delta^{98}\text{Mo} = -0.7\text{‰}$), anoxic ($\delta^{98}\text{Mo} = +1.6\text{‰}$), and euxinic ($\delta^{98}\text{Mo} = +2.3\text{‰}$) Mo isotope signatures and proposed Mo chemical behavior. Measured Mo isotope compositions of marine sediments from open-ocean settings appear to reflect a mixture of lithogenic Mo ($\delta^{98}\text{Mo} = 0.0\text{‰}$) and the authigenic Mo signature of either the oxic or anoxic Mo accumulation mechanisms. Measured Mo isotope values for restricted basin sediments suggest a change in the isotopic composition of dissolved Mo (dashed line at top) to heavier values as Mo is removed in the presence of dissolved sulfide.

$\text{MoO}_3\text{S}^{2-}$ and other subsequent thiomolybdates (such as MoS_4^{2-}) within sediments via diagenetically produced sulfide results in an anoxic authigenic Mo sediment isotope composition that is consistently 0.7‰ lighter than overlying water:

$$\delta^{98}\text{Mo}(\text{MoO}_4^{2-}\text{-aq}) - \delta^{98}\text{Mo}(\text{MoO}_x\text{S}_{4-x}^{2-}) = 0.7\text{‰}. \quad (2)$$

In euxinic environments, syngenetic formation of dissolved MoS_4^{2-} within the sulfidic water column is presumably quantitative; thus the fractionation between species (equation 2) is not observed in the underlying sediments.

Recognition of distinct environmentally dependent Mo isotopic signatures and the importance of a lithogenic Mo correction allow for a refined interpretation of previously measured Mo isotope data from sediments along the California margin (Siebert et al., 2006). After application of the lithogenic correction, all but one value can be resolved to either the oxic or anoxic signatures (Table 1). The exception is data from Tanner Basin, where the corrected Mo isotope value is $\delta^{98}\text{Mo} = +0.5\text{‰}$. We suggest that this value indicates either a mix of the oxic and anoxic Mo sources at this site, as proposed in Siebert et al. (2006), or another unidentified process that is dominating Mo accumulation. The corrected Mo isotope compositions of sediments from Santa Monica and San Pedro Basins are consistent with the anoxic signature observed in the Mexican margin sediments (Table 1), indicating that sulfidization of Mo is the dominant mechanism of authigenic Mo accumulation at these sites. In contrast, the corrected Mo isotope compositions of Mn-rich sediments from San Clemente Basin are consistent with the oxic Mo isotope signature as measured in Fe-Mn crusts (Barling et al., 2001; Siebert et al., 2003) (Table 1), indicating that Mo adsorption onto Mn oxyhydroxides is the dominant source for the accumulating Mo (Siebert et al., 2006). These observations lead us to conclude that for most marine sediments measured to date, the average recorded Mo isotope signature is indicative of the dominant authigenic Mo accumulation mechanism.

Molybdenum isotope data from Cariaco Basin sediments ($\delta^{98}\text{Mo} = +1.8\text{‰}$ [Arnold et al., 2004]) and shallow margin sediments of the Black Sea ($\delta^{98}\text{Mo} = +1.7\text{‰}$ [Näglér et al., 2005]) (Table 1) suggest that sediment Mo isotope compositions in restricted basin environ-

ments are heavier than the open-ocean anoxic value. Although these reported values are consistent with data from our anoxic sites, they have not been corrected for lithogenic Mo, and their authigenic Mo isotopic compositions are likely to be heavier. We propose that heavy Mo isotope compositions for sediments in restricted basin environments may reflect Mo limitation (Algeo and Lyons, 2006), such that inadequate resupply of dissolved MoO_4^{2-} drives aqueous Mo isotope compositions to heavier values as Mo sulfides are precipitated (dashed line in Fig. 3). We believe that the relative 0.7‰ fractionation between MoO_4^{2-} and authigenic Mo sulfide remains constant, and suggest that sediment Mo isotope values heavier than those observed at open-ocean sites reflect a shift in the isotopic composition of the dissolved MoO_4^{2-} pool. The fractionation between these Mo species is no longer observed in sediments when full euxinia is reached (as in the deep Black Sea) because the dissolved Mo pool has been quantitatively converted from MoO_4^{2-} to MoS_4^{2-} .

Previous application of the Mo isotope system in paleochemical reconstruction has relied on a simple mass balance between the oxic and reducing Mo sinks (Arnold et al., 2004). The recognition of a unique Mo isotope signature in open-ocean anoxic sediments, in conjunction with the potential impact of Mo limitation on Mo isotopic behavior in restricted environments, obfuscates the use of Mo isotopes to constrain paleoredox conditions. Further investigations to elucidate the affect of Mo limitation on sediment Mo isotope compositions are warranted before the Mo isotope system can be effectively employed as a paleochemical proxy.

CONCLUSIONS

We suggest that there are two primary Mo isotope fractionations recorded in marine sediments: an oxic fractionation ($\sim -3.0\%$) reflecting Mo adsorption to Mn oxides, and an anoxic fractionation ($\sim -0.7\%$) indicative of thiomolybdate ($\text{MoO}_x\text{S}_{4-x}^{2-}$) formation. As previously proposed, in environments where sulfide concentrations exceed $100 \mu\text{M}$, there appears to be quantitative conversion of aqueous MoO_4^{2-} to the MoS_4^{2-} phase, such that no observable fractionation is recorded in the sediments. We further note that authigenic signatures can be obscured by the lithogenic Mo contribution, and measured sediment Mo isotope compositions require correction for this effect.

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