



Molybdenum behavior during early diagenesis: Insights from Mo isotopes

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[1] We present molybdenum isotope and concentration data from 14 sites in the eastern Pacific from the central California to the Peru margin. The environments studied have been chosen to represent a broad range in oxidation-reduction (redox) potential, which provide a framework for the behavior of this redox-sensitive element. Manganese-rich hemipelagic sediments from the eastern tropical Pacific have a mean characteristic Mo isotope signature ($\delta^{98/95}\text{Mo} = -0.49 \pm 0.04\text{‰}$, two times the standard deviation of the mean (2 SDOM) with $n = 14$) that reflects fractionation between ocean water and authigenic Mo associated with Mn oxides. Authigenic Fe-Mo-S deposits from reducing continental margin settings also have a characteristic Mo isotopic signature ($\delta^{98/95}\text{Mo} = 1.64 \pm 0.04\text{‰}$, 2 SDOM with $n = 136$). Both of these values are in contrast to highly sulfidic ($>11 \mu\text{M H}_2\text{S}_{\text{aq}}$) restricted basin environments, which contain Mo isotope values analytically indistinguishable from seawater. In terms of the Mo isotope composition, the modern oceanic Mo sink is dominated by continental margin “type” environments where $\delta^{98/95}\text{Mo} = \sim 1.6\text{‰}$ and Mn-rich sediments where $\delta^{98/95}\text{Mo} =$ approximately -0.5‰ , with a minor contribution from euxinic settings where $\text{H}_2\text{S}_{\text{aq}} > 11 \mu\text{M}$.

Components: 22,086 words, 9 figures, 7 tables.

Keywords: molybdenum; isotopes; diagenesis.

Index Terms: 4825 Oceanography: Biological and Chemical: Geochemistry.

Received 21 July 2008; **Revised** 1 April 2009; **Accepted** 14 April 2009; **Published** 18 June 2009.

Poulson Brucker, R. L., J. McManus, S. Severmann, and W. M. Berelson (2009), Molybdenum behavior during early diagenesis: Insights from Mo isotopes, *Geochem. Geophys. Geosyst.*, 10, Q06010, doi:10.1029/2008GC002180.

1. Introduction

[2] Under the oxygenated conditions that dominate the modern ocean, Mo exists primarily as the

soluble molybdate ion (MoO_4^{2-} ; Figure 1 [e.g., Emerson and Huested, 1991]), and it is the most abundant dissolved trace element in the contemporary ocean [Broecker and Peng, 1982]. Though

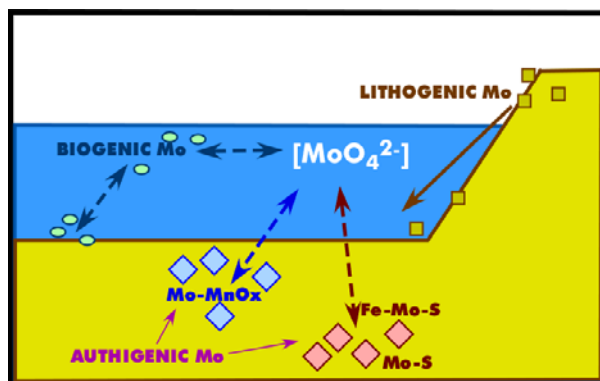


Figure 1. Major Mo sources to modern marine sediments: (1) lithogenic Mo, terrigenous material incorporated into bulk sediment; (2) biogenic Mo, sorbed to or incorporated into organic material; and (3) authigenic Mo, directly precipitated as a solid phase within the sediments (under both oxic and anoxic conditions).

considered an essential micronutrient [e.g., Mendel and Bittner, 2006, and references therein], Mo behaves conservatively in the open ocean water column with a concentration of ~ 105 nM and a

residence time of $\sim 800,000$ years [Collier, 1985; Emerson and Huested, 1991]. In addition, although there are currently only a limited number of analyses ($n = 6$), modern seawater is thought to have a homogenous Mo isotopic composition of $\delta^{98}\text{Mo}_{\text{SW}} = 2.3 \pm 0.1\text{‰}$ (Figure 2 [Barling et al., 2001; Siebert et al., 2003]; $\delta^{98}\text{Mo} = ([^{98/95}\text{Mo}_{\text{SAMPLE}}/^{98/95}\text{Mo}_{\text{STANDARD}} - 1] \times 1000)$), as would be expected given its long oceanic residence time.

[3] Unlike modern seawater, analyses to date show marine sediments to have a range of Mo concentrations and isotope compositions [e.g., Siebert et al., 2006; Poulson et al., 2006]. When interpreting the sediment record, it is important to recognize that bulk sediment Mo concentrations reflect multiple sources and processes that contribute to the total solid-phase Mo (Figure 1): (1) incorporation of lithogenic Mo into bulk sediment through continental weathering, (2) association of Mo with biological material that is delivered directly to the seafloor, and (3) precipitation or adsorption as an authigenic solid phase (under both oxic and anoxic conditions).

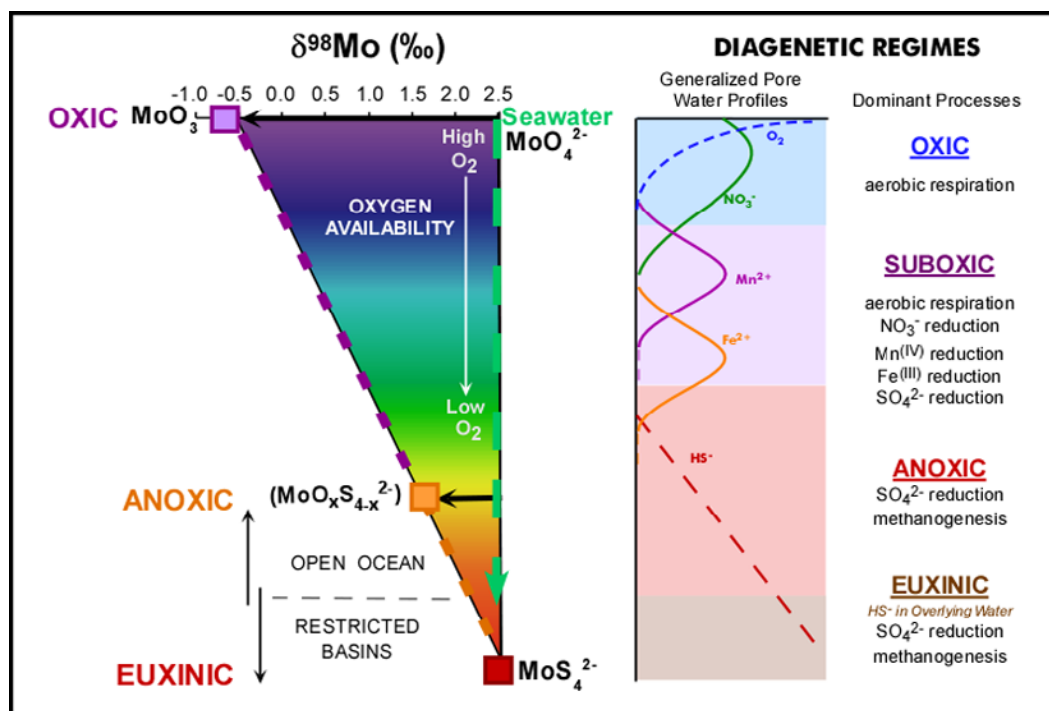


Figure 2. Previously published marine Mo isotope values and generalized depiction of associated diagenetic regimes. Isotope data plot adapted from Poulson et al. [2006] and generalized pore water profiles after Froelich et al. [1979]. The “oxic” Mo fractionation data (purple box) is taken from Fe-Mn crusts [Barling et al., 2001; Siebert et al., 2003], the “anoxic” Mo fractionation data (orange box) is from published reducing continental margin data [McManus et al., 2002; Poulson et al., 2006; Siebert et al., 2006], and the “euxinic” Mo data (red box) is from the deep Black Sea [Barling et al., 2001; Arnold et al., 2004]. The uniform seawater Mo isotope composition is shown as the green dashed line on the right side of the isotope diagram.

1.1. Lithogenic Mo

[4] Some fraction of all marine sediments contains a component of continental material, and the relative importance of a crustal component to any chemical constituent sedimentary budget (in our case molybdenum) depends on a number of processes. In many oceanic locations terrestrial sedimentation is small, but along the ocean-continent boundary this sedimentation can indeed be large. However, because of the low Mo concentration in lithogenic material, this material generally delivers only a small quantity of Mo to marine sediments [e.g., *Turekian and Wedepohl*, 1961; *Taylor and McLennan*, 1985]. Nevertheless, from an isotope budget perspective, the terrigenous contribution represents an isotopically discrete fraction of the total measured bulk sediment Mo (Figure 1) that needs to be quantified. Analyses of various terrigenous materials (e.g., granites, clastic sediments; $n = 12$) suggest a homogenous isotopic composition of $\delta^{98}\text{Mo} = 0.0 \pm 0.2\text{‰}$ [*Siebert et al.*, 2003], and for our purposes this value is assumed to represent the lithogenic Mo component in bulk sediment ($\delta^{98}\text{Mo}_{\text{LITH}}$). This assumption is necessary to constrain the isotopic composition of sedimentary authigenic Mo, because measurements of bulk sediment Mo isotope compositions in many continental margin settings require correction for dilution by the lithogenic contribution [*Poulson et al.*, 2006]. Despite this assumption, we fully recognize the possibility that the lithogenic reservoir may not be uniform in composition as the dissolved continental Mo input appears to fractionate during continental weathering [*Archer and Vance*, 2008].

1.2. Biogenic Mo

[5] Molybdenum is considered a biologically essential trace element, playing a key enzymatic role in a variety of processes, notably nitrogen fixation and nitrate reduction, as well as others [e.g., *Mendel and Bittner*, 2006, and references therein]. Like many nutritional elements, the relationship between organic matter and Mo is complex because Mo is not only incorporated into cells, but it can also be sorbed to organic material in the water column (Figure 1) [*Tribovillard et al.*, 2004]. Reported Mo:C ratios in the nitrogen-fixing bacteria *Trichodesmium erythraeum* show a range in the Mo:C ratios of natural and cultured samples (23 and 3 $\mu\text{mol/mol}$, respectively [*Tuit et al.*, 2004]). Additional studies report Mo:C ratios of ~ 9 nmol/mmol (Mazatlan margin [*Nameroff*,

1996]) and ~ 4 nmol/mmol (Santa Barbara Basin [*Zheng et al.*, 2000]) in sediment trap materials, but these studies do not distinguish between the biologically incorporated and adsorbed components. It is quite likely that Mo:C ratios in organic matter are variable, as they are dependent upon multiple environmental factors. In addition, it is also likely that the preservation of Mo associated with organic material will vary, as is seen for other redox-sensitive elements (e.g., U [*Zheng et al.*, 2002]). Recent experimental work has reported a -0.5‰ $\delta^{98}\text{Mo}$ isotope fractionation associated with biological assimilation of Mo [*Wasylenki et al.*, 2007; *Liermann et al.*, 2005]. Therefore, we might expect to observe an expression of this isotope fractionation under some conditions. However, Mo associated with biological material is generally only a small fraction of the total sediment Mo pool, making identification of the isotope expression of this fraction quite difficult. Nevertheless, it is possible that its isotopic contribution could be significant, thus we attempt to consider that pool here.

1.3. Authigenic Mo

[6] Authigenic enrichment of Mo occurs through different mechanisms under both oxic and anoxic conditions (Figure 1). In the presence of oxygen, Mo has been shown to associate with solid-phase Mn and Fe oxides [e.g., *Bertine and Turekian*, 1973; *Calvert and Pedersen*, 1993; *Chappaz et al.*, 2008], and adsorption to Mn oxides results in both sediment Mo enrichment and Mo isotope fractionation [e.g., *Barling et al.*, 2001] (Figure 2). Experimental work by *Barling and Anbar* [2004] and *Wasylenki et al.* [2008] revealed a large (2.7‰) fractionation between soluble molybdate (MoO_4^{2-}) and Mo sorbed to Mn oxides in the laboratory; that is, Mn-associated Mo had a light isotopic signature relative to the dissolved molybdate phase. These experimental findings are consistent with field results [*Barling et al.*, 2001; *Siebert et al.*, 2003], which demonstrate a similar fractionation between seawater molybdate and Mn-associated Mo in ferro-manganese crusts or nodules (Figure 2). The specific mechanism responsible for the observed isotope fractionations is not well understood, though quantum mechanical calculations suggest the fractionation may reflect adsorption of a minor aqueous species (MoO_3 or $\text{MoO}_3(\text{H}_2\text{O})_3$) to the Mn oxide surface ($\Delta^{98}\text{Mo}_{\text{MoO}_4-\text{MoO}_3} = 2.4\text{‰}$ [*Tossell*, 2005]; $\Delta^{98}\text{Mo}_{\text{MoO}_4-\text{MoO}_3(\text{H}_2\text{O})_3} = 2.0\text{‰}$ [*Weeks et al.*, 2007]). Though the mechanisms remain un-

clear, Mn-controlled authigenic Mo enrichments ($\delta^{98}\text{Mo}_{\text{Mn-AUTH}}$) have the most negative sediment Mo isotope compositions measured to date.

