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# Molybdenum isotope signatures in continental margin marine sediments

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## Abstract

We present molybdenum isotope data for four sediment profiles from continental margin settings. Each profile has a distinctive average isotope composition ranging from $\delta^{98/95}$Mo −0.5‰ to 1.3‰ (relative to J and M laboratory standard). This range lies between the modern ocean water value (2.3‰) and the values typical of Mo adsorbed onto Mn oxides (−0.7‰ ± 0.1‰). An important finding of this study is the apparent co-variation between the Mo isotope composition and the accumulation rate of authigenic Mo under reducing conditions. This relationship suggests that the chemical processes responsible for Mo accumulation under reducing conditions produce an isotope signature in marine sediments. In addition to the relationship between Mo accumulation and the Mo isotope signature there is also a relationship between these parameters and the rate of organic carbon oxidation and burial. These relationships suggest that the Mo isotope signature of reducing sediments may serve as a tracer for the cycling of organic carbon in continental margin sediments; however, additional data will be required to refine any such relationships.

*Keywords:* Molybdenum; Isotopes; Diagenesis; Sediments

## 1. Introduction

Under the well oxygenated conditions that prevail over much of the Earth's surface, molybdenum (Mo) is a highly soluble element, resulting in its being the most concentrated (~100 nM) of the dissolved trace metals in the ocean and Mo having an exceptionally long residence time (~0.8 Ma) (e.g., [1,2]). In contrast to its high solubility in ocean water, Mo is relatively insoluble under the reducing conditions that exist in sediments that line the ocean basin boundaries or marginal basins ([3–14], and others). The resulting sedimentary Mo enrichments thus represent a potential signature of past reducing conditions. In addition to Mo uptake under reducing conditions, Mo is also adsorbed to Mn oxides, and this particular removal pathway may scavenge up to 70% of the Mo from the oceans with the remainder being precipitated in reducing sediments (e.g., [13–19]).

The Mo isotope signature for each of the above sinks is thought to be distinct, with oxic sediments having a

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light Mo isotope composition ($\delta^{98/95}$Mo of $= -0.7‰$) and euxinic sediments having a heavy isotope value closer to that of ocean water (modern value is 2.3‰) (e.g., see review in [17] and references therein). Because the two Mo sinks have unique isotope signatures, the Mo isotope value in geologic deposits has been proposed to record the fraction of ocean reducing conditions through time (e.g., [15,17–22]). This initial idea regarding Mo isotopes assumes a mass balance between the oxic and anoxic Mo sinks. However, recent work (reviewed in [16]) suggests that another important Mo sink could be continental margin reducing sediments; sediments that are commonly termed "suboxic". These sediments span a range of electron transport reactions that can include those typical of both oxic and euxinic sediments, i.e., oxidation of reduced organic material can include oxic respiration as well as sulfate reduction. This report focuses on the isotope signature of Mo in

