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# Molybdenum Stable Isotopes:
# Observations, Interpretations and Directions

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## INTRODUCTION

The unusual chemistry of molybdenum (Mo) makes this trace element interesting to both geochemists and biochemists. Geochemically, Mo is relatively unreactive in oxygenated, aqueous solutions, and hence is a nominally conservative element in the oceans. In fact, Mo is removed so slowly from seawater that it is the most abundant transition metal in the oceans despite being a ppm-level constituent of the crust. In contrast, Mo is readily removed from solution in anoxic-sulfidic ("euxinic") settings, so that Mo enrichments in sediments are considered diagnostic of reducing depositional conditions. Few elements possess such bimodal redox behavior at the Earth's surface.

Biochemically, Mo draws attention because it is an essential enzyme cofactor in nearly all organisms, with particular importance for nitrogen fixation, nitrate reduction and sulfite oxidation. Such biochemical ubiquity is surprising in view of the general scarcity of Mo at the Earth's surface.

Isotopically, Mo initially catches the eye because it has seven stable isotopes of 10–25% abundance, covering a mass range of ~8% (Fig. 1). Thus, from an analyst's perspective, Mo offers both an unusually large mass spread and a number of options for isotope ratio
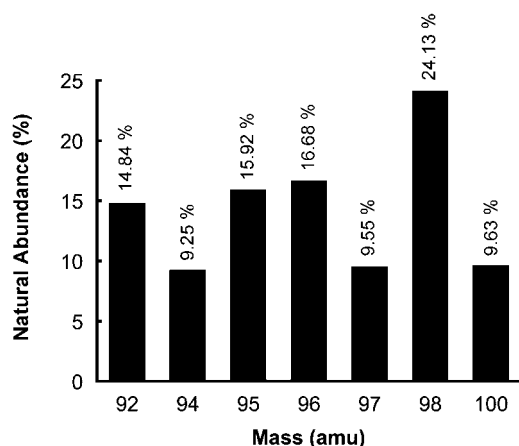


**Figure 1.** The average natural abundances of the stable isotopes of Mo as recommended by IUPAC, based on (Moore et al. 1974).

determination. Combined with rich redox chemistry and covalent-type bonding, both of which tend to drive isotope fractionation, these factors make the Mo isotope system a particularly promising target for stable isotope investigation.

In the environment, Mo isotope research began in earnest with the application of multiple-collector inductively coupled plasma mass spectrometry. While much work remains to be done, this early research points to promising applications in paleoceanography, and beyond.

This review is intended to provide an overview of this emerging stable isotope system in the context of Mo environmental biogeochemistry. Special attention is given to Mo in marine systems because this is where most initial work has focused. We begin by reviewing the environmental biogeochemistry of Mo, emphasizing the ocean budget and the role of this element in biology, and drawing comparisons and contrasts with other elements. Subsequent sections discuss analytical methods, summarize Mo isotope observations in natural samples and laboratory experiments, provide a first-order interpretation of Mo isotope systematics in the oceans, and consider logical directions for future investigations.

## MOLYBDENUM IN THE ENVIRONMENT AND IN BIOLOGY: SETTING THE STAGE

### Molybdenum environmental geochemistry

The distribution of Mo at the Earth's surface is unique among the transition metals. Mo is a trace constituent of the upper crust, with an average abundance of 1–2 ppm (Taylor and McLennan 1985). Yet, Mo is the most abundant transition metal in the oceans, with a concentration of ~105 nmol kg$^{-1}$ (Morris 1975; Bruland 1983; Collier 1985). In seeking to understand this distribution, we gain insight into fundamental aspects of Mo geochemistry.

As for all elements, the distribution of Mo in the environment depends critically on chemical speciation, including oxidation state (Bertine and Turekian 1973; Morford and Emerson 1999). However, Mo is somewhat unusual in both respects. In terms of ligand coordination, Mo is one of a small number of transition metals that commonly form oxyanions and coordinate only weakly with other environmentally common ligands such as Cl$^-$ or OH$^-$. Other such metals include Cr and W, which sit above and below Mo, respectively, in Group VI of the Periodic Table, as well as Tc, Re, Os and U. Hence, Mo chemistry has some analogies with these metals, as well as with nonmetals such as S, Se, P and As which also form oxyanions.

However, in terms of redox chemistry, Mo differs significantly from Cr, Se and many other elements in that it is so easily oxidized that its most highly oxidized form, Mo(VI), is prevalent when Eh > 0 V in solutions with pH > 5 (Fig. 2). As a result, Mo speciation in most oxygenated waters is believed dominated by the tetrahedrally coordinated oxyanion $MoO_4^{2-}$. Protonated species such as $HMoO_4^-$ or $H_2MoO_4$ ("molybdic acid') are quantitatively important only at pH < 5 (Fig. 2). Polynuclear Mo species such as $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$ are observed when pH < 6, but only at Mo concentrations too high to be generally relevant in the environment (e.g., >10$^{-3}$ M). Mo environmental chemistry in oxygenated systems is therefore loosely analogous to S, for which the dominant species is $SO_4^{2-}$. In particular, both elements are readily transferred to solution during oxidative weathering, are highly mobile in oxidizing fluids, and relatively non-reactive in the oceans. In fact, the chemical similarities between $MoO_4^{2-}$ and $SO_4^{2-}$ (e.g., charge; coordination; ionic radii) have led to the suggestion that biological assimilation of Mo may be inhibited by $SO_4^{2-}$ (e.g., Marino et al. 2003).