[7] In marine sediments, Mn and Fe oxides are a disseminated phase and the molybdenum associated with these metal oxides can undergo additional cycling during early diagenesis, potentially leaving an isotopic expression of this cycling. Once oxygen is consumed during organic matter oxidation, Mn and Fe reduction may ensue, releasing oxide-sorbed Mo back into solution. If Mn or Fe is then reoxidized within the sedimentary column during diagenesis, some dissolved Mo may readsorb to this reoxidized metal. Alternatively, some dissolved Mo may be removed from pore water deeper in the sediment column if there is an additional sedimentary Mo sink. The impact of metal cycling on Mo isotope compositions has previously been demonstrated by *Reitz et al.* [2007], who argued that diagenetic Mn cycling impacts the Mo isotopic compositions of affected sediments. Their data suggest that if fractionated Mn-bound Mo ($\delta^{98}\text{Mo}_{\text{Mn-AUTH}}$) is released during Mn reduction and subsequently deposited in authigenic phases at depth, such secondary diagenetic processes can drive sediment Mo isotope compositions to increasingly fractionated values.

[8] Another type of authigenic Mo deposit is generated under anoxic sedimentary conditions where sulfate reduction is the dominant microbially mediated organic matter degradation process. Here Mo is sequestered into sediments through complexation with sulfide (Figure 1), forming thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) that are scavenged by organic matter or Fe sulfide phases such as pyrite [*Helz et al.*, 1996, 2004; *Zheng et al.*, 2000; *Algeo and Lyons*, 2006; *Tribouillard et al.*, 2004, 2006]. *Helz et al.* [1996] proposed a sulfide-controlled geochemical action point switch (APS) for Mo at $\sim 11 \mu\text{M H}_2\text{S}_{(\text{aq})}$, where the dominant dissolved Mo phase abruptly transitions from molybdate (MoO_4^{2-}) to tetrathiomolybdate (MoS_4^{2-}) [see also *Erickson and Helz*, 2000]. The pore water work of *Zheng et al.* [2000] proposed two thresholds for Mo sulfide formation; at $\text{H}_2\text{S}_{(\text{aq})}$ concentrations of $\sim 0.01 \mu\text{M}$ these authors proposed that Mo is removed from solution via coprecipitation of Fe-Mo-S phases, whereas at higher $\text{H}_2\text{S}_{(\text{aq})}$ concentrations ($\sim 10 \mu\text{M}$) they postulate that Mo precipitates independent of iron. It may be that the sulfide thresholds proposed by *Zheng et al.* [2000] reflect changes in aqueous Mo speciation that impact solid-phase Mo behavior. At low sul-

fide concentrations, thiomolybdate intermediate species ($\text{MoO}_x\text{S}_{4-x}^{2-}$) may dominate the aqueous phase and be scavenged by solid-phase Fe sulfides, while at higher sulfide concentrations tetrathiomolybdate (MoS_4^{2-}) is likely to dominate, precipitating independently as a solid phase Mo sulfide.

[9] Indeed, it appears that the sulfide APS has a strong impact on sediment Mo isotope compositions. In the deep Black Sea, where euxinic conditions persist and sulfide concentrations are well above the APS in the overlying water column, measured sediment Mo isotope compositions are analytically indistinguishable from the seawater $\delta^{98}\text{Mo}$ value (Figure 2) [*Barling et al.*, 2001; *Arnold et al.*, 2004; *Neubert et al.*, 2008]. This has been attributed to complete removal or conversion of MoO_4^{2-} from the water column, resulting in no observable fractionation between the sediment Mo inventory and the aqueous Mo source [e.g., *Barling et al.*, 2001; *Arnold et al.*, 2004]. Studies by *Nägler et al.* [2005] and *Neubert et al.* [2008] showed that Black Sea sediments only record the seawater $\delta^{98}\text{Mo}$ value in water depths below the APS ($\sim 400 \text{ m}$). In shallower sediments, Mo isotope values are fractionated relative to a seawater $\delta^{98}\text{Mo}$ source ($\delta^{98}\text{Mo} = -0.6\text{‰}$ to 1.6‰ [*Neubert et al.*, 2008]). This distinction is important in that the euxinic sediments recording the seawater $\delta^{98}\text{Mo}$ value represents only a small fraction ($<10\%$) of the total “reducing” sink in the modern global ocean Mo budget [e.g., *McManus et al.*, 2006].

[10] Other results from environments with sulfide concentrations well below the APS, or where both oxygen and sulfide are low to negligible in overlying waters, also suggest significant Mo isotopic fractionation between authigenic sedimentary Mo deposits and a seawater $\delta^{98}\text{Mo}$ source. An investigation of pore waters from Santa Monica Basin modeled a fractionation of -0.7‰ between pore fluids and sediment Mo deposits under reducing conditions [*McManus et al.*, 2002]. Furthermore, sediments from three sites underlying low-oxygen waters on the Mexican continental margin suggest a constant Mo isotopic signature of $\delta^{98}\text{Mo} = 1.6\text{‰}$ [*Poulson et al.*, 2006], consistent with the fractionation modeled from pore water Mo profiles [*McManus et al.*, 2002] (Figure 2).

[11] Authigenic Mo enrichment in all of these environments is likely controlled by the formation and deposition of Mo sulfides [e.g., *Helz et al.*, 1996], but the exact geochemical mechanisms responsible for this fractionation remain ill defined.

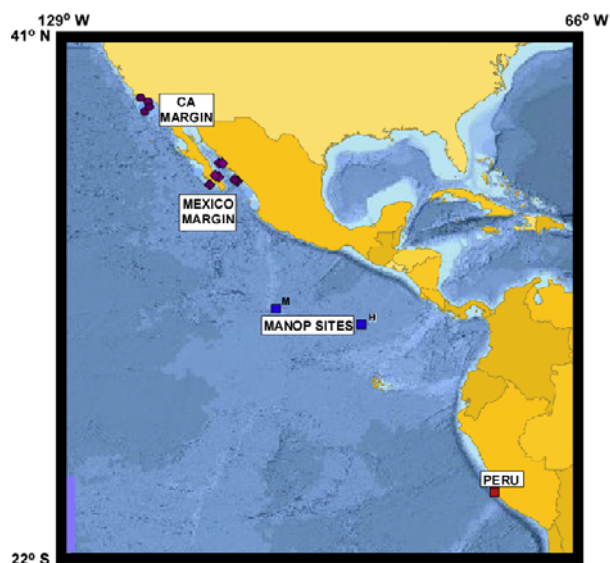


Figure 3. Map of study areas showing approximate locations of all sites investigated. Base map generated using <http://www.planiglobe.com>.

It has been suggested, however, that the formation of thiomolybdate species ($\text{MoO}_x\text{S}_{4-x}^{2-x-}$) fractionates Mo isotopes in the aqueous phase [e.g., Neubert *et al.*, 2008]. In fact, quantum mechanical calculations predict a large ($\sim 7\%$) fractionation between MoO_4^{2-} and MoS_4^{2-} species [Tossell, 2005]. Experimental work has shown that, in the presence of both H_2S and S^0 electron donors, thiomolybdate Mo(VI) may be reduced to Mo(V) or Mo(IV) polysulfide anions [Vorlicek *et al.*, 2004]. Changes in bonding around the Mo atom, whether associated with S and O substitutions or with reduction of Mo, could result in isotopic fractionation between dissolved Mo species. Subsequent scavenging and deposition of these fractionated Mo species may be responsible for the observed authigenic signature.

[12] Despite uncertainties about the governing mechanisms, in combination, the pore water work of McManus *et al.* [2002] and the observed fractionation in previously published Mexico margin sediments [Poulson *et al.*, 2006] and shallow Black Sea sediments [Nägler *et al.*, 2005; Neubert *et al.*, 2008] suggest a unique Mo isotope signature exists for authigenic Mo deposits in reducing continental margin settings ($\delta^{98}\text{Mo}_{\text{S-AUTH}}$), with a common value of $\sim 1.6\%$. However, and in contrast to this assertion, reported Mo isotope compositions from surface sediments of the California continental margin span the full range between Mn-dominated

and more reducing (where sulfate reduction is important for electron transport) environments [Siebert *et al.*, 2006; Poulson *et al.*, 2006]. Although sediments from two low-oxygen, high carbon flux basins (Santa Monica and San Pedro) do indeed have Mo isotope signatures consistent with those observed on the Mexican and shallow Black Sea margin (core average $\delta^{98}\text{Mo}$ values of 1.4‰ and 1.6‰; respectively), sediments from the well-oxygenated and Mn-rich San Clemente basin have reported Mo isotope values consistent with Mn-associated Mo (core average $\delta^{98}\text{Mo} = -0.8\%$ [Siebert *et al.*, 2006; Poulson *et al.*, 2006]). In addition, in Tanner basin, a site where environmental conditions are between these two extremes, sediment Mo isotope compositions are intermediate and more variable than those reported in other settings (core average $\delta^{98}\text{Mo} = 0.5\%$ [Siebert *et al.*, 2006; Poulson *et al.*, 2006]).

[13] The range of Mo isotope compositions measured on the California margin, and our incomplete understanding of the mechanisms responsible for this variability, demonstrate the need for further refinement of the Mo isotope system in marine sediments. Because reducing continental margin environments may represent a substantial sink for Mo in the modern ocean [e.g., McManus *et al.*, 2006], it is important to assess the range of isotope values in these settings and determine if there is indeed a dominant authigenic signature recorded in continental margin sediments. This study aims to further constrain Mo distributions and isotopic fractionation in the marine environment through observations from a number of continental margin settings (Figure 3). As described in detail below, we have selected sites that represent a range of diagenetic settings that are prevalent along the open ocean-continent boundary.

2. Methods

[14] All sediment cores from the California, Mexico, and Peru margins were collected using a multicorer [Barnett *et al.*, 1984]. Organic carbon was measured using an elemental analyzer, with samples first acidified to remove inorganic carbon prior to analysis [after Verardo *et al.*, 1990]. Solid-phase metal analyses were performed on 50–100 mg of dry ground bulk sediment samples digested using a series of HCl, HNO_3 , and HF digestion steps (either on a hot plate or by microwave digestion (CEM, MARS 5000)). These two methods are generally analytically indistinguish-

able (Tables A1–A3). Major element compositions (Al, Ca, Fe, Mn, and Ti) were measured on total sample digestions by inductively coupled plasma optical emission spectrometry (ICP-OES, Teledyne Leeman Prodigy; Tables A1 and A3). For the same bulk sediment sample digestions, trace element concentrations were determined by inductively coupled plasma mass spectrometry (ICPMS, Thermo PQ ExCell; Tables A1 and A2).

[15] The reproducibility of analytical techniques was evaluated by performing replicate analyses of multiple standard reference materials (Table A1). Major element concentrations (Al, Fe, Mn, and Ti) analyzed by ICP-OES for all standard reference materials are typically reproducible within 5% (1 SD), and agree reasonably well with previously reported values (Table A1). For Mo concentrations determined by ICPMS, as well as those produced during isotopic analyses, standard reference materials were typically reproducible to $\leq 12\%$ (1 SD) and agree with published values, with the exception of the standard reference material NBS-1645 (Table A1). This material is a river sediment standard, and it has been the most difficult matrix for our group to reproduce analytically (as noted by its relatively high uncertainty; Table A1); our Mo concentration data for NBS-1645 does not agree with the published value (34 ppm, *Potts et al.*, 1992). As there is no available certified reference value for this standard, we have confidence in our value (18 ± 2 ppm), but note this discrepancy. For this particular material, our value represents replicate digestions, multiple analytical techniques, and analyses of 39 separate sample aliquots (Table A1).