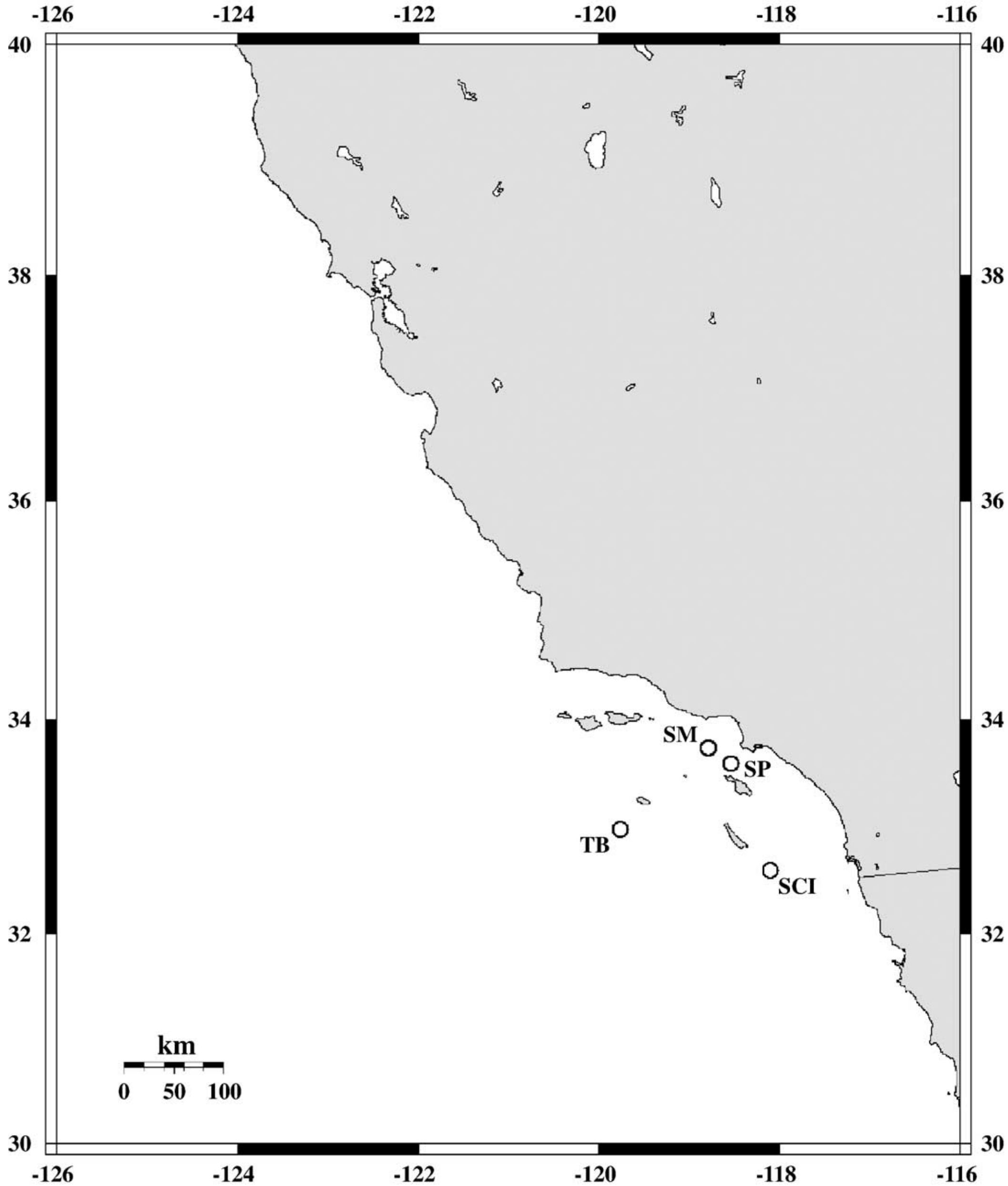

Fig. 1. Map of the study area showing the approximate locations of the four investigated sites. SM is Santa Monica Basin, SP is San Pedro Basin, TB is Tanner Basin, and SCl is the San Clemente Basin.

four continental margin marine settings. The Mo isotope signature in these environments is shown to vary and lies between the typical oxic and euxinic signatures. In addition, there also appears to be a relationship between the isotope signature and organic carbon cycling, and if this observation proves to be robust, Mo isotopes could be a powerful proxy for biogeochemical processes in continental margin settings.

## 2. Study sites

Our study sites are four submarine basins that lie within the California Borderlands region (Fig. 1). Organic carbon decomposition within these basins is dominated by diagenetic pathways that include oxygen, manganese, nitrate, iron, and sulfate as electron acceptors, but oxygen penetration depths are typically <2 cm (Table 1) and the concentration of dissolved sulfide is undetectable in the upper few tens of centimetres of these sediments (e.g., [23–26]). Santa Monica (SM) and San Pedro (SP) are the two most reducing basins with each basin typically having bottom water oxygen concentrations <10 μM and organic carbon decomposition rates near ~2 mmol $m^{-2}$ $day^{-1}$ (Table 1). Tanner Basin (TB) is furthest from shore having the lowest organic carbon decomposition rate and a higher bottom water oxygen concentration than the Santa Monica and San Pedro sites (Table 1). San Clemente (SCl) basin is distinct among our sites in that the upper few centimetres of sediment have a layer rich in solid-phase manganese [27,28]. This basin also has low organic decomposition rates and the highest bottom water oxygen concentration of all four sites.

## 3. Methods

Sediments used in this particular study were collected with a multi-corer [29]. These sediments were processed for pore water analyses immediately after retrieval [26,28]. The remaining sediment was freeze-dried and ground after returning to shore. Analyses of these sediments and their pore fluids resulted in a number of publications detailing core and study site information, and those data are not reproduced here [25–28,30].

For solid-phase metal concentrations, ~0.025–0.100 g of sediment were digested using a series of HF, $HNO_3$, and HCl hot digestions (80–85 °C) on a hot plate or using a microwave digestion technique (CEM, MARS 5000) [16]. Analyses were done using ICP-MS (Mo) or ICP-AES (Al, Ti, Fe, Mn). For Mo isotopes we used a modification of an existing sample preparation technique [31]. Because this technique was not successful for all of our samples, we made two primary modifications to the original method; (1) the addition of a 6 N HCl digestion step, and (2) the addition of a concentrated $HNO_3$ digestion step in combination with $H_2O_2$. Column separation of Mo from the sedimentary matrix was also accomplished using an adaptation of the previously published technique [31], with the primary change to that procedure being the use of 0.5 N $HNO_3$ as an eluent as opposed to 2 N $HNO_3$ as previously proposed. It is important to iterate that these modifications proved essential in our analyses of some marine sediments. In the absence of these modifications we experienced a number of recovery and column elution problems with the more organic-rich matrix that is typical of continental margin sediments as opposed to the low organic carbon matrix typical of other geologic materials [31].

Samples for Mo isotope analysis were spiked with a $^{97}Mo$ and $^{100}Mo$ double isotope tracer (after [31]). Mo isotope measurements were made on the Nu instruments® MC-ICP-MS at the Keck Collaboratory at Oregon State University. Our isotope measurements were made relative to a Johnson Matthey ICP (JMC)

Table 1
Study site characteristics[a]

| Study sites | Depth (m) | Latitude (°N) | Longitude (°W) | BW $O_2$[b] (μM) | $C_{ox}$[c] (mmol $m^{-2}$ $d^{-1}$) | $O_2$ penetration depth[d] (cm) |
|---|---|---|---|---|---|---|
| San Pedro | 897 | 33.6 | 118.5 | 3 | 1.8 ± 0.4 | |
| Santa Monica | 905 | 33.7 | 118.8 | 9 | 1.9 ± 0.2 | 0.26 |
| San Clemente | 2070 | 32.6 | 118.1 | 65 | 1.0 ± 0.1 | 1.28 |
| Tanner Basin | 1514 | 33.0 | 119.7 | 27 | 1.0 ± 0.3 | 0.57 |

[a] Data taken from [16,25,26].