The geochemical character of Mo changes sharply in $H_2S$-bearing systems, so much so that it has been likened to a "geochemical switch" (Helz et al. 1996; Erickson and Helz 2000). This change is seen in the concentration depth profiles of these elements in the Black Sea
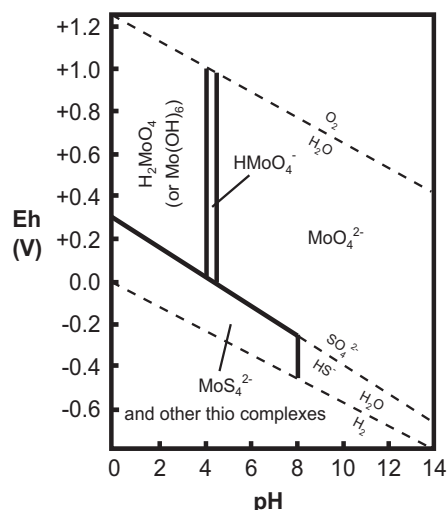
**Figure 2.** Eh-pH diagram of dissolved Mo speciation in the system Mo-$H_2O$-S. $\Sigma Mo = 10^{-6}$ M; $\Sigma S = 10^{-4}$ M. Modified after Manheim and Landergren (1974), using molybdate protonation constants from Baes and Mesmer (1986). $H_2MoO_4$ is related to $Mo(OH)_6$ by addition of two water molecules (see text). $MoO^{2+}$, included in earlier Eh-pH diagrams, is omitted because this and other Mo(V) species are typically unstable except as dimers (e.g., $Mo_2O_4^{2+}$) at higher $\Sigma Mo$ than common in nature. Speciation at Eh below the $SO_4^{2-}$ - $H_2S$ transition is not well characterized and is commonly out of equilibrium. The boundary between $MoS_4^{2-}$ and $MoO_4^{2-}$ is based on Erickson and Helz (2000); intermediate oxythiomolybdates are metastable and hence not indicted.

(Fig. 3) (Emerson and Huested 1991). Here, oxygenated surface waters give way to anoxia and [$H_2S$] > 100 μmol kg$^{-1}$ below ~100 m. The total Mo concentration across this redox transition declines from ~40 nmol kg$^{-1}$ at the surface to ~3 nmol kg$^{-1}$ below the chemocline. Investigations of Mo in marine sediments and porewaters indicate that Mo is also removed from solution under less intensely reducing conditions; in general, authigenic accumulation of Mo occurs in sediments overlain by waters in which $O_2$ < 5 μmol kg$^{-1}$ (Emerson and Huested 1991; Crusius et al. 1996; Dean et al. 1997; Zheng et al. 2000a; Nameroff et al. 2002).

The Mo removal mechanisms in reducing settings are not well understood, in part because Mo speciation in such settings is complicated by slow reaction kinetics. The reduction of Mo(VI) to form insoluble $MoS_2$ appears to play less of a role than might be intuitively expected, as a result of kinetic hindrances (Helz et al. 1996). Instead, interactions with HS$^-$ are probably important; Mo may be removed as particle-reactive oxythiomolybdates ($MoO_{4-x}S_x^{2-}$) which form when [$H_2S$] exceeds a "switch point" of ~10 μmol kg$^{-1}$ (Helz et al. 1996; Erickson and Helz 2000). Additionally, a general association of Mo with $C_{org}$ is commonly observed which could reflect a direct connection between Mo and organic compounds in reducing environments (e.g., Brumsack and Gieskes 1983). Interestingly, most Mo removal apparently occurs below the sediment-water interface rather than in
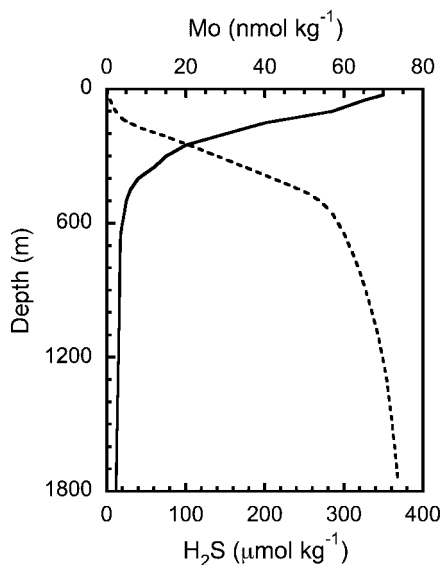


**Figure 3.** Depth profiles of Mo (solid line) and $H_2S$ (dashed line) in the Black Sea (Mo: Emerson and Huested 1991; $H_2S$: Neretin et al. 2001). The concentration of Mo falls sharply in the euxinic zone.

the water column even when the water column is strongly reducing (Francois 1987; Emerson and Huested 1991; Crusius et al. 1996), a phenomenon that may result from acid-catalysis of oxythiomolybdate formation in low-pH sediment pore waters (Erickson and Helz 2000).