[16] Separate bulk sediment samples (~ 100 mg) were digested for Mo isotopic analyses (Tables A1 and A4). Samples were spiked with a ^{97}Mo and ^{100}Mo double isotope tracer and Mo was separated from the sediment matrix using a previously published column separation technique [*Siebert et al.*, 2001, 2006]. Mo isotope compositions were analyzed on a Nu Instruments HR multicollector inductively coupled plasma mass spectrometer (MC-ICPMS). All Mo isotope measurements are reported relative to a Claritas PPT ICPMS Mo standard solution (Lot #CL2–44MO). At present there is not an accepted standard for interlaboratory comparison; thus, normalizing measured values to different standards could potentially generate offsets between reported Mo isotope values from different lab groups.

[17] Four of the standard reference materials have also been run several times to evaluate the reproducibility of Mo isotope analyses (PACS-2, $n = 10$, SDO-1, $n = 10$, SX-12280, $n = 23$ and NBS-1645, $n = 39$); long-term reproducibility for these standards is $\leq 0.3\%$ (long-term average 1-SD errors for all separate digestions; Table A1). We present these different reference materials in part because there is no internationally accepted standard reference material for Mo, and wish to offer a baseline of comparison for our data. Because of this lack of an international standard, it is important to consider the comparability of the data we report to that of other groups, in as much as is possible. The USGS standard SDO-1 has been run repeatedly by the group at Arizona State University (ASU) and their value for that standard is $\delta^{98/95}\text{Mo} = 1.14 \pm 0.15\%$ ($n = 248$ (G. Gordon, personal communication, 2009)). Our value of $1.2 \pm 0.3\%$ (Table A1) is in agreement with their value.

[18] In general it appears that our sediment data are comparable with prior work; however, we recommend that the reader extend a certain level of caution when comparing the absolute value of our numbers to those of other values. Much of the comparisons employed herein lean on comparisons internal to our work, and it is worth noting that in general, analyses of individual samples tended to reproduce better than the standard reference materials with an average 1-SD error of 0.1% (e.g., Table A4). It is also worth noting that the empirically derived Mo isotope fractionation factor ($\Delta^{98}\text{Mo}$) reported for Mo sorption to Mn oxides [*Barling and Anbar*, 2004; *Wasylenki et al.*, 2008] is a relative offset between measured values. The magnitude of this offset should be applicable across data sets; as discussed in detail below, the reported fractionation factor generally agrees with the offset observed between the reported seawater Mo isotope value ($\delta^{98}\text{Mo}_{\text{SW}} = 2.3 \pm 0.1\%$ [*Barling et al.*, 2001; *Siebert et al.*, 2003]) and the Mn-rich sediment data of this study.

[19] Replicate digestions and ICP-OES, ICPMS, and MC-ICPMS analyses were performed on $\sim 20\%$ of all natural sediment samples in this study (Tables A2–A4). The average reproducibility of these data for Mo concentrations is better than 10% (1 SD). There are a number of samples within the data set for which analyses reproduced poorly, but are nonetheless part of the average. In general, these analytical anomalies have little impact on the primary signatures that emerge from the overall

data set, given its large size and breadth of environmental coverage.

3. Results and Discussion

[20] The bulk Mo in any sediment sample represents an admixture of different Mo pools. Here we assume that each pool has a unique Mo isotopic composition (Figure 1). On the basis of the available data, we generate a mass balance of the fractions of each Mo component relative to the total sediment Mo concentration (X_n) and their isotopic signatures ($\delta^{98}\text{Mo}_n$):

$$\begin{aligned} \delta^{98}\text{Mo}_{\text{MEAS}} = & \delta^{98}\text{Mo}_{\text{LITH}}(X_{\text{LITH}}) + \delta^{98}\text{Mo}_{\text{BIO}}(X_{\text{BIO}}) \\ & + \delta^{98}\text{Mo}_{\text{Mn-AUTH}}(X_{\text{Mn-AUTH}}) \\ & + \delta^{98}\text{Mo}_{\text{S-AUTH}}(X_{\text{S-AUTH}}) \end{aligned} \quad (1)$$

[21] In this model X is the fraction of each Mo pool (all X s add up to 1): Mo_{LITH} represents the lithogenic Mo associated with continental weathering, Mo_{BIO} represents the biogenic Mo fraction associated with organic matter deposition, and the authigenic Mo enrichments are represented as $\text{Mo}_{\text{Mn-AUTH}}$ (Mo associated with Mn oxides) and $\text{Mo}_{\text{S-AUTH}}$ (Mo sulfides formed in reducing sediments). It is often possible to simplify this equation; for example, Mn-controlled authigenic Mo deposits occur under oxygenated conditions where Mo sulfide formation is negligible. Therefore the relative importance of each source to the total bulk Mo reservoir is dependent upon geochemical conditions specific to the sedimentary environment.

3.1. Lithogenic Mo

[22] For many continental margin sedimentary settings the fraction of Mo that is associated with lithogenic material can be quite significant, thereby obscuring the authigenic Mo signature. In terms of considering the global authigenic burial budget, this problem is not trivial, as it can significantly impact the interpretation of the continental margin burial flux [e.g., *McManus et al.*, 2006]. For this study we estimate the fraction of lithogenic Mo in bulk sediment samples from a regional background Mo:Al ratio [e.g., *McManus et al.*, 2006]. For all sites in this study, a lithogenic Mo:Al ratio of 11×10^{-6} was used, which is the median value from a range of background Mo:Al values (8 to 14×10^{-6}) previously observed in sediments from the Californian and Chilean margins [*McManus et al.*, 2006]. This value is also consistent with typical

reported values for igneous rocks and sandstones (Mo:Al = 6 to 19×10^{-6} in the work by *Turekian and Wedepohl* [1961]; Mo:Al = $\sim 19 \times 10^{-6}$ in the work by *Taylor and McLennan* [1985]). We therefore estimate the total sedimentary lithogenic Mo contribution from the measured sediment Al concentrations, and calculate the lithogenic fraction (X_{LITH}) as the fraction of lithogenic Mo relative to the total bulk Mo pool. For all sites in this study, the estimated lithogenic Mo contribution was ≤ 1 ppm Mo (Table A5). On average, the lithogenic fraction (X_{LITH}) is less than 15% of the total bulk sediment Mo (Table 1).

[23] For the lithogenic fraction we assumed a $\delta^{98}\text{Mo}$ value of 0.0‰ [after *Siebert et al.*, 2003]. Measured Mo isotope compositions of bulk sediment samples are therefore corrected for “dilution” by the lithogenic fraction [*Poulson et al.*, 2006], and the resulting simplified mass balance (equation (1)) would have the form:

$$\delta^{98}\text{Mo}_{\text{MEAS}} = \delta^{98}\text{Mo}_{\text{LITH}}(X_{\text{LITH}}) + \delta^{98}\text{Mo}_{\text{ENRICH}}(X_{\text{ENRICH}}) \quad (2)$$

where $\text{Mo}_{\text{ENRICH}}$ represents the sediment Mo enrichment over any lithogenic contribution. For all sedimentary environments, $\text{Mo}_{\text{ENRICH}}$ represents some combination of authigenic enrichment (either Mn- or S-controlled) and Mo that is associated with biological material (Figure 1), such that:

$$\begin{aligned} \delta^{98}\text{Mo}_{\text{ENRICH}} = & \delta^{98}\text{Mo}_{\text{BIO}}(X_{\text{BIO}}) + \delta^{98}\text{Mo}_{\text{Mn-AUTH}}(X_{\text{Mn-AUTH}}) \\ & + \delta^{98}\text{Mo}_{\text{S-AUTH}}(X_{\text{S-AUTH}}) \end{aligned} \quad (3)$$

This lithogenic Mo correction allows for more accurate interpretation of Mo isotopic variability in sediment Mo enrichments, reported herein as $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values (Tables 1 and A5). At least three pieces of evidence that suggest more isotopic variability in the lithogenic signature than we can currently constrain include; the recent work of *Archer and Vance* [2008] who showed that chemical weathering does indeed generate some isotope fractionation, the work of *Hannah et al.* [2007] and *Malinovsky et al.* [2007] who showed considerable variation in the Mo isotope composition of molybdenites, and of course the fact that shale deposits can have a range of isotope compositions [e.g., *Arnold et al.*, 2004; *Siebert et al.*, 2005; *Wille et al.*, 2007, 2008].

Table 1 (Sample). General Site Characteristics and Average Sediment Mo_{ENRICH} Data^a [The full Table 1 is available in the HTML version of this article]

	Depth (cm)	Latitude (°N)	Longitude (°W)	Depth (m)	BW O ₂ (μM)	Average Mo _{ENRICH} (ppm)	X _{LITH}	δ ⁹⁸ Mo _{ENRICH} (‰)	Mo _{ENRICH} :C _{org} (ppm/%)
MANOP sites									
Site H		06.5	92.8	3600	110–150				
	0.5					55.6	0.01	−0.5	68.6
	1.5					52.7	0.01	−0.4	71.5
	3.5					45.1	0.01	−0.4	54.7
	3.5					49.8	0.01	−0.4	
	4.5					62.3	0.01	−0.5	78.0
	4.5					55.4	0.01	−0.5	
	6.0					62.1	0.01	−0.4	70.4
	8.0					36.8	0.02	−0.6	53.6
	10.0					28.3	0.02	−0.6	37.6
	12.0					13.9	0.04	−0.4	16.5
	14.0					5.9	0.10	−0.4	6.1
	16.0					5.7	0.10	−0.6	5.5
	18.0					5.9	0.10	−0.5	5.3
	20.0					5.6	0.11	−0.6	4.9
Site M		08.8	104.0	3100	110–150				
	0.8					15.0	0.04	−0.2	10.3
	2.0					13.9	0.04	−0.3	9.5
	4.0					13.1	0.04	−0.4	8.9
	6.0					6.0	0.09	−0.4	3.8
	8.0					2.6	0.21	−0.3	1.5
	10.0					2.1	0.25	0.2	1.1
	12.0					2.0	0.27	−0.1	1.1
	14.0					1.6	0.35	0.2	0.7
	16.0					1.2	0.46	0.3	0.5
	18.0					0.6	0.88	−0.4	0.1
Peru margin		−13.7	76.7	264	<10				
	1.3					87.3	0.00	1.0	6.0
	3.3					81.5	0.00	1.2	5.6
	5.3					79.5	0.00	1.0	5.4
	7.3					58.4	0.00	1.1	4.0
	9.3					59.7	0.01	1.4	4.1
	12.5					58.6	0.01	1.3	4.0
	14.5					30.0	0.02	1.7	2.0
	21.0					26.6	0.02	1.7	1.8
	25.0					29.3	0.01	1.6	2.0
	33.0					37.5	0.02	1.3	2.5
California margin									
Santa Barbara		34.3	120.0	493	≤1				
	1.3					3.7	0.18	1.4	1.1
	4.3					4.4	0.17	1.5	1.1
	6.3					6.4	0.12	0.8	1.8
	8.3					4.9	0.15	1.5	1.3
	10.5					7.3	0.10	1.4	2.0
	14.5					4.5	0.16	1.8	1.3
	18.5					4.3	0.18	1.5	1.2
	25.0					4.3	0.19	1.6	1.2
	33.0					4.0	0.26	1.7	1.0
	41.0					3.8	0.27	1.8	0.9
Santa Monica		33.7	118.8	910	2.0				
	0.5					3.2	0.19	1.6	
	0.9					3.3	0.18	1.7	0.6

^aBottom water oxygen data for all Mexican margin sites (and Santa Monica) from *Berelson et al.* [2005]. All other bottom water oxygen values compiled from *Bender and Heggie* [1984], *Berelson et al.* [1987, 2005], and *McManus et al.* [2006]. Average sediment Mo_{ENRICH} concentrations, isotopic compositions, and Mo:C ratios from Table A5. Fractions of lithogenic Mo (X_{LITH}) calculated in Table A5; assumed Mo:Al ratio for lithogenic background is 1.1×10^{-5} [*McManus et al.*, 2006; *Poulson et al.*, 2006]. Details of lithogenic correction (δ⁹⁸Mo_{ENRICH} values) described in text. The italicized Mo:C ratios from MANOP Site M and the Peru margin are calculated from a single average organic carbon value for the whole core (see Table A5).