[b] BW is bottom water.

[c] $C_{ox}$ is the organic carbon oxidation rate and is calculated from the evolution of respiratory $CO_2$ during the course of benthic incubations [25]. The value for each site is a compilation of previously published data [16].

[d] Oxygen penetration depths are calculated as described in [25] from oxygen flux data and bottom water oxygen concentrations. For San Pedro Basin on this occasion there were no oxygen flux data; however, based on the carbon flux and bottom water oxygen we estimate that this value will be similar to that of Santa Monica Basin.

standard solution (lot 602332B). We present all data in the delta notation as reported previously [31,32] where $\delta^{98/95}\text{Mo} = [[^{98}\text{Mo}/^{95}\text{Mo}_{\text{sample}} - ^{98}\text{Mo}/^{95}\text{Mo}_{\text{standard}}]/^{98}\text{Mo}/^{95}\text{Mo}_{\text{standard}} - 1] \times 10^3$. The external standard reproducibility of the isotope values is generally at or below 0.1‰ ($2\sigma$) for the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio. However, the reproducibility of a single sediment standard (NBS 1645) for this particular data set is ~± 0.25‰. This value is a more appropriate measure of the long-term reproducibility of our particular sedimentary matrix. This value is also less precise compared to previously published values [15,31], but it is a reasonable representation of the precision of this particular data set. Based on subsequent work in our laboratory we anticipate that this value can be improved to ~0.1–0.2‰. However, the variability of Mo isotope compositions within the cores from each of our study sites (where $n = 8$–22 individual analyses, see below) is within the precision obtained for the NBS 1645 standard and may reflect the natural variability observed for the Mo isotope values within each of our study sites.

## 4. Results

Each of our four study sites exhibits sedimentary Mo enrichments over “background” Mo concentrations (Fig. 2). We define the background Mo : Al ratio as the lowest regional value seen in our sediment cores [16]. This Mo : Al value for the southern California margin is $8 \times 10^{-6}$ (g g$^{-1}$). Using this background Mo : Al ratio we estimate the authigenic Mo ($\text{Mo}_{\text{auth.}}$) signature from the relationship: $\text{Mo}_{\text{auth.}} = \text{Mo}_{\text{measured}} -$

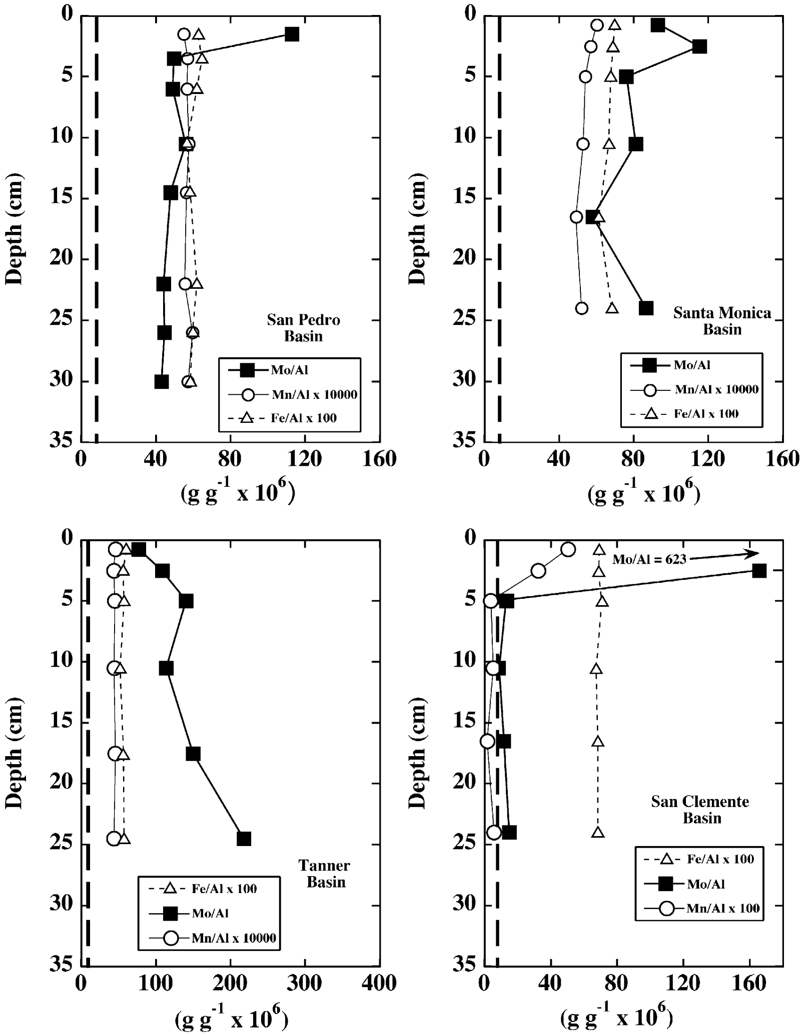

Fig. 2. Metal to Al ratios plotted as a function of sediment depth at our study sites. Dashed line is the lithogenic Mo : Al ratio as described in the text.