Regardless of mechanistic uncertainties, sedimentation under low-$O_2$ waters is a critical part of the global Mo ocean budget. Despite their scarcity in the oceans, such sedimentary settings account for removal of 10−50% of the Mo entering the oceans via rivers each year (Bertine and Turekian 1973; Morford and Emerson 1999). Most of this removal probably occurs in sulfidic ("euxinic") basins like the Black Sea or the Cariaco Basin. Hence, relative to its average crustal abundance, Mo is strongly enriched in black shales, saprolites and other carbonaceous sediments, with concentrations invariably >10 ppm and often exceeding 100 ppm.

Some 10–20% of Mo removal may also occur in so-called "suboxic" settings of intermediate redox potential, where bottom water $O_2$ is <5 µmol kg$^{-1}$ and $H_2S$ << 10 µmol kg$^{-1}$ (Morford and Emerson 1999; Emerson personal communication).

Surprisingly in view of the stability of $MoO_4^{2-}$ in solution, Mo enrichment to concentrations of 100's–1000's of ppm, correlated with Mn content, is seen in ferromanganese oxide sediments, especially crusts, nodules and some oxic pelagic sediments (Bertine and Turekian 1973; Calvert and Price 1977; Cronan 1980; Calvert and Piper 1984; Shimmield and Price 1986). Such enrichment most likely reflects authigenic accumulation of Mo by adsorption to and/or coprecipitation with Mn oxide phases. This phenomenon is observed in the laboratory (Chan and Riley 1966; Barling and Anbar 2004). Therefore, the bulk of Mo not removed to euxinic sediments is generally thought to be removed in association with sedimentary Mn oxides (Bertine and Turekian 1973; Morford and Emerson 1999). Ferromanganese crusts and nodules are probably not themselves dominant sinks because these sediments accumulate very slowly; Mo associated with Mn oxides in widely disseminated pelagic sediments may be quantitatively more important although Mo enrichments in pelagic sediments are relatively small.

The net result of these considerations is that Mo is thought to have a comparatively straightforward ocean budget (Fig. 4), entering largely dissolved in river waters and leaving primarily in association with authigenic Mn-oxides and anoxic sediments. The accumulation of Mo in the oceans relative to other transition metals therefore reflects the strongly bimodal character of Mo geochemistry with respect to redox conditions. Essentially, Mo is readily transferred from crust to oceans during oxidative weathering but, because settings in which bottom water $O_2$ < 5 µmol kg$^{-1}$ cover only ~0.3% of the modern seafloor, Mo is only slowly removed from the oceans. Hence, the Mo ocean residence time is ~10$^5$−10$^6$ years (Morford and Emerson 1999), and the largest variations in Mo concentration in oxygenated seawater are only ~5% on a salinity-normalized basis (Tuit and Ravizza 2003). Re and U have similar budgets, reflecting similar geochemical considerations (Klinkhammer and Palmer 1991; Anbar et al. 1992; Colodner et al. 1993).

A consequence of this geochemical behavior is that the abundance of Mo in sediments (as well as the abundances of U and Re) can be used as an
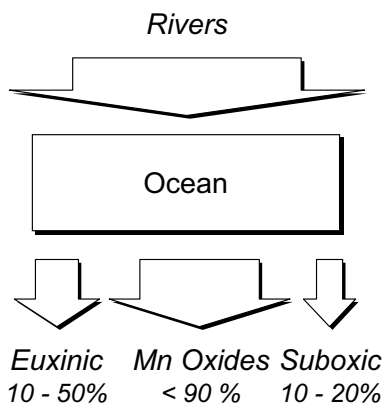


**Figure 4.** A schematic depiction of the Mo elemental budget in the modern oceans. Rough estimates of the percent removal to each sediment type, drawn from the literature, are indicated (see text).

indicator of local bottom water redox conditions (e.g., Crusius et al. 1996; Dean et al. 1997; Dean et al. 1999; Yarincik et al. 2000; Zheng et al. 2000b; Calvert et al. 2001; Werne et al. 2002; Algeo and Maynard 2003; Lyons et al. 2003; Sageman et al. 2003). Broadly speaking, Mo enrichments of 10s to 100s of ppm in sediments (typically normalized to tracers of detrital input, such as Al) may indicate water column Eh below the "switch point" during sediment deposition.