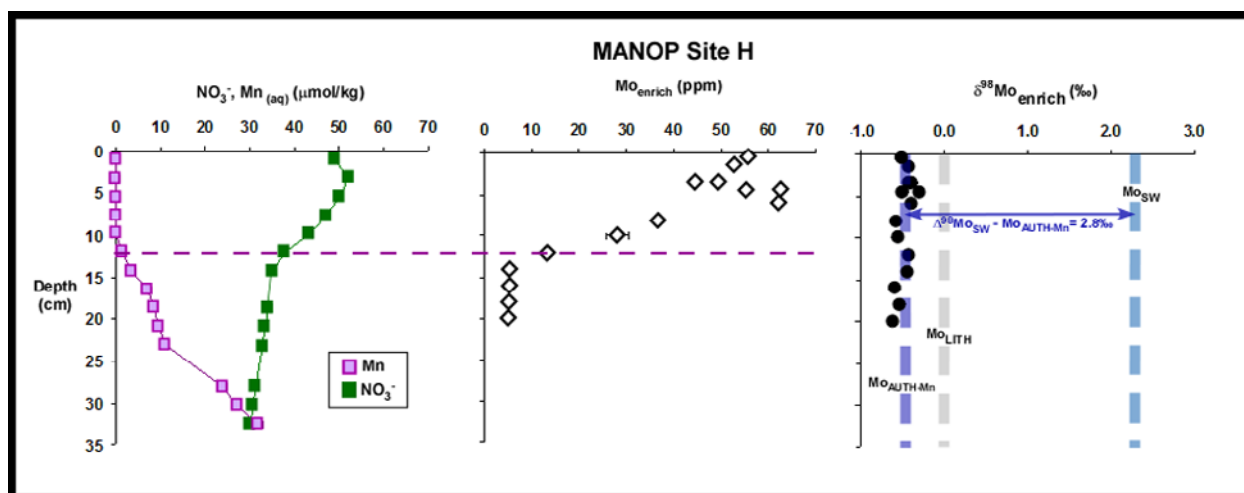


Figure 4. MANOP site H profiles. (left) All pore water data from *Klinkhammer* [1980]. Dashed line indicates estimated depth of Mn reduction (~ 12 cm). (middle) Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and (right) $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values from Table A5. All error bars (ppm and ‰) are 1-SD errors for average replicate sample digestions. Light blue dashed line labeled Mo_{SW} is the average isotopic composition of seawater ($\delta^{98}\text{Mo}_{\text{SW}} = 2.3 \pm 0.1\text{‰}$ [Barling *et al.*, 2001; Siebert *et al.*, 2003]). Gray dashed line labeled Mo_{LITH} is the average isotopic composition of terrestrial materials ($\delta^{98}\text{Mo}_{\text{LITH}} = 0.0 \pm 0.2\text{‰}$ [Siebert *et al.*, 2003]). Blue dashed line labeled $\text{Mo}_{\text{AUTH-Mn}}$ is the average isotopic composition of these MANOP H samples ($\delta^{98}\text{Mo}_{\text{AUTH-Mn}} = -0.5\text{‰}$).

[24] Future work may provide a different estimate for the lithogenic component, both in terms of concentration and isotopic composition; however, it is also important to appreciate that for many of the sites reported here, the potential inaccuracies in this estimate are small when compared to the bulk signature.

3.2. MANOP Sites: Marine Sedimentary Authigenic Mo-Manganese Signature

[25] Two sediment cores from the eastern tropical Pacific (cores collected as part of the Manganese Nodule Program, MANOP sites M and H) represent the least reducing sites analyzed in this study. These sites are characterized as being hemipelagic Mn-rich sites (1–7 wt % Mn [Lyle *et al.*, 1984]) lying below a well-oxygenated water column (110–150 μM [e.g., Bender and Heggie, 1984]). Both sites are from water depths greater than 3000 m; site M is located ~ 25 km east of the East Pacific Rise, and site H is located in the Guatemala Basin (Figure 3 and Table 1). Site M was selected for the original MANOP study to investigate hydrothermal sedimentation [Lyle *et al.*, 1984]. Site H, originally selected as a representative hemipelagic site, is marked by the presence of Mn-rich ferromanganese nodules [Finney *et al.*, 1984].

[26] Surface sediments from both MANOP sites have significant $\text{Mo}_{\text{ENRICH}}$ concentrations associ-

ated with Mo sorbed to Mn oxides (Table 1). Site H, in particular, may be considered “prototypical” Mn-rich sediment, with Mn concentrations of ~ 5 wt % [Lyle *et al.*, 1984] (Table A3). Likewise, pore water Mn data at site H imply that sediments are oxygenated to ~ 12 cm, with Mn reduction below this depth [Klinkhammer, 1980] (Figure 4). Sediment Mo concentrations reflect the process of Mn reduction at depth; the upper ~ 10 cm are highly enriched in Mo (>50 ppm) with $\text{Mo}_{\text{ENRICH}}$ concentrations decreasing below this depth (Figure 4 and Table 1). This solid phase Mo decrease suggests Mo is released back into pore fluids as the host Mn oxide is reduced. We take Site H to represent an end-member case for open-ocean authigenic Mo enrichment associated with Mn oxides ($\text{Mo}_{\text{Mn-AUTH}}$), such that (from equation (3)) $\delta^{98}\text{Mo}_{\text{ENRICH}} = \delta^{98}\text{Mo}_{\text{Mn-AUTH}} (X_{\text{Mn-AUTH}})$.

[27] Consistent with the dominance of Mn cycling, site H sediments have the most negative Mo isotopic compositions measured in this study (Table 1) with an average $\delta^{98}\text{Mo}_{\text{ENRICH}}$ value for all site H samples of $-0.49 \pm 0.04\text{‰}$ (2 SDOM with $n = 14$, where $2 \text{ SDOM} = [2 \times (\text{stdev}/(\text{sqrt } n))]$; Table 1 and Figure 4). This value suggests a fractionation between a seawater aqueous Mo source and the authigenic Mo pool of $\Delta^{98}\text{Mo}_{\text{SW-Mn-AUTH}} = 2.8\text{‰}$; consistent with previously reported Mo isotope data from Fe-Mn crusts (Figure 2) [Siebert *et al.*, 2003; Barling *et al.*, 2001], previously

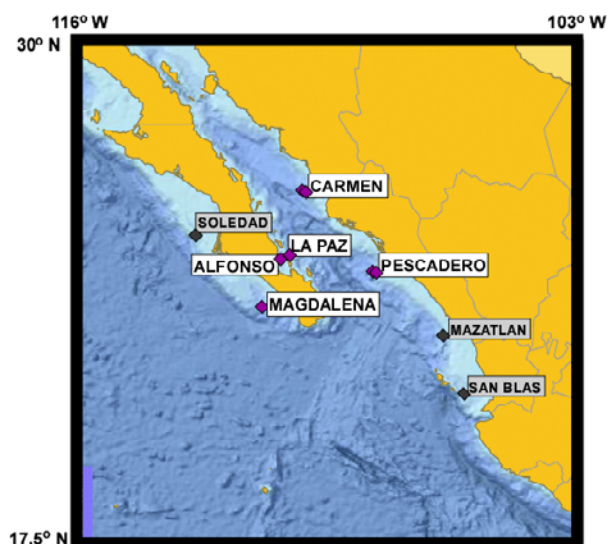


Figure 5. Map of Mexico margin study areas showing approximate locations of all sites investigated. Sites reported in this study are shown in colored symbols; sites with previously published Mo isotope data are shown in gray [Poulson *et al.*, 2006]. Base map generated using <http://www.planiglobe.com>.

reported data from Mn-rich sediments [Siebert *et al.*, 2006; Poulson *et al.*, 2006], and experimental work [Barling and Anbar, 2004; Wasylenzi *et al.*, 2008].

[28] Site M sediments are less fractionated relative to seawater ($-0.1 \pm 0.2\text{‰}$; 2 SDOM with $n = 10$; Table 1) than those measured at site H; nevertheless, $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values from site M are generally negative, suggesting Mn cycling is a primary control on Mo behavior at this site (Table 1). Pore water data suggest Mn reduction at a depth of only ~ 5 cm at site M [Klinkhammer, 1980] and solid phase $\text{Mo}_{\text{ENRICH}}$ concentrations also decrease below this depth (Table 1).

3.3. Mexico and Peru Margins: Open Ocean Authigenic Mo Sulfide Signature

[29] The Mexico margin sediment samples investigated in this study were all subsamples of cores previously studied by Sansone *et al.* [2004] and Berelson *et al.* [2005] (Figure 5 and Table 1). One station is located off the west coast of Southern Baja on the open margin (Magdalena); the remaining four sites are located within the Gulf of California (Figure 5). Of the four sites located within the Gulf of California, two lie within depositional basins (Alfonso and La Paz), and

two are from the open margin on the eastern side of the Gulf (Carmen and Pescadero).

[30] Along the Mexico margin oxygen-deficient North Pacific Intermediate Water dominates subsurface currents and establishes an OMZ between depths of 500 and 1000 m [Thunell, 1998]. This low-oxygen core extends >1500 km off the coast of Mexico [Sansone *et al.*, 2004], and anoxic or very low oxygen ($<1 \mu\text{M}$) bottom waters throughout this region limit bioturbation and allow for the preservation of laminated sediments underlying the OMZ [e.g., Calvert, 1966]. Because the sediments on this margin are bathed in low-oxygen waters, decomposition of organic carbon via aerobic processes is presumably limited. Evidence of denitrification and Mn reduction has been reported within the water column off mainland Mexico [e.g., Nameroff *et al.*, 2002; Hartnett and Devol, 2003], suggesting that diagenesis within the sediments is dominated by reactions associated with Fe and S cycling. The diagenetic production of methane at these sites also confirms highly reducing conditions within the sediments [Sansone *et al.*, 2004; Berelson *et al.*, 2005]. All the Mexican margin sites are thus presumed to contain anoxic sediments. Bottom water oxygen concentrations are low ($<5 \mu\text{M}$) and laminated sediments are present at all but the Magdalena site [Berelson *et*

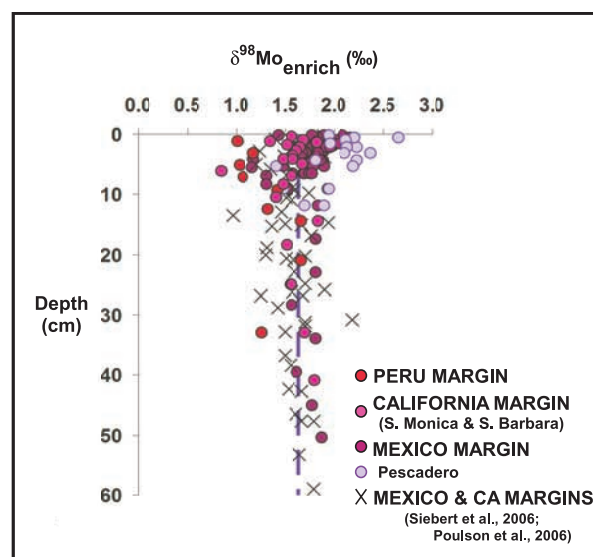


Figure 6. Sediment $\text{Mo}_{\text{ENRICH}}$ isotope compositions from all anoxic margin sites. All Mo isotope data (circles) from this study are from Table A5; data from previous studies (crosses [Siebert *et al.*, 2006; Poulson *et al.*, 2006]) are from Table A6. Purple dashed line represents average value (1.64‰) for all sediment data shown ($n = 136$; excludes Pescadero sediments).

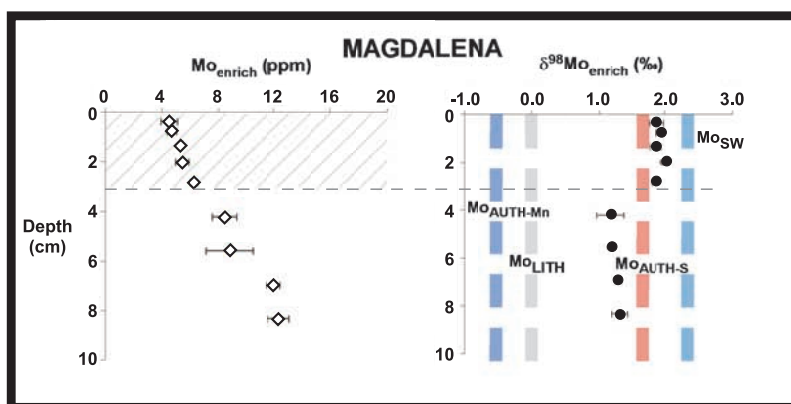


Figure 7. Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and isotope compositions from Magdalena margin. Hatched section and dashed line indicate bioturbated layer (0–3 cm). Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values are from Table A5. All error bars (ppm and ‰) are 1-SD errors for average replicate sample digestions. Light blue dashed line labeled Mo_{SW} is the average isotopic composition of seawater ($\delta^{98}\text{Mo}_{\text{SW}} = 2.3 \pm 0.1\text{‰}$ [Barling *et al.*, 2001; Siebert *et al.*, 2003]). Gray dashed line labeled Mo_{LITH} is the average isotopic composition of terrestrial materials ($\delta^{98}\text{Mo}_{\text{LITH}} = 0.0 \pm 0.2\text{‰}$ [Siebert *et al.*, 2003]). Blue dashed line labeled $\text{Mo}_{\text{AUTH-Mn}}$ is the average isotopic composition of the MANOP H samples ($\delta^{98}\text{Mo}_{\text{AUTH-Mn}} = -0.5\text{‰}$). Red dashed line labeled $\text{Mo}_{\text{AUTH-S}}$ is the average isotopic composition of the Mexico margin samples ($\delta^{98}\text{Mo}_{\text{AUTH-S}} = 1.7\text{‰}$).

al., 2005]. These conditions suggest Fe/S-controlled rather than Mn/ O_2 reduction processes are likely to dominate authigenic Mo enrichment at most if not all of these sites.