Table 2
Accumulation rate, carbon rain rate, and average Mo isotope values

| Study sites | MAR[a] (mg $cm^{-2}$ $y^{-1}$) | $Mo_{MAR}$ (nmol $m^{-2}$ $day^{-1}$) | $C_{burial}$ (mmol $m^{-2}$ $day^{-1}$) | $C_{rain}$ (mmol $m^{-2}$ $day^{-1}$) | $\delta^{98/95}Mo$ (core average) |
|---|---|---|---|---|---|
| San Pedro[b] | 29 | 24 | 2.6 | 4.4 | 1.3 ± 0.2 |
| Santa Monica[c] | 16 | 20 | 1.8 | 3.7 | 1.2 ± 0.3 |
| San Clemente[c] | 15 | 1 | 0.9 | 1.9 | −0.5 ± 0.4 |
| Tanner Basin[c] | 12 | 18 | 1.4 | 2.4 | 0.5 ± 0.3 |

[a] Mass accumulation rates (MAR) and carbon burial rates ($C_{burial}$) are taken from [25]. Carbon rain ($C_{rain}$) is calculated as the sum of $C_{burial}$ and $C_{ox}$ in Table 1 [16].

[b] Mo isotope data were collected on a cruise in July 2001 [30].

[c] Sediment data were collected on a cruise in November 1995 [26].

[Mo/$Al_{lithogenic}$ × Al]. We recognize the operational nature of this definition. For example, this definition assumes that there is no authigenic Al formed in marine sediments. This definition also assumes that the site where our chosen regional minimum is selected there is no authigenic Mo, and that such a minimum is regionally applicable. By comparison to other continental margins, Mo : Al ratios at sites along the central California margin and the Chile margin range between 8 and $14 \times 10^{-6}$ [16]. Despite the operational nature of this value, any definition that we would choose, whether based on chemical extractions or alternative Mo : Al values, would be equally operational (see Section 5.1 for further discussion).

San Clemente basin contains the highest Mo enrichment over background of any of the sites; however, the highest enrichment zone is associated with a manganese rich layer (Fig. 2). Below the Mn-rich zone, this core goes through a minimum in the Mo : Al ratio (the regional background value) and increases slightly below ~10 cm. We suggest that this deeper Mo enrichment is generated by Mo authigenesis under the reducing conditions that likely operate at this depth (i.e., it is below the Mn reduction zone). Tanner basin has the highest non-Mn associated Mo enrichment throughout the core of all the sites followed closely by Santa Monica and San Pedro basins. The authigenic accumulation rates, however, are similar for these sites (Table 2 and [16]). In terms of carbon cycling these basins have carbon rain rates that range from 2 to 4 mmol $m^{-2}$ $day^{-1}$, with roughly 50% of the organic carbon that reaches the seafloor in each basin being buried [25].

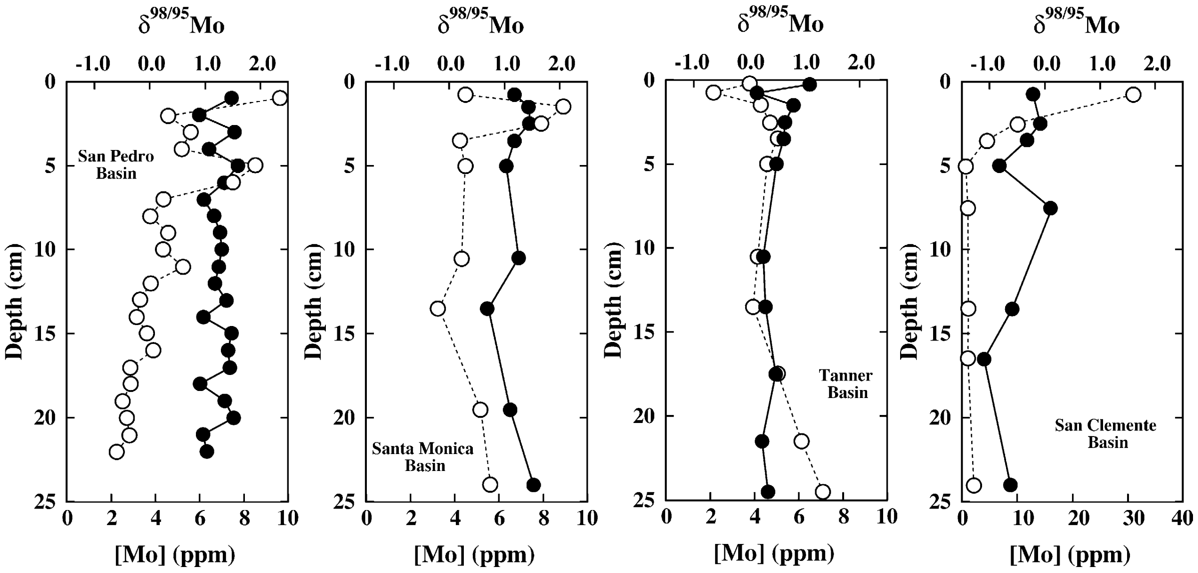

Fig. 3. Molybdenum concentrations (ppm) and $\delta^{98/95}$Mo values plotted as a function of sediment depth. Data from the San Pedro study site presented here are taken from a different core than the data presented in Fig. 2. We do not have Mn and Al data for the site in Fig. 3; however, we do not expect there to be differences sufficiently significant as to cause a reinterpretation of the diagenetic setting. Open symbols are the Mo concentrations and closed symbols are the isotope values.