Finally, because the Mo ocean budget should be strongly sensitive to bottom water redox conditions, particularly perturbations associated with expanded deep sea anoxia, determination of Mo concentrations or their variations in ancient seawater, via sedimentary proxies, has been proposed as an indicator of global ocean paleoredox change (e.g., Emerson and Huested 1991).

## Molybdenum in biology

Biologically, Mo, like Fe, has a prominent role in biochemical pathways that impact global biogeochemical cycles, particularly the nitrogen and sulfur cycles (Stiefel 1997; Frausto da Silva and Williams 2001). However, unlike Fe, or Mn, Mo is not widely used as a terminal electron receptor or donor in microbial respiration. This is probably the result of the low reduction potentials of the Mo oxidation states compared to other metals (Frausto da Silva and Williams 2001) (Fig. 5); the fact that multiple Mo oxidation states can be accessed over a narrow range of voltages makes Mo relatively "redox labile" at low environmental Eh, but also means that the energy gain from Mo redox transformations is small compared to many other elements.

At the same time, this redox lability makes Mo well suited as a cofactor in enzymes that catalyze redox reactions. An example is the prominence of Mo in nitrogen fixation. This prokaryotic metabolism, the dominant pathway for conversion of atmospheric $N_2$ to biologically-useful $NH_3$, utilizes Mo (along with Fe) in the active site of the nitrogenase enzyme that catalyzes $N_2$ reduction. Alternative nitrogenases that do not incorporate Mo have been identified, but are markedly less efficient (Miller and Eady 1988; Eady 1996).

The redox properties of Mo also make it useful in enzymes that catalyze reactions involving two-electron or oxygen-atom transfer (Frausto da Silva and Williams 2001). Such enzymes include nitrate reductase, sulfite oxidase, formate dehydrogenase and aldehyde oxidase (Hille 1996; Stiefel 1997; Kroneck and Abt 2002). Hence, while Mo is rarely a terminal electron
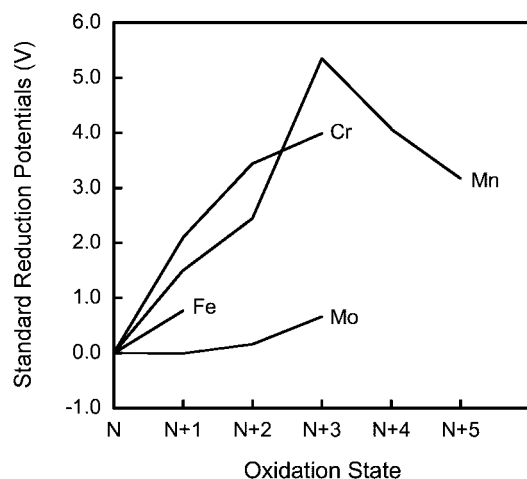


**Figure 5.** An oxidation state diagram for Mo, Cr, Fe and Mn. For Mo and Cr, N = III; for Fe and Mn, N = II. Potentials are given at standard states in acid solution relative to the hydrogen electrode. On such a diagram, the slope between any two points equals the redox potential. In contrast to most other metals, multiple Mo oxidation states are accessible over a small range of potentials. Note also that Mo is oxidized to Mo(VI) at relatively low potential (similar to Fe(III)). Figure modified after Frausto da Silva and Williams (2001).

acceptor or donor, it does have a role in respiratory metabolism by microorganisms that reduce nitrate or oxidize reduced forms of sulfur to sulfate.

Mo use is not confined to prokaryotes; similar enzymes are also found in eukaryotes (including humans). Mo deficiency is rare, as are disorders of Mo metabolism, but symptoms may be induced if diets are rich in Cu or W, which are Mo antagonists. The direct toxicity of Mo is low, but Mo is an antagonist for Cu in cattle, where thiomolybdates formed in the rumen act as high-affinity ligands for Cu. Hence intake of foods high in Mo can induce the disease molybdenosis (Mills and Davis 1987).

It is intriguing that Mo is an important element in biology despite its scarcity at the Earth's surface—indeed, no element of similar scarcity is so biochemically ubiquitous. The reason for this paradoxical combination is unknown. Possible explanations include the unique chemical character of this element, evolutionary adaptation to the abundance of Mo in oxygenated oceans relative to other transition metals, a legacy of prebiotic chemical evolution in Mo-rich environments (e.g., in association with sulfide minerals), or some combination of these factors. Regardless, this paradox has inspired creative hypotheses about the importance of Mo in evolution (Crick and Orgel 1973; Anbar and Knoll 2002).