[31] Molybdenum isotope values consistent with the previously reported “anoxic” sediment Mo isotope signature ($\delta^{98}\text{Mo} = 1.6\text{‰}$ [Poulson *et al.*, 2006]; Figure 2) are measured at depth (greater than ~15 cm) in almost all sites analyzed in the Mexico margin (Figure 6 and Table 1). However, there are sufficient data to suggest that there is a near-surface sedimentary pool of Mo that is closer to the ocean water isotope value than the more typical continental margin value (Figure 6). These heavy Mo isotope values lead us to speculate that there may be a biogenic Mo (Mo_{BIO}) sedimentary component that dominates the bulk Mo pool in the uppermost sediments at some locations. In particular, sediments from both cores taken on the Pescadero slope have the lowest concentrations of $\text{Mo}_{\text{ENRICH}}$ (2.8 ± 0.2 ppm, 2 SDOM with $n = 19$) and the lowest observed sediment $\text{Mo}_{\text{ENRICH}}:\text{C}_{\text{org}}$ ratios (~0.5) of all sites analyzed on the Mexico margin (Table 1). These low $\text{Mo}_{\text{ENRICH}}:\text{C}_{\text{org}}$ ratios are lower than those reported for sediment trap materials [Nameroff, 1996; Zheng *et al.*, 2000] and nitrogen fixing biota [Tuit *et al.*, 2004], indicating that these sediments are the least likely to be impacted by other authigenic Mo enrichment. Sediments from both Pescadero sites have the heaviest $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values measured on the margin, specifically in the uppermost ~4 cm, averaging

$\delta^{98}\text{Mo}_{\text{ENRICH}} = 2.2 \pm 0.1\text{‰}$ for all samples over this depth range (2 SDOM with $n = 11$; Figure 6 and Table 1). If this value represents the Mo isotopic composition of sedimenting organic material ($\delta^{98}\text{Mo}_{\text{BIO}}$), the data suggest that there is likely little or no fractionation between seawater Mo and biogenic Mo. We recognize that statistically it is difficult to discern whether or not there is an offset from the ocean water value, but more importantly the mean of both these sites is indeed different from the down-core continental margin value (~1.6‰). We further note that the small to negligible fractionation implied here (~0.1‰) differs from the 0.5‰ reported for biological uptake of Mo from solution in laboratory experiments [Wasylenki *et al.*, 2007; Liermann *et al.*, 2005]. However, it would be imprudent to interpret either this study or previous work as implying a single isotopic composition for biogenic material. Furthermore, other sites also offer an indication that there may be a Mo sedimentary component that is enriched in the heavy Mo isotopes. For example, down-core data from the Magdalena margin suggest that there may be two sedimentary Mo components in the upper sediment column having different isotope values (Figure 7). These sediments are bioturbated in the uppermost 2–3 cm [Berelson *et al.*, 2005], and mixing may inhibit the formation of Fe/S-controlled authigenic Mo deposits in the most surficial sediments. Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations remain low throughout the uppermost ~3 cm, increasing below this depth (Figure 7 and Table 1). Sediment $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values are heaviest within

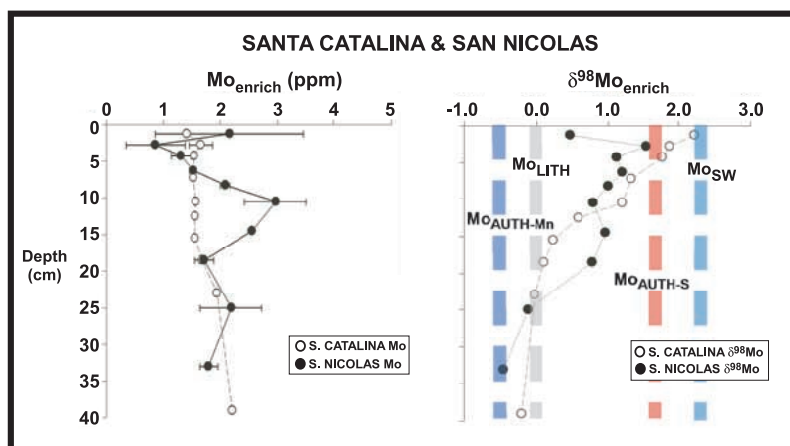


Figure 8. Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and Mo isotope compositions from Santa Catalina and San Nicolas basins. (left) Sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and (right) $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values from Table A5. All error bars (ppm and ‰) are 1-SD errors for average replicate sample digestions. Light blue dashed line labeled Mo_{SW} is the average isotopic composition of seawater ($\delta^{98}\text{Mo}_{\text{SW}} = 2.3 \pm 0.1\text{‰}$ [Barling *et al.*, 2001; Siebert *et al.*, 2003]). Gray dashed line labeled Mo_{LITH} is the average isotopic composition of terrestrial materials ($\delta^{98}\text{Mo}_{\text{LITH}} = 0.0 \pm 0.2\text{‰}$ [Siebert *et al.*, 2003]). Blue dashed line labeled $\text{Mo}_{\text{AUTH-Mn}}$ is the average isotopic composition of the MANOP H samples ($\delta^{98}\text{Mo}_{\text{AUTH-Mn}} = -0.5\text{‰}$). Red dashed line labeled $\text{Mo}_{\text{AUTH-S}}$ is the average isotopic composition of the Mexico margin samples ($\delta^{98}\text{Mo}_{\text{AUTH-S}} = 1.7\text{‰}$).

the mixed layer ($1.9 \pm 0.1\text{‰}$ (1 SD); $n = 5$; Figure 7 and Table 1). Below the mixed layer, sediments are more fractionated (relative to seawater), suggesting that an Fe/S-controlled authigenic Mo phase dominates the sediment Mo pool in the deepest portions of the core (average $1.2 \pm 0.1\text{‰}$ (1 SD); $n = 4$; Figure 7 and Table 1). Parenthetically, it is worth noting that this site also has the highest sediment Ca concentrations of all sites analyzed (~ 13 wt % Ca; Table A3), and carbonate mineral phases may play an as yet undefined role in the sediment Mo isotope compositions observed. Sediment data from Alfonso basin also suggest a transition from surface sediments with low Mo concentrations and heavier isotope values ($\delta^{98}\text{Mo}_{\text{ENRICH}} 1.9 \pm 0.1\text{‰}$ (1 SD), $n = 7$) to values consistent with Fe/S-controlled authigenic enrichment below 4 cm ($1.72 \pm 0.07\text{‰}$, 2 SDOM with $n = 12$; Table 1). In sum, there are several sites that imply that there is a near-surface molybdenum pool that differs in isotope composition from the mean continental margin pool. These values could reflect the composition of a transient and perhaps varying pool of Mo that is associated with organic material, but it is premature to reach such a conclusion at this point.

[32] Despite the presence of a slightly heavier near-surface sedimentary Mo isotope pool, the ultimate fate of this component remains unclear, as this loosely defined biogenic Mo may not survive early diagenetic processes and may have little impact in

the rock record. We make this point because even though there is variability observed in near-surface sediments at some locations, the deeper core data from the Mexico margin appear to converge on a common value (Figure 6). In fact, the mean $\delta^{98}\text{Mo}_{\text{ENRICH}}$ value for all Mexico margin sediments below 5 cm (all sites, including Pescadero) is $1.70 \pm 0.09\text{‰}$ (2 SDOM with $n = 28$; Table 1). This average value from the Mexican margin suggests fractionation between a seawater aqueous Mo source and the authigenic Mo pool of $\Delta^{98}\text{Mo}_{\text{SW-AUTH-S}} = 0.6\text{‰}$, consistent with the results of pore water data modeled assuming Rayleigh fractionation ($\Delta^{98}\text{Mo} = 0.7\text{‰}$ [McManus *et al.*, 2002]). It therefore appears that anoxic authigenic Mo deposits that are fractionated by $\sim 0.6\text{‰}$ from their Mo source, in this case ocean water, likely represent the ultimate or at least dominating Mo phase recorded in reducing continental margins.

[33] The Peru margin is a region of wind-driven perennial upwelling, resulting in high productivity in the surface waters and an associated intense water column oxygen minimum zone (OMZ, $< 5 \mu\text{M O}_2$) [Suess *et al.*, 1986]. Sediments of the Peru margin investigated in this work were collected from a shelf site near 13°S cored at 264 m water depth (Figure 3 and Table 1). This site represents the most reducing open-ocean conditions of our study sites, because of the high organic

carbon content ($>14\%$ C_{org} ; Table A5), and sulfidic nature of the sediments in this region [e.g., *Reimers and Suess*, 1983; *Froelich et al.*, 1988]. Several authors have noted the presence of free sulfide in pore waters from surface sediments (<15 cm) on this margin, but sulfide is absent from the bottom water [e.g., *Froelich et al.*, 1988; *Fossing*, 1990; *Böning et al.*, 2004]. Pore water data from a similar site on the Peru margin reveal H_2S concentrations > 1 mM within the uppermost ~ 20 cm, with the highest sulfate reduction rates observed within a few cm of the sediment surface [*Fossing*, 1990].

[34] Authigenic Mo dominates the bulk sediment Mo pool throughout the Peru margin core ($X_{LITH} \leq 0.02$; Table 1), presumably reflecting authigenic Mo enrichment associated with Fe-Mo-S and/or Mo-S precipitation (Mo_{S-AUTH}). Interestingly, the isotopic composition of the Peru sediments display a down-core trend opposite that observed in many of the Mexico margin sites; that is, the uppermost sediments have isotopic compositions slightly lighter than those measured at depth (Table 1 and Figure 6). In fact, the uppermost 13 cm have the highest authigenic Mo contents (71 ± 13 ppm) and an average Mo isotope composition of $\delta^{98}Mo_{ENRICH} = 1.2 \pm 0.2\%$ (both errors 1 SD, $n = 6$; Table 1 and Figure 6). Notably, these lighter isotope values are similar to those measured in the Mo-enriched sediments of the Magdalena site (Table 1 and Figure 7). However, we cannot say at present what mechanism is responsible for generating these lighter Mo isotopic values. In addition, we note that these values are only marginally lighter than the average continental margin value. Deeper in the core, sediment Mo concentrations decrease (31 ± 5 ppm; 1 SD, $n = 4$) and the measured Mo isotope compositions are consistent with the authigenic Mo signature observed in the Mexico margin sites ($\delta^{98}Mo_{ENRICH} = 1.5 \pm 0.2\%$; 1 SD, $n = 4$; Table 1 and Figure 6).

3.4. California Margin: Authigenic Mo Sulfide Signature and the Impact of Mn Cycling

[35] Off the coast of California, seasonal upwelling enhances biological productivity, and the associated high-productivity zone bordering the East Pacific (combined with circulation patterns) results in a water column OMZ between depths of 200 and 1000 m [e.g., *Sverdrup and Allen*, 1939]. The four basins investigated along the California margin are all part of a larger complex known as the Borderland Basins region [e.g., *Emery*, 1960] (Figure 3

and Table 1). A general deepening of the basins with distance offshore characterizes the Borderland region. In general, the nearshore basin sites are the most reducing with bottom water oxygen contents increasing in basins with distance offshore [e.g., *Berelson et al.*, 1996].

[36] The nearshore basins investigated here, Santa Barbara and Santa Monica, have sill depths within the OMZ, and these sites have the lowest measured bottom water oxygen concentrations in the region ($<10 \mu M$) [*Reimers*, 1987; *Berelson et al.*, 1987; *Jahnke*, 1990]. These inner basins are the most reducing environments studied on this margin, with sulfate reduction dominating organic matter remineralization [e.g., *Kaplan et al.*, 1963; *Berelson et al.*, 1987; *Jahnke*, 1990]. Santa Barbara and Santa Monica basins both have relatively invariant average down core $\delta^{98}Mo_{ENRICH}$ values ($1.5 \pm 0.2\%$ and $1.6 \pm 0.1\%$, respectively; both down-core variations are 2 SDOM with $n = 10$; Figure 6 and Table 1) consistent with the authigenic Mo sulfide signature ($\delta^{98}Mo_{AUTH-S}$) observed on the Mexico margin.