The Mo isotope composition varies from site to site as well as within each core. This variability suggests differences in either the extent of isotope fractionation or the processes that govern fractionation. The San Clemente basin (−0.5‰) is the only core with an average $\delta^{98/95}$Mo that is less than 0‰, which is the assumed crustal Mo isotope composition [15,17,19]. The other sites have distinctive average $\delta^{98/95}$Mo values greater than crustal values but less than ocean water (2.3‰) ranging from 0.5‰ to 1.3‰ (Table 2). For most of the sites, Mo isotope values co-vary with Mo concentrations, but such is not always the case, in particular the San Pedro basin does not exhibit a strong covariance (Fig. 3).

## 5. Discussion

### 5.1. Molybdenum authigenesis in continental margin settings

Mo is an unusual element in the oceans in that it is highly enriched in sedimentary solid phases under both oxidizing and reducing conditions and both situations are captured within our data set. Under oxidizing conditions, Mo adsorbs to Mn oxides; thus, Mn-oxide rich layers in marine sediments tend to be enriched in Mo as well (e.g., [7]). This particular type of authigenic enrichment is, however, transient. This transience arises from the fact that Mn-oxide layers are continually undergoing dissolution and re-precipitation in hemi-pelagic settings because the solid-phase $Mn^{4+}$ is continually being reduced during organic matter electron transport leading to $Mn^{2+}$ diffusion followed by re-precipitation in the shallower sediment column as an oxidized phase (e.g., [33]). Thus this type of authigenic Mo is not likely to be observed deeper in the sediment column. Data from San Clemente basin characterize this scenario in that these sediments have a layer (top 5 cm) where the Mn : Al ratio is one to two orders of magnitude higher than the other sites (Fig. 2). Assuming that most of the Mo within these sediments is indeed adsorbed onto Mn oxides we would expect the isotope value of these sediments to be approximately 3‰ lower than parent seawater based on observations from Mn crusts [15,19] and laboratory experiments [22]. With an average isotope composition of −0.5‰ ± 0.4‰ (1$\sigma$ variation) for San Clemente basin sediments, this expectation is met (Fig. 3 and Table 2). Based on theoretical considerations [34] we speculate that the chemical mechanism for isotope fractionation associated with this particular adsorption process is related to a speciation and coordination change whereby the minor $MoO_3$ species is adsorbed rather than the dominant $MoO_4^{2-}$ species. It has been predicted that this coordination change should result in an isotope shift of 2.4‰ [34], which agrees with the range of the isotope shift reported for Mo adsorption onto Mn oxides and with the range seen in our core.

Although San Clemente captures the scenario of Mo associated with a Mn-rich layer, which results in light isotope compositions, many continental margins are sufficiently reducing that we would not expect a significant oxidized Mn layer to be present within the sediments. This expectation arises because oxidized Mn is used in electron transport processes and continental margin settings are often sufficiently reducing that there is little oxidized Mn present in the upper sediment column [33]. This assertion will be particularly true for suboxic continental margin sediments that are shallow (<2 km) and lie below highly productive surface waters. Thus environments like San Clemente basin, characterized as having Mn-rich sediments, are more likely to be typical of deeper hemipelagic settings than of the shallower continental margin settings.

Under reducing conditions, Mo authigenesis occurs where dissolved sulfide is present in marine pore fluids (e.g., [4,5,8,10,11,35–47]). More specifically, previous workers [39] suggest that Mo is removed from sedimentary pore fluids under reducing sediments where dissolved sulfide concentrations exceed 0.05 μM. This concentration is likely to be approached in many suboxic continental margin settings and indeed recent evidence indicates that a number of continental margin settings are accumulating sulfidized authigenic Mo (e.g., [16,36,39,48,49]). Our data suggest that each of our sites may be undergoing this type of authigenic Mo accumulation (Table 2). In the particular case of San Clemente basin, where there is Mo associated with Mn oxides in the surface sediments, we predict that this type of authigenic enrichment is occurring below the Mn-rich layer near the base of our sampling range. As evidence for this idea we note an increase in the Mo : Al ratio over the depth range of ~15 to 25 cm (Fig. 2). In the case of the other sites we hypothesize that this type of authigenesis is occurring throughout the sediment column. The mechanism for this enrichment remains somewhat speculative but the balance of experimental and field data suggest that in the presence of low concentrations of sulfide, which can be generated during the early diagenesis of organic carbon during sulfate reduction, Mo is converted to a particle-reactive thiomolybdate complex ($MoO_xS_{4-x}^{2-}$) [45–47]. This complex could be scavenged by sulfidized organic matter or Fe–S phases or both [47]. Regardless of the specific pathway, the balance of evidence suggests that where sufficient reduced sulfur phases are available, authigenic Mo can accumulate, and it appears that the conditions are sufficiently reducing at each of our sites for the accumulation of authigenic Mo via this pathway.