### Isotopic expectations

From such chemical and biological considerations it is apparent *a priori* that Mo stable isotope studies could provide novel biogeochemical insights if natural Mo isotope variations are measurable. Measurable isotope variations are seen for Se and Cr (reviewed in Johnson et al. 2004), other elements with Mo-like oxyanion-dominated environmental chemistry. Mo isotope variations might provide information on ancient ocean redox conditions (Barling et al. 2001; Siebert et al. 2003), or on changes in the availability of this bioessential element (particularly in response to changing redox conditions (e.g., Anbar and Knoll 2002)). Mo isotopes could also provide insights into Mo biochemistry (Williams and Frausto da Silva 2002), an issue of non-trivial importance.

As discussed at length in this review, Mo isotope variations are now known to be pervasive. This finding was not unexpected. First, the Mo isotope system spans a mass range of ~8% (Fig. 1), which compares favorably with many other stable isotope systems. Second, the dynamic redox chemistry of Mo, and the fact that Mo-ligand interactions have strong covalent character, lends itself to chemical isotope effects. Finally, with seven stable isotopes of relative abundance ~10–25%, high-precision Mo isotope analyses are analytically tractable.

Less expected, initial Mo isotope variations in ocean sediments (and seawater) are proving to be quite systematic and, at least to a first approximation, interpretable in terms of a limited number of fractionation processes. This situation presumably reflects the relatively straightforward ocean geochemical cycle of Mo and its long ocean residence time. In addition, it is probably important that Mo is fundamentally a catalyst in respiration rather than a reductant or oxidant, so that Mo isotope systematics are not strongly complicated by isotope effects associated with microbial respiration. Regardless, early observations already point to important geoscience applications for this emerging non-traditional isotope system.

## ANALYTICAL CONSIDERATIONS

### Data reporting conventions

The stable isotopes of Mo include $^{92}$Mo, $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo and $^{100}$Mo (Fig. 1) (with a half life of $10^{19}$ yr, $^{100}$Mo is effectively stable). Because of this large number of stable isotopes, the Mo isotope analyst is presented with a number of options in both analysis and data reporting. It is common to analyze the relative abundances of as many isotopes as

possible to confirm that observed variations are, indeed, mass dependent. Such confirmation is particularly important because of potential polyatomic interferences at masses 95 and 96 from $^{40}Ar^{55}Mn^+$ and $^{40}Ar^{56}Fe^+$ in ICP-MS if residual Mn or Fe are present after Mo preconcentration (an occasional problem given the high abundances of Mn and Fe relative to Mo in many geological samples). Isobaric interferences from Zr are also a potential problem in many geological samples, and particularly when using Zr as an "element spike" (see below). Interferences from Ru are less problematic in natural samples because of low abundance. However, these interferences can be corrected to high degree of accuracy (Anbar et al. 2001).

Reporting conventions vary. Some workers report variations as $\delta^{97/95}Mo$ ($= [(^{97}Mo/^{95}Mo)_{sample}/(^{97}Mo/^{95}Mo)_{standard} - 1] \times 1000$) because $^{97}Mo$ and $^{95}Mo$ are the only Mo isotopes completely free of isobaric interferences from other elements (Anbar et al. 2001; Barling et al. 2001). Because $^{97}Mo$ is used by Siebert et al. (2001) in their isotope double spike procedure (see below), this group reports $\delta^{98/95}Mo$ ($= [(^{98}Mo/^{95}Mo)_{sample}/(^{98}Mo/^{95}Mo)_{standard} - 1] \times 1000$) in their publications (Siebert et al. 2001; McManus et al. 2002; Siebert et al. 2003). These conventions are related by $\delta^{97/95}Mo \sim 2/3 \times \delta^{98/95}Mo$ (although this relationship is not exact for all fractionation laws, e.g., Criss 1999, Young et al. 2001). Data are presented here as $\delta^{97/95}Mo$.

There is no internationally-certified Mo isotope standard. Various groups have used different working laboratory standards. Data are reported here relative to the Rochester JMC standard (Barling et al. 2001), a laboratory standard which seems similar to average crustal Mo and therefore is a convenient reference point. Rochester JMC Mo is also similar to the JMC Mo standard used by Siebert et al. 2003 in reporting their data, based on cross-comparison of $\delta^{97/95}Mo$ of similar samples measured by both groups. As proposed by Siebert et al. (2003), data from different groups can also be compared with reference to the mean Mo isotope composition of seawater ("mean ocean Mo," a.k.a. MOMO; see below for discussion of uniformity of MOMO). However, MOMO is not a practical standard because the need for significant preconcentration of Mo from seawater creates a risk of contamination during sample handling or chromatographic isotope fractionation, because $\delta^{97/95}Mo$ of seawater is isotopically heavier than most other materials (see below), and because it is possible that measurable $\delta^{97/95}Mo$ variations in the oceans remain to be discovered. Certification of a international reference standard for inter-lab comparison should be a high priority for the Mo stable isotope community.