[37] The other two Borderland Basins investigated in this study, Santa Catalina and San Nicolas, are located further offshore. Both basins have sill depths at or just below the base of the OMZ (1000–1200 m) [*Emery*, 1960], and measured bottom water concentrations are generally between 15 and 35 μM [*Reimers*, 1987; *Berelson et al.*, 1987]. At these sites, organic matter is primarily oxidized by suboxic reactions (Mn and Fe reduction) [e.g., *Berelson et al.*, 1987; *Shaw et al.*, 1990].

[38] Sediment $\delta^{98}Mo_{ENRICH}$ compositions from these outer basins span the full range of values previously observed in marine sediments (Figure 8 and Table 1). In general, sediment Mo isotope compositions are heaviest near the sediment-water interface, and approach values more consistent with Mn-associated authigenic Mo deposits ($\delta^{98}Mo_{AUTH-Mn}$) at depth (Figure 8 and Table 1). However, it is unlikely that Mn oxides are the final host phase for Mo at depth as pore water profiles from these sites suggest Mn oxides undergo reductive dissolution and are not preserved in these sediments [*McManus et al.*, 1998; S. Severmann, unpublished data, 2004]. The ultimate authigenic Mo phase at depth is likely associated with Fe-Mo-S/Mo-S precipitation (X_{AUTH-S}). The assumption of an Fe-Mo-S/Mo-S authigenic phase at depth is bolstered by observed increases in total reduced sulfur (up to ~ 0.5 wt %) in the uppermost 30 cm of

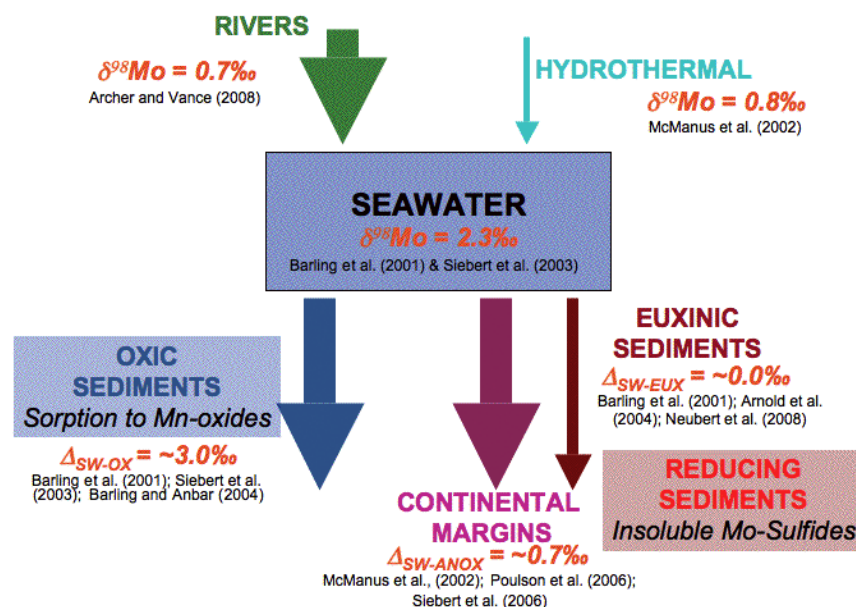


Figure 9. Schematic depiction of the revised modern marine Mo budget. All source term Mo isotope compositions or sink term relative fractionations (between seawater and sediment reservoirs) are from references as indicated. Arrow sizes indicate relative sizes of various sources and sinks in the modern marine system.

Santa Catalina sediments, which was interpreted as the ingrowth of authigenic pyrite during sediment burial [Leslie et al., 1990].

[39] We propose that the same mechanisms responsible for authigenic Mo sulfide enrichment in other reducing margin settings also impact Mo behavior at these sites, but that the aqueous Mo source is not necessarily seawater ($\delta^{98}\text{Mo}_{\text{SW}}$). Instead, we suggest that these sites typify environments where Mn cycling within the sediment column influences Mo isotopic behavior. It appears that some of the fractionated Mo released during Mn reduction ($\delta^{98}\text{Mo}_{\text{Mn}}$) likely supplies the aqueous Mo that is subsequently deposited in authigenic phases at depth; that is, the initial source of aqueous Mo to these sediments is isotopically fractionated (relative to seawater), altering the ultimate Mo isotope composition of authigenic Fe-Mo-S phases (Figure 8). As previously suggested by Reitz et al. [2007] to explain similar observations from the Eastern Mediterranean, it appears that secondary diagenetic processes drive Mo isotope compositions to highly fractionated values. Such a process would also lead to the relatively large scatter in the previously published values from the San Clemente Basin [Siebert et al., 2006].

[40] Despite the interesting Mo isotope behavior observed in these sites, it is worth noting that they

have some of the lowest $\text{Mo}_{\text{ENRICH}}$ concentrations of all sites analyzed in this study (Table 1). Therefore these types of environments are unlikely to represent a significant sedimentary sink for Mo. More reducing environments (like the inner basins on the California margin) have higher $\text{Mo}_{\text{ENRICH}}$ concentrations and isotopic compositions consistent with the authigenic, open ocean Mo sulfide signature, e.g., $\sim 1.6\text{‰}$ (Table 1 and Figure 6). Ultimately, it appears that sediments that bear the authigenic $\delta^{98}\text{Mo}_{\text{AUTH-S}}$ signature likely dominate the reducing continental margin sedimentary sink.

3.5. Modern Marine Mo Isotope Budget

[41] Average $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values from all sediment samples on the Mexican margin (excluding Pescadero), as well as those from the Peru margin and the two inner basin California margin sites, define a mean Mo isotope signature of $\delta^{98}\text{Mo}_{\text{ENRICH}} = 1.68 \pm 0.05\text{‰}$ (2 SDOM with $n = 84$; Table 1). Including published data from three additional sites on the Mexican margin (Table A6) [Poulson et al., 2006], and two additional reducing inner basins of the California margin (San Pedro and Santa Monica; Table A6 [Siebert et al., 2006; Poulson et al., 2006]), the average is $1.64 \pm 0.04\text{‰}$ (2 SDOM with $n = 136$; Table 1 and Figure 6). It

thus appears that Fe/S-controlled authigenic Mo enrichments with a seawater aqueous Mo source bear a Mo isotopic signature ($\delta^{98}\text{Mo}_{\text{AUTH-S}}$) that is ultimately recorded in marine sediments. This final distinction is important. Although surface sediments (upper 5 cm) are more heterogeneous in their enriched $\delta^{98}\text{Mo}$ (ranging from $\sim 1.2\%$ at Peru to $\sim 2.2\%$ at Pescadero), many of the sites converge on a single $\delta^{98}\text{Mo}_{\text{AUTH-S}}$ value. This convergence occurs despite a significant range in Mo concentrations, variable pore water sulfide concentrations, and presumably differences in the relative contributions of $\text{Mo}_{\text{AUTH-S}}$ and Mo_{BIO} .

[42] In light of the unique Mo isotope fractionation observed in continental margin sediments, and the recently published riverine Mo isotope inputs [Archer and Vance, 2008], we can further revise the modern marine Mo budget. Assuming steady state conditions, we can construct a mass balance: $F_{\text{RIVER}}\delta_{\text{RIVER}} + F_{\text{HYDRO}}\delta_{\text{HYDRO}} = F_{\text{OXIC}}\delta_{\text{OXIC}} + F_{\text{EUXINIC}}\delta_{\text{EUXINIC}} + F_{\text{MARGIN}}\delta_{\text{MARGIN}}$ where δ and F represent the isotopic compositions and fluxes of the source and sink terms (Figure 9). Archer and Vance [2008] recently reported a discharge-weighted global riverine average $\delta^{98}\text{Mo}_{\text{R-RIVER}}$ of 0.7% , corresponding to a total reported global Mo riverine input flux of $\sim 1.8 \times 10^8$ mol/a [Bertine and Turekian, 1973] (Figure 9). The estimated Mo input flux from low-temperature hydrothermal systems is $\sim 0.2 \times 10^8$ mol/a, with a reported isotopic composition of $\delta^{98}\text{Mo}_{\text{HYDRO}} = 0.8\%$ [McManus et al., 2002] (Figure 9). Together, these represent a total marine Mo input flux of $\sim 2.0 \times 10^8$ mol/a.

[43] Bertine and Turekian [1973] estimated that the two primary sinks for Mo in the modern ocean, oxic and reducing sediments, are relatively balanced. The total flux of Mo into oxic, Mn-rich sediments is estimated to be $\sim 0.9 \times 10^8$ mol/a (as reported by Morford and Emerson [1999]). On the basis of our observations from MANOP site H, we assume this flux corresponds to an isotopic composition of $\delta^{98}\text{Mo}_{\text{OXIC}} = -0.5\%$ (Figure 9). The remaining output flux, $\sim 1.1 \times 10^8$ mol/a, is the “reducing sediment” Mo sink [e.g., Bertine and Turekian, 1973], which represents both euxinic restricted basins and reducing continental margin environments (Figure 9). If sediments from euxinic basins have sediment Mo isotope compositions indistinguishable from the seawater $\delta^{98}\text{Mo}$ value ($\delta^{98}\text{Mo}_{\text{EUXINIC}} = 2.3\%$ [Barling et al., 2001; Arnold et al., 2004; Neubert et al., 2008]), and

continental margins bear the authigenic signature observed in this study ($\delta^{98}\text{Mo}_{\text{MARGIN}} = 1.6\%$), mass balance requires a continental margin sink comparable to the oxic sink ($\sim 0.9 \times 10^8$ mol/a; Figure 9).

[44] It is important to bear in mind that from the perspective of Mo isotopes, the margin sink is any sedimentary sink underlying waters with sulfide concentrations below the APS. A previous estimate [McManus et al., 2006] puts the euxinic sink at approximately $<0.2 \times 10^8$ mol/a; however, this upper limit value is probably a gross overestimate and a more reasonable upper limit is probably 0.1×10^8 mol/a; that is, the modern euxinic sink (i.e., the “APS sink”) is likely to be less than 5% of the total Mo sink. This reduced estimate for the size of the total euxinic sink is further strengthened by the observations of Neubert et al. [2008], who demonstrated that euxinic Mo deposition (sediments with $\delta^{98}\text{Mo} = 2.3\%$) is limited to sediments below ~ 400 m water depth in the Black Sea, which is consistent with previous work in the Black Sea [e.g., Nägler et al., 2005] and the requirement of the overlying water column sulfide needing to be above the chemically defined APS to achieve euxinia. In addition, we note here the Mo elemental budget recently reported by Scott et al. [2008]. This budget differs slightly with our own synthesis, but the general sense of our budget is similar to that as well as other Mo elemental budgets [e.g., Morford and Emerson, 1999; McManus et al., 2006].