Our data exhibit a co-variation between the accumulation rate of sulfidized Mo and the Mo isotope value (Fig. 4). This co-variation suggests that the dominant reactions leading to authigenesis are the reactions responsible for isotope variability. This similarity in chemistry will be expressed to some degree as coincident changes in the Mo concentration and the isotope composition with depth in an individual core, which is observed most notably in the Santa Monica and Tanner Basin cores. However, because of the importance of the accumulation rate in setting the authigenic signature (Fig. 4), there is no a priori reason to expect a strict covariance between Mo concentration and the isotope composition, and such a lack of covariance is observed for the San Pedro site where the concentration changes from 10 to 2 ppm but the isotope composition varies comparatively little (Fig. 3). One interpretation of these data is that the San Pedro basin is a location where sediment accumulation rates are decreasing with time, a possibility that has been raised during prior work [50].

At face value the Mo isotope data for these sites could suggest that the isotope fractionation process is different for each of our sites, and we recognize this as a possible interpretation of our data. However, we prefer the interpretation that the isotope value at any one specific site is a mixture between two (or perhaps more) isotope signatures. We prefer this particular interpretation because it does not require multiple and unique fractionation processes. We propose that one sedimentary signature that is likely part of that mixture is the Mo derived from the adsorbed phase $MoO_3$, which we have hypothesized above as being driven by the fractionation associated with the coordination change that occurs between the dominant dissolved species $MoO_4^{2-}$ and the adsorbed $MoO_3$ (Fig. 4). Any Mo that is adsorbed onto solid surfaces as $MoO_3$ will have an isotope composition of $\sim -0.7$‰. If this phase is released and subsequently removed as a sulfidized phase it should maintain this isotopic signature. Thus in suboxic continental margins the Mo that does pass through an intermediate $MoO_3$ adsorption phase could be part of an isotope mixture in continental margin sediments.

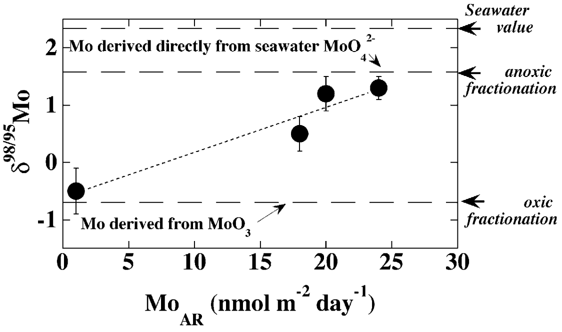

Fig. 4. $\delta^{98/95}Mo$ plotted as a function of the Mo mass accumulation rate. Dashed lines represent the seawater isotope value (top), the fractionation from the seawater value predicted from the calculated fractionation factor derived from pore water Mo and Mo isotope data [32] (middle), and the oxic fractionation as assembled from a number of sources (Table 3) (bottom). The figure suggests that there could be a mixture of two (or more) authigenic components, each with a unique isotope signature.

A second isotopic end-member would be represented by the isotopic fractionation associated with the removal of ocean water $MoO_4^{2-}$ as a sulfidized phase ($MoO_xS_{4-x}^{2-}$). Evidence for this type of isotope fractionation under reducing conditions comes from the dissolved Mo isotope signature in marine pore fluids [32]. In that study the authors calculate a fractionation factor from the change in pore fluid Mo and Mo isotope composition at Santa Monica basin. If we assume that the results from that study are broadly applicable, we would expect to observe a fractionation of $-0.7$‰ relative to the ocean water value for continental margin sediments—i.e., sediments where the entire Mo pool is formed via sulfidization would have a $\delta^{98/95}Mo$ value of 1.6‰ (Fig. 4). Under this two end-member mixing model all continental margin suboxic sediments should lie somewhere between $\sim -0.7$‰ and 1.6‰ (Fig. 4). Given the limited data currently available, we treat this idea as a working hypothesis; however, it is consistent with present thinking regarding the chemical mechanisms for Mo enrichment in marine sediments and the limited estimates available for fractionation in sedimentary solid phases.

An important implication of the co-variation observed in Fig. 4 is that the isotope data support the idea that these sediments are indeed undergoing authigenesis. We make this point based on the observation that the Mo isotope value varies from site to site and is significantly different from 0‰, which we assume to be the value of lithogenic material (Table 3). The importance of this point is that our estimated authigenic accumulation rate of Mo (Table 2 and Fig. 3) is based in part on selection of an appropriate background or lithogenic Mo concentration for these

Table 3
Mo isotope values

| | $\delta^{98/95}$Mo | |
|---|---|---|
| | Range | Average |
| | (‰) | (‰) |
| Lithogenic[a] | −0.4 to 0.4 | 0.1 ± 0.2 |
| Fe–Mn crusts[b] | | −0.7 ± 0.1 |
| Euxinic[c] | 1.3 to 2.6 | 1.95 |
| Seawater[d] | | 2.3 |
| Suboxic[e] | −0.45 to 1.6 | |

[a] Lithogenic values are derived from [19] and [15] and included clastic sediments, subduction basalts, granites, and molybdenites.