**Historical perspective**

Efforts to measure Mo isotope variations, using thermal ionization mass spectrometry (TIMS), can be traced back to the early 1960s. Early studies were provocative: Murthy (1962; 1963) reported that the Mo isotope composition in some iron meteorites deviated from that of others, and from terrestrial Mo, by ~10 ‰/amu, while Crouch and Tuplin (1964) reported mass dependent variations and mass independent isotopic anomalies among terrestrial molybdenites. As discussed below, Wetherill (1964) subsequently demonstrated isotopic uniformity among iron meteorites to better than 1 ‰/amu. It is likely that earlier reports were affected by analytical artifacts due to inadequate correction of Mo isotope fractionation during analysis.

Although TIMS-based studies of Mo isotopic composition continued (Turnlund et al. 1993; Lu and Masuda 1994; Dauphas et al. 2002a,b; Yin et al. 2002), little attention was given to the possibility of mass-dependent variations until the advent of multiple-collector inductively coupled plasma mass spectrometery (MC-ICP-MS) in the mid 1990s. MC-ICP-MS is generally preferred over TIMS for Mo isotope studies because of the high ionization efficiency of Mo in the ICP source (permitting sample sizes <1 μg), the elimination of blank contamination from Mo in TIMS filaments, and more rapid sample throughput (Halliday et

al. 1995; Lee and Halliday 1995). As discussed below, MC-ICP-MS also offers more than one approach to correct for analytical mass fractionation to extremely high precision.

## Chemical separations

Preconcentration of Mo is necessary from most natural samples, in which typical Mo abundances ranges from 1 ppm (e.g., average crust) to ~100 ppm (e.g., black shales and marine ferromanganese crusts and nodules). The major exception is the Mo-bearing mineral molybdenite ($MoS_2$) which can be found in hydrothermal deposits and igneous rocks. Purification is also essential for most natural samples (again, molybdenite is the major exception). Removal of Fe and Mn is particularly critical to minimize formation of their argides which potentially generate significant interferences at masses 94–97.

Both preconcentration and purification are accomplished with traditional ion exchange chromatographic methods. More than one procedure has been used—the interested reader is referred to relevant publications for analytical details (Barling et al. 2001, Siebert et al. 2001).

A key finding is that Mo isotopes can be fractionated during elution in at least some ion exchange systems (Anbar et al. 2001; Siebert et al. 2001), similar to observations of Ca, Cu and Fe isotope effects (Russell and Papanastassiou 1978; Maréchal et al. 1999; Anbar et al. 2000). Therefore, it is often necessary to ensure that yields through these chemical processes are essentially quantitative.

## Analytical mass fractionation

The major analytical complication in Mo isotope analysis is precise correction for isotope fractionation during Mo purification and mass spectrometric analysis. This subject is reviewed in general by Albarède and Beard (2004), and is discussed here in particular reference to Mo. It is important to recognize that this challenge is fundamentally different in mass dependent stable isotope studies as compared to investigations of mass-independent Mo isotope variations produced by nucleosynthesis. The latter have received attention in recent years for high-precision determination of Mo isotope composition (e.g., Dauphas et al. 2002a,b; Yin et al. 2002), but are not relevant here.

***Sample-standard bracketing.*** In the earliest Mo isotope studies (Murthy 1962; Murthy 1963; Crouch and Tulpin 1964), analytical mass fractionation was assumed to be identical for samples and standards even when analyzed separately. However, in TIMS this assumption is risky because the isotopic composition of an analyte changes continuously during analysis, a result of isotope enrichment during thermal evaporation and ionization (a problem acknowledged by Murthy). The time-course of this fractionation is highly sensitive to sample purity and operating conditions.

Sample-standard comparison is more applicable in MC-ICP-MS, in which instrument mass fractionation is fundamentally a "steady state" phenomenon (Maréchal et al. 1999). This method has been used successfully for some non-traditional stable isotopes, particularly involving Fe, in which analyses of samples are bracketed by standards to cope with systematic instrumental drift (e.g., Zhu et al. 2002; Beard et al. 2003). However, other methods have been used for Mo stable isotope work published to date because of concerns about non-systematic changes in instrument mass fractionation, particularly arising from differences in matrices, between samples and standards. Such concerns are more acute for Mo than for Fe and many other elements because Mo is a trace constituent of most samples, increasing the challenge of rigorous, high-yield sample purification.

***Element spike.*** An additional benefit of MC-ICP-MS is the ability to use an "element spike" approach. In this method, the isotopic composition of a different element, added to the sample, is to monitor variations in instrument mass fractionation (Longerich et al. 1987; Maréchal et al. 1999). This method is possible with MC-ICP-MS because the relative

fractionation behavior of different elements in ICP sources is more-or-less constant, although it is critical to note that the data reduction must account for the fact that the absolute fractionation behavior of each element may be different (Maréchal et al. 1999; Anbar et al. 2001).

The first modern observations of Mo isotope fractionations in geological materials were made using this method (Barling et al. 2001), employing Zr and Ru spikes with on-line correction for isobaric interferences from these spikes (Anbar et al. 2001). Precision of ±0.25‰ was reported in measurement of $\delta^{97/95}$Mo, with comparable results for other ratios.