[45] What does our interpretation of the modern Mo balance mean for the utility of Mo isotopes in the geologic record? The simple answer is that it merely alters the interpretation of that record. The field has certainly been cognizant of the potential importance of this sink [e.g., Siebert et al., 2003; Arnold et al., 2004]; thus, our work here is merely building upon and refining that work. A simplified mass balance points to the likely change in interpretation of the oceanic Mo isotope balance, i.e., $F_{\text{RIVER}}\delta_{\text{RIVER}} = F_{\text{OXIC}}\delta_{\text{OXIC}} + F_{\text{MARGIN}}\delta_{\text{MARGIN}}$. Here we remove the small contributions of low-temperature hydrothermal inputs and euxinic sinks. Clearly the balance is set by the input term and a varying ratio of oxic and “reducing” sinks. We generically use the term “reducing” following the lead of Bertine and Turekian [1973]. With respect to Mo “euxinia” is defined by the APS, because this definition is built upon a functional chemical

Table A1. Standard Reference Materials for Mo, Al, Ca, Fe, Mn, and Ti^a

	ICPMS			MC-ICPMS			Al		Ca		Fe		Mn		Ti	
	n	Mo (ppm)	1 SD	n	Mo (ppm)	1 SD	Percent	1 SD	Percent	1 SD	Percent	1 SD	Percent	1 SD	Percent	1 SD
MAG-1																
Average	7	1.1	0.1				16	8.5	0.6	1.1	0.1	5.0	0.2	0.08	0.01	0.47
<i>McManus et al.</i> [2006]	11	1.14	0.08					7	2	–	–	4.75	0.04	0.072	0.002	0.41
<i>Wieser and DeLaeter</i> [2000]		1.17	–					–	–	–	–	–	–	–	–	–
<i>Potts et al.</i> [1992]		1.6	–					8.67	–	0.98	–	4.82	–	0.08	–	0.45
SX-12280																
Average	23	2.6	0.4	23	3.1	0.4	–0.2	0.3	36	6.3	0.3	1.1	0.1	0.26	0.01	0.35
<i>McManus et al.</i> [2006]								5.8	0.3	–	–	3.6	0.2	0.24	0.01	0.30
<i>Robbins et al.</i> [1984]								6.22	–	1.1	–	4.18	–	0.26	–	0.38
BCR-1																
Average	4	1.5	0.2				6	7.2	0.2	1.1	0.1	9.5	0.3	0.152	0.004	1.39
<i>McManus et al.</i> [2006]	13	1.64	0.06					7.2	0.2	–	–	9.68	0.01	0.1470	0.0004	1.35
<i>Wieser and DeLaeter</i> [2000]		1.54	–					–	–	–	–	–	–	–	–	–
<i>Potts et al.</i> [1992]		1.60	–					7.23	–	5.1	–	9.42	–	0.14	–	1.34
NBS-1645																
Average				39	18	2	0.6	0.3	1	2.6	–	10.0	–	0.08	–	0.08
<i>Potts et al.</i> [1992]					34	–		2.3	–	–	–	11.3	–	0.08	–	0.05
PACS-2																
Average	26	5.2	0.7	10	5.9	0.4	1.3	0.3	26	6.6	0.3	2.1	0.1	0.046	0.002	0.45
NRC of Canada Certified Reference		5.4	0.3		5.4	0.3		6.6	0.3	2.0	0.2	4.1	0.1	0.044	0.002	0.44
SDO-1																
Average	21	133	12	10	124	9	1.2	0.3	17	6.5	0.2	0.78	0.02	0.032	0.001	0.42
USGS Certified Reference		134	21		134	21		6.1	0.1	0.75	–	6.50	0.2	0.033	0.004	0.43

^a Average values are from separate replicate digestions (n means number of samples); mix of hot plate and microwave digestion techniques (see text).



Table A2 (Sample). Sediment Mo Concentration Data^a [The full Table A2 is available in the HTML version of this article]

Depth (cm)	Sample Name	ICPMS			MC-ICPMS			Both		Mo	
		Run 1 (ppm Mo)	Run 2 (ppm Mo)	Run 3 (ppm Mo)	Run 1 (ppm Mo)	Run 2 (ppm Mo)	Run 3 (ppm Mo)	Run 1		Run 2	
								ppm	1 SD	ppm	1 SD
MANOP sites											
Site H	MP5301 AAZ				55.6						55.6
	MP5302 AAZ				52.7						52.7
	MP5304 AAZ				45.1						45.1
	MP8950 AAZ				49.8						49.8
	MP5305 AAZ				62.3						62.3
	MP8951 AAZ				55.4						55.4
	MP5306 AAZ				62.0	62.2					62.1
	MP5307 AAZ				36.8						36.8
	MP5308 AAZ				29.9	26.7					28.3
	MP5309 AAZ				13.9						13.9
Site M	MP5310 AAZ				5.9						5.9
	MP5311 AAZ				5.7						5.7
	MP5312 AAZ				5.9						5.9
	MP5313 AAZ				5.6						5.6
	PLUTO 20BC MP8966AAZ				15.0						15.0
	PLUTO 20BC MP8967AAZ				13.9						13.9
	PLUTO 20BC MP8968AAZ				13.0		13.2				13.1
	PLUTO 20BC MP8969AAZ				6.0						6.0
	PLUTO 20BC MP8970AAZ				2.6	2.6					2.6
	PLUTO 20BC MP8971AAZ				2.1						2.1
Peru margin	PLUTO 20BC MP8972AAZ				2.0						2.0
	PLUTO 20BC MP8973AAZ				1.6						1.6
	PLUTO 20BC MP8974AAZ				1.1	1.3					1.2
	PLUTO 20BC MP8975AAZ				0.6						0.6
	MC3 1–1.5	83.9			90.7						87.3
	MC3 3–3.5				80.1			82.8	9.2		81.5
	MC3 5–5.5	75.1			84.0						79.5
	MC3 7–7.5	55.7			61.0						58.4
	MC3 9–9.5				64.5			59.4	1.6	55.1	59.7
	MC3 12–13	53.4			58.3			64.2	15.3		58.6
MC3 14–15	26.9			31.0	29.1		32.9	8.5		30.0	
MC3 20–22	23.3	23.8		28.2			28.8	7.8	28.7	26.6	
MC3 24–26	27.0			31.8	29.2					29.3	
MC3 32–34	35.4			39.7						37.5	

^a All reported values are from separate total sediment digestions (analyzed by either ICPMS or MC-ICPMS as indicated). Errors on average Mo concentrations are 1 SD for all analyses. For some samples, aliquots of the same sediment digestion were analyzed by both methods; the average of these two analyses (and 1-SD error) are listed under “both” so as not to place undue weight on a single digestion when calculating the final sample Mo concentration average. Samples listed in bold font were processed by microwave digestion; all other samples processed by hot plate digestion.

Table A3 (Sample). Sediment Major Element Compositions and Lithogenic Mo Fractions^a [The full Table A3 is available in the HTML version of this article]

Depth (cm)	Sample Name	Run 1										Run 2										Run 3										Al		Ca		Fe		Mn		Ti																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																
		Al		Ca		Fe		Mn		Ti		Al		Ca		Fe		Mn		Ti		Al		Ca		Fe		Mn		Ti		Al		Ca		Fe		Mn		Ti																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)

Table A4 (Sample). Sediment Mo Isotope Compositions^a [The full Table A4 is available in the HTML version of this article]

			Run 1		Run 2		Run 3		Mo _{BULK} δ ⁹⁸ Mo	
	Depth (cm)	Sample Name	δ ⁹⁸ Mo (‰)	2SE	δ ⁹⁸ Mo (‰)	2SE	δ ⁹⁸ Mo (‰)	2SE	Average (‰)	1 SD
MANOP sites										
Site H	0.5	MP5301 AAZ	−0.5	0.1					−0.5	
	1.5	MP5302 AAZ	−0.4	0.1					−0.4	
	3.5	MP5304 AAZ	−0.4	0.1					−0.4	
	3.5	MP8950 AAZ	−0.4	0.0					−0.4	
	4.5	MP5305 AAZ	−0.5	0.1					−0.5	
	4.5	MP8951 AAZ	−0.5	0.0					−0.5	
	6.0	MP5306 AAZ	−0.6	0.0	−0.2	0.0			−0.4	0.2
	8.0	MP5307 AAZ	−0.6	0.0					−0.6	
	10.0	MP5308 AAZ	−0.6	0.0	−0.5	0.0			−0.6	0.0
	12.0	MP5309 AAZ	−0.4	0.1					−0.4	
	14.0	MP5310 AAZ	−0.4	0.1					−0.4	
	16.0	MP5311 AAZ	−0.5	0.1					−0.5	
	18.0	MP5312 AAZ	−0.5	0.1					−0.5	
Site M	20.0	MP5313 AAZ	−0.5	0.1					−0.5	
	0.8	PLUTO 20BC MP8966AAZ	−0.2	0.0					−0.2	
	2.0	PLUTO 20BC MP8967AAZ	−0.3	0.0					−0.3	
	4.0	PLUTO 20BC MP8968AAZ	−0.5	0.0	−0.3	0.1			−0.4	0.1
	6.0	PLUTO 20BC MP8969AAZ	−0.3	0.0					−0.3	
	8.0	PLUTO 20BC MP8970AAZ	−0.1	0.1	−0.4	0.1			−0.2	0.2
	10.0	PLUTO 20BC MP8971AAZ	0.1	0.1					0.1	
	12.0	PLUTO 20BC MP8972AAZ	−0.1	0.1					−0.1	
	14.0	PLUTO 20BC MP8973AAZ	0.1	0.1					0.1	
	16.0	PLUTO 20BC MP8974AAZ	0.2	0.1	0.1	0.1			0.2	0.1
18.0	PLUTO 20BC MP8975AAZ	−0.1	0.1					−0.1		
Peru margin	1.3	MC3 1–1.5	1.0	0.1					1.0	
	3.3	MC3 3–3.5	1.0	0.1	1.4	0.0			1.2	0.2
	5.3	MC3 5–5.5	1.0	0.0					1.0	
	7.3	MC3 7–7.5	1.1	0.1					1.1	
	9.3	MC3 9–9.5	1.0	0.0	1.5	0.1	1.7	0.1	1.4	0.4
	12.5	MC3 12–13	1.1	0.1	1.6	0.1			1.3	0.4
	14.5	MC3 14–15	1.4	0.0	1.8	0.1	1.6	0.1	1.6	0.2
	21.0	MC3 20–22	1.4	0.1	1.8	0.1	1.7	0.1	1.6	0.2
	25.0	MC3 24–26	1.4	0.0	1.7	0.0			1.5	0.2
	33.0	MC3 32–34	1.2	0.1					1.2	
California margin										
Santa Barbara	1.3	MC17_1	1.1	0.2					1.1	
	4.3	MC17_4	1.2	0.1					1.2	
	6.3	MC17_6	0.7	0.1					0.7	
	8.3	MC17_8	1.3	0.1	1.3	0.1			1.3	0.0
	10.5	MC17_10	1.3	0.0					1.3	
	14.5	MC17_14	1.5	0.1					1.5	
	18.5	MC17_18	1.2	0.1	1.3	0.1			1.3	0.1
	25.0	MC17_24	1.3	0.1					1.3	
	33.0	MC17_32	1.3	0.1					1.3	
	41.0	MC17_40	1.3	0.1					1.3	
Santa Monica	0.5	2MC 3–4	1.3	0.1					1.3	
	0.9	2MC 6–7	1.4	0.1					1.4	
	1.3	2MC 9–10	1.6	0.1					1.6	
	1.7	2MC 12–13	1.3	0.1					1.3	
	2.3	2MC 16–17	1.5	0.1					1.5	
	2.8	2MC 20–21	1.5	0.1					1.5	
	3.5	2MC 25–26	1.4	0.0					1.4	
	4.2	2MC 30–31	1.3	0.1					1.3	
	4.9	2MC 35–36	1.4	0.1					1.4	
	6.9	2MC 50–51	1.3	0.1					1.3	

^a All reported values are from separate total sediment digestions. Errors on average values are 1 SD for all analyses; errors reported for individual Mo isotope analyses are 2SE instrumental errors from individual runs.