[b] We have elected to use the isotope signature from surface samples taken from Fe–Mn crusts [15,19] to represent the isotope signature for oxic sediments.

[c] The range in euxinic isotope values includes values from an array of anoxic basins [15,21,51]. However, we have excluded values from [51] for the average as these are from the shallow Black Sea where the sulfide concentrations are significantly lower than for the deeper Black Sea.

[d] Reported in [15].

[e] This study and [19].

sediments, as discussed above, and we freely admit that the selected background value could be different from the one that we have selected. However, if the Mo at each of these sites was exclusively lithogenic, we would not expect there to be any variation in the Mo isotope value and we would expect that the isotope value would be approximately 0‰, which it is not. Part of the limitation encumbered by the isotope data is that the crustal or lithogenic isotope signature is based on a limited data set; however, this value is the current best estimate for the lithogenic component. Despite these limitations, what is important to articulate is that the apparent relationship between Mo accumulation rate and Mo isotopes (Fig. 4) does indeed point to Mo authigenesis in continental margin settings. This importance is highlighted by the fact that the data pointing to Mo authigenesis in continental margin settings are still limited [16,39,48,49], and the isotope data add further support for those data.

### 5.2. Implications for the molybdenum isotope budget

A number of the applications for Mo isotopes as a proxy for ocean chemistry rely on a knowledge of the processes that control the Mo isotope balance in the ocean through time. However, as has been pointed out on a number of occasions there still remain a significant number of uncertainties regarding the modern Mo and Mo isotope budget [13,17,21]. These uncertainties revolve primarily around the oceanic burial reservoir for Mo. Mo ocean inputs are rivers, at $1.8 \times 10^8$ mol y$^{-1}$ [52 as reviewed in 14], and low temperature hydrothermal weathering at $0.2 \times 10^8$ mol y$^{-1}$ [32,53]. The sinks for Mo have been proposed to be oxic sediments ($0.9 \times 10^8$ mol y$^{-1}$) and anoxic sediments (0.2–$0.8 \times 10^8$ mol y$^{-1}$) [14]. If we assume the maximum burial term for anoxic sediments ($0.8 \times 10^8$ mol y$^{-1}$) is the appropriate value and that the estimate for oxic sediments is correct, then these numbers imply a nearly balanced Mo budget, but that balance would require a near even mixture between the oxic and anoxic sinks. In contrast to this requirement, the existing isotope balance [15] suggests that the sinks should be ~70% oxic and 30% anoxic.

Recent reports that continental margin reducing sediments may also be an important Mo sink [16,39,48,49] may provide a more refined geochemical budget. It is difficult, however, to extrapolate Mo accumulation rates from one region to a global scale; thus, making such budgetary constraints highly uncertain. Assuming a moderately low Mo uptake rate of 5 nmol m$^{-2}$ day$^{-1}$, based on a compilation of existing sediment and pore water data, and assuming that this is the average Mo removal rate for ocean margin sediments between depths of 0.2 and 2 km, it has been estimated that the Mo burial rate in continental margin sediments is $0.6 \times 10^8$ mol Mo y$^{-1}$ [16]. An alternative approach uses the molybdenum to organic carbon burial ratio in sediments and the organic carbon burial budget to estimate the global molybdenum burial rate [16]. This approach yields a Mo burial rate of approximately 0.6–$0.9 \times 10^8$ mol Mo y$^{-1}$ for non-deltaic reducing continental margin settings. A similar approach based on carbon burial in anoxic or euxinic basins suggests that Mo removal in these systems is likely to be less than $0.4 \times 10^8$ mol Mo y$^{-1}$ [16]. Although a full Mo isotope budget is premature at this point we suggest, based on the work reviewed here, that the oxic removal of Mo is $0.9 \times 10^8$ mol Mo y$^{-1}$, with a $\delta^{98/95}$Mo value of approximately −0.7‰. Likewise Mo removal in reducing continental margin settings is approximately $0.7 \times 10^8$ mol Mo y$^{-1}$, and assuming that the pore water fractionation [32] is representative of the continental margin removal process that Mo will have an isotope value of 1.6‰. Euxinic basin removal is $0.4 \times 10^8$ mol Mo y$^{-1}$ with an uncertain isotope value that likely lies between 1.6‰ and 2.3‰ (Table 3). Given the scarcity of Mo isotope data for marine systems the isotope signatures are at best loose approximations at this point (i.e., the continental margin value is based on a Rayleigh fit to a single pore water profile [32]; Fig. 4).

### *5.3. Relationship between molybdenum and organic carbon*

Molybdenum is an element that appears to be sensitive to the cycling of sulfur in marine sediments [10,11,43–47]. Because organic carbon can be decomposed via pathways that include sulfate reduction in continental margin settings (e.g., [25,33]) it follows that there could be a relationship between Mo accumulation and either the delivery of reactive organic material to the sediments or the burial of sulfur and organic material within the sediments [16]. For the California borderlands region this expectation is met (Fig. 5). Likewise because of the correlation between the accumulation rate of Mo and the isotope signature at these sites (Fig. 4), there is a correlation between organic carbon and the isotope signature (Fig. 6). As discussed above this covariance likely points to a common mechanism for both Mo enrichment and isotope fractionation.