***Isotopic double spike.*** The most rigorous approach is to use an isotopic "double spike", in which samples are doped with a known quantity of "spike" Mo which consists of two isotopes in a known ratio (Wetherill 1964; Siebert et al. 2001). These spike isotopes serve as an internal standard to monitor mass fractionation of the sample subsequent to spiking. The fundamental advantage over the element spike is that the spike isotopes follow exactly the same fractionation behavior as the isotopes of interest. A disadvantage is the need to carefully prepare and calibrate the double spike.

Mo is particularly suitable for double spike analysis because it has a large number of stable isotopes. It is not surprising, therefore, that Wetherill (1964) used this approach to demonstrate isotopic homogeneity between terrestrial and meteorite Mo samples, employing a $^{95}$Mo-$^{98}$Mo spike and TIMS. This study was one of the earliest applications of the double spike method.

In a more recent TIMS Mo isotope double spike study using a multiple collector system, Wieser and de Laeter (Wieser and DeLaeter 2003) reported precision of better than ±0.1 ‰/ amu mass difference (±2σ) using a $^{94}$Mo-$^{100}$Mo spike.

The utility of the double spike is not limited to TIMS. The method has also been applied very successfully in MC-ICP-MS (Siebert et al. 2001). Using a $^{97}$Mo-$^{100}$Mo spike, precision of ±0.1‰ (±2σ) was reported in measurement of $\delta^{98/95}$Mo, and has been applied to a range of natural materials (McManus et al. 2002; Siebert et al. 2003).

***Methods compared.*** Looking to the future, when working with geological samples the double spike has an important practical advantage over both the sample-standard bracketing and the element spike methods. It can obviate the need for high yield chemistry if the spike isotopes are added prior to Mo purification and extraction, thereby providing an internal reference point for isotope fractionation produced by the instrument as well as by the separation chemistry. This advantage is important because it is difficult in practice to design Mo chemical separation schemes that achieve both high yield and high purity for a wide range of sample types.

In terms of the existing database, the element spike and isotope double spike methods have both been used successfully for Mo isotope surveys in nature (Barling et al. 2001; Siebert et al. 2003). The reason for the lower precision of the element spike data (±2σ of ±0.25‰ vs. ±0.1‰) is unclear. This difference may reflect inherent limitations of the element spike technique, performance differences among MC-ICP-MS instruments of differing designs, or matrix complications from sample impurities residual from the higher yield chemistry used in initial Mo isotope element spike research. However, within these uncertainties, $\delta^{97/95}$Mo (or $\delta^{98/95}$Mo) offsets observed between similar sample types using both methods are statistically indistinguishable (Barling et al. 2001; Siebert et al. 2003; see next section).

## OBSERVATIONS

Examinations of Mo isotope variations in nature include the initial reconnaissance of Barling et al. (2001), the more comprehensive survey of Siebert et al. (2003), and some more

focused studies of specific sample types (McManus et al. 2002; Wieser and DeLaeter 2003; Arnold et al. 2004). These studies emphasized reservoirs, sources and sinks important to the Mo ocean geochemical cycle, including igneous rocks, ferromanganese oxide sediments, euxinic sediments, suboxic sediments and seawater. Laboratory studies have emphasized associated fractionation mechanisms.

The findings are summarized below, and in Figures 6, 7 and 8. Complete references are provided in the text and in the figure captions. Implications of these data for understanding Mo geochemical cycling, and for application of this understanding to paleoredox questions, are discussed in the subsequent section.