Table A5 (Sample). Average Sediment $\text{Mo}_{\text{ENRICH}}$ Concentrations and Isotopic Compositions^a [The full Table A5 is available in the HTML version of this article]

	Depth (cm)	Sample Name	Mo_{BULK} (ppm)	Average $\text{Mo}_{\text{BULK}}\delta^{98}\text{Mo}$ (‰)	Average Al (%)	Mo_{LITH} (ppm)	X_{LITH}	X_{ENRICH}	$\text{Mo}_{\text{ENRICH}}$ (ppm)	$\delta^{98}\text{Mo}_{\text{ENRICH}}$ (‰)	% C_{org}	$\text{Mo}_{\text{E}}:\text{C}$ (ppm/‰)
MANOP sites Site H	0.5	MP5301 AAZ	55.6	-0.5	6.01	0.7	0.01	0.99	54.9	-0.5	0.8	68.6
	1.5	MP5302 AAZ	52.7	-0.4	6.09	0.7	0.01	0.99	52.0	-0.4	0.7	71.5
	3.5	MP5304 AAZ	45.1	-0.4	6.05	0.7	0.01	0.99	44.4	-0.4	0.8	54.7
	3.5	MP8950 AAZ	49.8	-0.4		0.6	0.01	0.99	49.1	-0.4		
	4.5	MP5305 AAZ	62.3	-0.5	6.07	0.7	0.01	0.99	61.7	-0.5	0.8	78.0
	4.5	MP8951 AAZ	55.4	-0.5		0.6	0.01	0.99	54.8	-0.5		
	6.0	MP5306 AAZ	62.1	-0.4	5.94	0.7	0.01	0.99	61.4	-0.4	0.9	70.4
	8.0	MP5307 AAZ	36.8	-0.6	5.72	0.6	0.02	0.98	36.2	-0.6	0.7	53.6
	10.0	MP5308 AAZ	28.3	-0.6	5.41	0.6	0.02	0.98	27.7	-0.6	0.7	37.6
	12.0	MP5309 AAZ	13.9	-0.4	5.45	0.6	0.04	0.96	13.3	-0.4	0.8	16.5
	14.0	MP5310 AAZ	5.9	-0.4	5.18	0.6	0.10	0.90	5.3	-0.4	0.9	6.1
	16.0	MP5311 AAZ	5.7	-0.5	5.21	0.6	0.10	0.90	5.2	-0.6	0.9	5.5
	18.0	MP5312 AAZ	5.9	-0.5	5.48	0.6	0.10	0.90	5.3	-0.5	1.0	5.3
Site M	20.0	MP5313 AAZ	5.6	-0.5	5.42	0.6	0.11	0.89	5.1	-0.6	1.0	4.9
	0.8	MP8966AAZ	15.0	-0.2	4.96	0.5	0.04	0.96	14.4	-0.2	1.4	10.3
	2.0	MP8967AAZ	13.9	-0.3		0.5	0.04	0.96	13.4	-0.3		9.5
	4.0	MP8968AAZ	13.1	-0.4		0.5	0.04	0.96	12.6	-0.4		8.9
	6.0	MP8969AAZ	6.0	-0.3		0.5	0.09	0.91	5.4	-0.4		3.8
	8.0	MP8970AAZ	2.6	-0.2		0.5	0.21	0.79	2.1	-0.3		1.5
	10.0	MP8971AAZ	2.1	0.1		0.5	0.25	0.75	1.6	0.2		1.1
	12.0	MP8972AAZ	2.0	-0.1		0.5	0.27	0.73	1.5	-0.1		1.1
	14.0	MP8973AAZ	1.6	0.1		0.5	0.35	0.65	1.0	0.2		0.7
	16.0	MP8974AAZ	1.2	0.2		0.5	0.46	0.54	0.7	0.3		0.5
Peru margin	18.0	MP8975AAZ	0.6	-0.1		0.5	0.88	0.12	0.1	-0.4		0.1
	1.3	MC3 1-1.5	87.3	1.0	2.71	0.3	0.00	1.00	87.0	1.0	14.6	6.0
	3.3	MC3 3-3.5	81.5	1.2	2.60	0.3	0.00	1.00	81.2	1.2		5.6
	5.3	MC3 5-5.5	79.5	1.0	2.49	0.3	0.00	1.00	79.2	1.0		5.4
	7.3	MC3 7-7.5	58.4	1.1	2.32	0.3	0.00	1.00	58.1	1.1		4.0
	9.3	MC3 9-9.5	59.7	1.4	3.45	0.4	0.01	0.99	59.3	1.4		4.1
	12.5	MC3 12-13	58.6	1.3	3.11	0.3	0.01	0.99	58.3	1.3		4.0
	14.5	MC3 14-15	30.0	1.6	6.56	0.7	0.02	0.98	29.2	1.7		2.0
	21.0	MC3 20-22	26.6	1.6	5.17	0.6	0.02	0.98	26.0	1.7		1.8
	25.0	MC3 24-26	29.3	1.5	3.99	0.4	0.01	0.99	28.9	1.6		2.0
California margin Santa Barbara	33.0	MC3 32-34	37.5	1.2	5.29	0.6	0.02	0.98	36.9	1.3		2.5
	1.3	MC17_1	3.7	1.1	6.14	0.7	0.18	0.82	3.0	1.4	2.7	1.1
	4.3	MC17_4	4.4	1.2	6.64	0.7	0.17	0.83	3.6	1.5	3.3	1.1

^a Average bulk sediment Mo concentrations from Table A2, average bulk Mo isotope compositions from Table A3, and average %Al from Table A4. Assumed Mo:Al ratio for lithogenic background is 1.1×10^{-5} [McManus *et al.*, 2006; Poulson *et al.*, 2006]. %Al (Table A4) and %C_{org} values for MANOP H (Vulcan BC37, same core) and MANOP M (Pluto 25BC, companion to Mo core) from Lyle *et al.* [1984]; data not corrected for carbonate dilution. %C_{org} value for Peru is average from McManus *et al.* [2006]; companion core. Mo_{LITH} and X_{LITH} values in italics do not have corresponding %Al data; reported values calculated from core average %Al values.



Table A6 (Sample). Detailed Sediment Data From Previously Published California and Mexico Margin Sites^a [The full Table A6 is available in the HTML version of this article]

Depth (cm)	Sample Name	ICPMS			Nu Run 1 Mo	Nu Run 2 Mo	“Both” Mo	Mo _{BULK}		Run 1		Run 2		Mo _{BULK} δ ⁹⁸ Mo	
		Run 1 Mo	Run 2 Mo	Run 3 Mo				Average (ppm)	1 SD	δ ⁹⁸ Mo (‰)	2SE	δ ⁹⁸ Mo (‰)	2SE	Average (‰)	1 SD
Soledad	10MC-0-2cm	4.2			3.5			3.8	0.5	1.4	0.1			1.4	
	4.0 10MC-5	5.3			4.4			4.8	0.6	1.4	0.1			1.4	
	9.8 10MC-6	6.7	5.9		3.9	7.3		5.9	1.5	1.6	0.1	1.6	0.1	1.6	0.0
	15.3 10MC-7	17.8	16.3		12.7	18.2		16.3	2.5	1.3	0.0	1.3	0.0	1.3	0.0
	20.8 10MC-8	8.0			6.6			7.3	1.0	1.4	0.0			1.4	
	26.3 10MC-9	8.1	7.9		6.4			7.5	0.9	1.5	0.1			1.5	
	31.8 10MC-10	9.5			7.7			8.6	1.3	1.6	0.0			1.6	
	10MC-11	8.3	8.2					8.3	0.1						
	42.8 10MC-12	10.3	10.3		8.6	11.6		10.2	1.2	1.5	0.1	1.7	0.1	1.6	0.1
	46.5 10MC-last	18.8	18.3		15.7	20.4		18.3	2.0	1.6	0.1	1.6	0.1	1.6	0.0
Mazatlan	29MC-0-2	6.3						6.3							
	29MC-1	8.9						8.9							
	29MC-2	10.1						10.1							
	14.8 29MC-3	9.4	7.9		8.8			8.7	0.7	1.8	0.1			1.8	
	20.3 29MC-4	12.0	10.4		11.0			11.1	0.8	1.6	0.0			1.6	
	25.8 29MC-5	11.1	9.8		9.7			10.2	0.8	1.8	0.1			1.8	
	31.3 29MC-6	12.6			11.5			12.1	0.8	1.6	0.0			1.6	
	36.8 29MC-7	14.3	12.5		12.8	15.2		13.7	1.3	1.4	0.0	1.5	0.1	1.4	0.0
	42.3 29MC-8	14.3	15.5		15.2	18.2		15.8	1.7	1.5	0.0	1.4	0.1	1.5	0.1
	47.8 29MC-9	16.8	22.6		14.3			17.9	4.2	1.6	0.1			1.6	
San Blas	53.3 29MC-10	15.8	13.2		13.7	17.6		15.1	2.0	1.5	0.1	1.6	0.0	1.6	0.0
	59.0 29MC-11	16.6			15.1			15.8	1.0	1.7	0.1			1.7	
	31MC 0-3mm	5.0						5.0							
	1.2 31MC-3mm to 2cm	5.9			5.2			5.5	0.5	1.5	0.1			1.5	
	3.8 31MC-1	9.2	8.5		7.4			8.4	0.9	1.6	0.1			1.6	
	9.3 31MC-2	8.3			6.9			7.6	1.0	1.4	0.1			1.4	
	15.0 31MC-3	9.8	9.0		8.0			8.9	0.9	1.5	0.1			1.5	
	26.8 31MC-4	11.9	11.8		9.5	12.3		11.4	1.3	1.5	0.1	1.6	0.1	1.6	0.0
	38.3 31MC-5	15.9	14.0		12.8			14.2	1.5	1.5	0.0			1.5	
	47.8 31MC-6	12.0			10.2			11.1	1.3	1.7	0.1			1.7	

^a All previously published data listed in italics [Siebert *et al.*, 2006; Poulson *et al.*, 2006]; all other data are from replicate recent sample digestions. All Mo values listed represent separate total sediment digestions (analyzed by either ICPMS or MC-ICPMS as indicated). Errors on average Mo concentrations are 1 SD for all analyses. For some samples, aliquots of the same sediment digestion were analyzed for Mo by both methods; the average of these two analyses (and 1-SD error) are listed under “both” so as not to place undue weight on a single digestion when calculating the final sample Mo concentration average. All Mo isotope values reported are separate total sediment digestions. Errors on average values are 1 SD for all analyses; errors reported for individual Mo isotope analyses are 2SE instrumental errors from individual runs. All Al, Ca, Fe, and Mn values are replicate digestions and analyses of the same bulk sediment sample. Errors (1 SD) listed when more than one replicate digestion was performed. Assumed Mo:Al ratio for lithogenic background is 1.1×10^{-5} [McManus *et al.*, 2006; Poulson *et al.*, 2006].

shift [e.g., *Helz et al.*, 1996], and in the modern ocean the APS is met in quite limited localities.

4. Conclusions

[46] Our primary emphasis for this paper has been to identify the major components of Mo that are buried in marine sediment and their corresponding isotope compositions. It is quite likely that our operational compartmentalization is an oversimplification. However, on the basis of previous work on Mo geochemistry, our crude definitions are at least consistent with what has previously been hypothesized regarding Mo geochemistry. Along these lines there are likely to be at least four pathways or components that contain Mo within a sedimentary column: lithogenic Mo associated with terrestrial material (Mo_{LITH}), biogenic Mo associated in some way with organic matter (Mo_{BIO}), and authigenic Mo deposited via either oxic (sorption to Mn oxides, $\text{Mo}_{\text{AUTH-Mn}}$) or anoxic (precipitation of Fe-Mo-S solids, $\text{Mo}_{\text{AUTH-S}}$) mechanisms. These sources each appear to have characteristic Mo isotope compositions, and all modern marine sediments appear to reflect some mixture of these components.

[47] For the purposes of defining a “typical” manganese oxide sediment we measured sediments from MANOP site H. Because of its highly enriched Mo concentrations and relatively invariant $\delta^{98}\text{Mo}_{\text{ENRICH}}$ values, we presume that this site reflects the characteristic Mo isotopic signature of the $\text{Mo}_{\text{AUTH-Mn}}$ component, and the average measured $\delta^{98}\text{Mo}_{\text{ENRICH}}$ value is indeed consistent with previous experimental studies as well as measurements made on manganese crusts. The characteristic Mo isotopic signature of the anoxic authigenic sedimentary $\text{Mo}_{\text{AUTH-S}}$ component is herein defined by the wealth of data presented from the Mexico, Peru, and California margins. Together, the data from all reducing margin sites converge on a single Mo isotope value ($\delta^{98}\text{Mo}_{\text{MARGIN}} = 1.6\text{‰}$), providing strong evidence for a characteristic Mo isotope signature associated with authigenic Mo in these open-ocean settings.

Appendix A

[48] Tables A1–A6 include quality control data from several standard reference materials (Table A1), as well as supplementary sediment data from all sites discussed in the text (Tables A2–A6). Table A2 includes sediment Mo concentration data from all ICPMS and MC-ICPMS analyses of this

study. Table A3 lists the sediment major element compositions measured by ICP-OES and the Al-based estimates for the sediment lithogenic Mo fractions. Table A4 includes all measured sediment Mo isotope compositions from this study, and Table A5 lists the average sediment $\text{Mo}_{\text{ENRICH}}$ concentrations and calculated $\text{Mo}_{\text{ENRICH}}$ isotopic compositions. Table A6 includes additional supplementary data from previously published California and Mexico margin sites [*Siebert et al.*, 2006; *Poulson et al.*, 2006].

Acknowledgments

[49] This work benefited from the generous collaborations with Thomas Nägler and Christopher Siebert; without both of their efforts this work would not have been possible. We would also like to extend our gratitude to the editor John Tarduno, one anonymous reviewer, and Ariel Anbar for their thoughtful and constructive reviews. The California margin work took place on the R/V *Pt. Sur*, and we are indebted to the captain and crew of that vessel for their tireless support. Chris Moser helped in the field with core collection. Bobbi Conard provided MANOP samples through the Oregon State University core repository. This research was funded by the National Science Foundation under NSF grants OCE-0219651, EAR-0518322, and OCE-0721102. This material was partially based on work supported by the National Science Foundation, while J.M. was working at the foundation. Any opinion, finding, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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