Although intuitive at some level, the fact that both Mo accumulation and its isotope values seem to track the carbon cycle imply that their combination may end up being particularly powerful as a paleoproxy. For example, although Mo is only moderately enriched in typical continental margin settings [16,38,48,49], the potential to use Mo as a quantitative proxy is encumbered because it is necessary to know the sediment accumulation rate (Fig. 5). To put this statement another way, Mo concentrations are sensitive to mass accumulation rates; thus, concentrations alone will not reveal quantitative information regarding biogeochemical processes. In contrast to this limitation, one of the promises held by Mo isotopes as a paleoproxy for the carbon cycle is that sediment accumulation rates are not required for conversion of the proxy signature to the process of interest. Although our data represent only a single region characterized by suboxic depositional basins, by removing the requirement for accurate sedimentation rate information, Mo isotopes open a new possibility for developing a quantitative tracer of the marine carbon cycle.

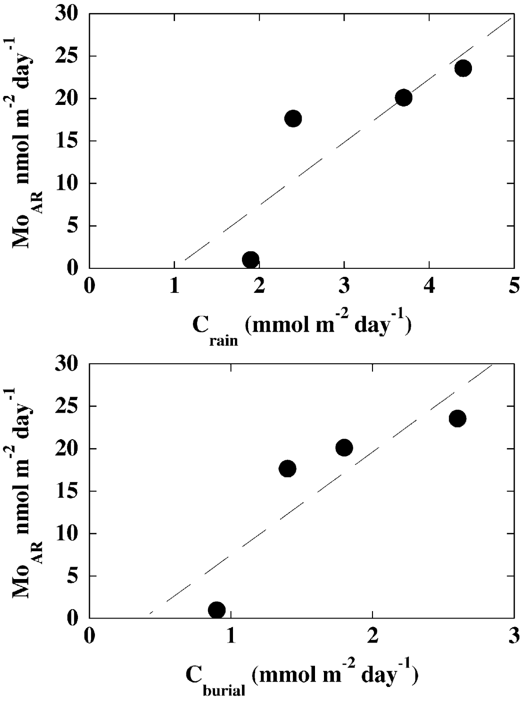

Fig. 5. Mo mass accumulation rate plotted as a function of the organic carbon rain rate (top) and the organic carbon burial rate (bottom). The organic carbon rain rate is a calculated parameter based on the sum of the organic carbon oxidation rate ($C_{ox}$) and the organic carbon burial rate ($C_{burial}$) (Tables 1 and 2).

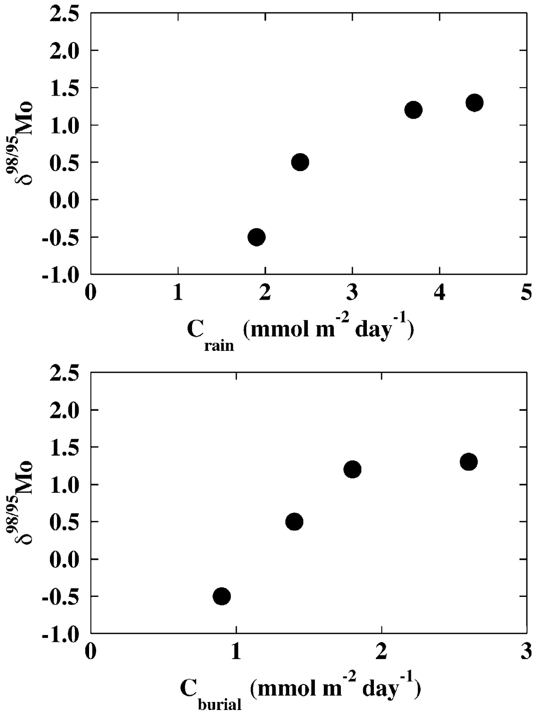

Fig. 6. $\delta^{98/95}$Mo plotted as a function of the organic carbon rain rate (top) and the organic carbon burial rate (bottom). The organic carbon rain rate is calculated as in Fig. 5. The figure shows that the sedimentary Mo isotope value varies as a function of the organic carbon rain and burial rates, which when considered in light of Fig. 5, implies that Mo authigenesis and its isotope signature are related to either the organic carbon delivery rate to the sediments ($C_{rain}$) or to the factors that influence carbon preservation ($C_{burial}$).

## 6. Conclusions

Analysis of four sediment cores from a continental margin area shows that (1) Mo authigenesis is occurring in these suboxic sediments and (2) that authigenesis produces fractionation of Mo isotopes. The down-core profiles of Mo isotope compositions are the first reported for continental margin settings. At one site where manganese cycling occurs in close proximity to the sediment–water boundary a Mn-rich zone is produced and the average Mo isotope composition at that site is negative. This negative value is consistent with previous work on Mo isotope fractionation associated with Mn oxides. At the other sites, the data suggest a relationship between the accumulation rate of sulfidized Mo and the Mo isotope signature. The apparent covariance between these parameters suggests that the chemistry that leads to Mo accumulation is recorded as an isotope signature. Furthermore, there is an observed relationship between carbon cycling and the isotope composition of the sediments. If this relationship continues to hold under a variety of conditions it would mean that Mo isotopes could be a powerful proxy for carbon cycling in environments where there is sufficient carbon oxidation to initiate Mo authigenesis.

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