### Igneous rocks

*Granites and basalts.* Mo isotope data from igneous rocks are sparse but revealing (Siebert et al. 2003). A number of basalts and granites have $\delta^{97/95}$Mo close to 0‰ (relative to the Rochester JMC standard). Although the basalts are all subduction volcanics from Kamchatka, and hence from a single, geographically coherent suite, the granite samples are
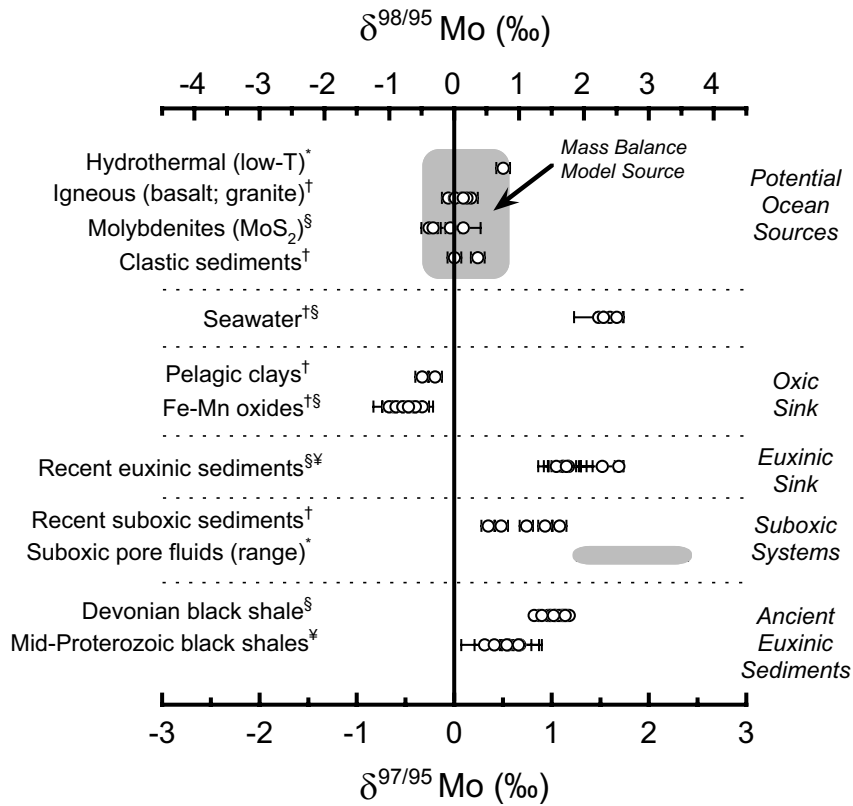


**Figure 6.** Summary of existing Mo isotope data from natural samples. Isotopic composition of ocean source is based on mass balance (see text). Data are presented as $\delta^{97/95}$Mo and $\delta^{98/95}$Mo relative to the Rochester JMC standard ($\delta^{97/95}$Mo ~2/3 × $\delta^{98/95}$Mo). References: (*) McManus et al. 2002; (†) Siebert et al. 2003; (§) Barling et al. 2001; (¥) Arnold et al. 2004. Molybdenite values of Wieser and DeLaeter (2003) are omitted because of standard normalization problems (see text). Data obtained by different research groups using different standards are cross-calibrated by comparing seawater δ values.

Archean and Himalayan (Tertiary). The coherence of these samples suggests that Mo isotope fractionation during igneous processing is small compared to current analytical limits (Siebert et al. 2003).

***Molybdenites.*** Detectable Mo isotope variation is seen in molybdenites from hydrothermal ore deposits (Barling et al. 2001; Wieser and DeLaeter 2003). Unfortunately, the results of Wieser and DeLaeter (2003) cannot be directly compared to those of Barling et al. (2001) because no common materials were analyzed. However, if it is assumed that the JMC Mo standard of Wieser and DeLaeter (2003) is identical to other JMC Mo standards (Barling et al. 2001; Siebert et al. 2003), then the total range of $\delta^{97/95}$Mo is nearly 1‰. It is plausible that the variations among these samples are somewhat larger than among granites and basalts because formation temperatures for hydrothermal molybdenites are 350–600°C, substantially cooler than silicate melting temperatures (Wieser and DeLaeter 2003). Additionally, hydrothermal molybdenites commonly occur in veins, raising the possibility of Rayleigh effects during progressive precipitation of $MoS_2$ from migrating fluids. Such effects could amplify variations relative to expectations from single-stage fractionation factors. Consistent with this scenario, the molybdenite $\delta^{97/95}$Mo overlap those of granites and basalts.

## Marine sediments

***Ferromanganese oxides.*** An extensive Mo isotope dataset is now available for ferromanganese crusts and nodules, which are enriched in Mo and hence are logical targets for early isotopic investigations (Barling et al. 2001; Siebert et al. 2003). These include nodules from the Pacific and Atlantic Oceans, and crusts from the Pacific, Atlantic and Indian Oceans. Nodule data are of bulk samples, but Pacific and Atlantic crust data are time-resolved at ~1–3 million year intervals from the present back to 60 million years ago.

This dataset has three striking features. First, the Mo isotope composition of all these samples is remarkably uniform. Overall, Mo in these sediments varies within a range of ±<0.25‰. This uniformity includes the 60 million year records in the two crusts. Non-systematic variations in Mo concentration through these crusts and comparison with U diffusion models suggest that this uniformity is not the result of diffusional homogenization of an originally variable isotope signal (Siebert et al. 2003). Second, there is no significant offset between the isotopic compositions of crusts and nodules despite the greatly different accumulation rates of these sediment types. Third, the mean isotopic composition of these samples is offset from $\delta^{97/95}$Mo of igneous rocks by approximately −0.5‰.

The only significant $\delta^{97/95}$Mo variation in these samples is a small offset of ~0.15‰ seen between Pacific and Atlantic crusts, just outside the ±2σ uncertainties of Siebert et al. (2003). A similar offset is seen in nodule data, although well within the analytical uncertainties of Barling et al. (2001). Such offsets seem unlikely to reflect variations in $\delta^{97/95}$Mo in seawater in view of the long ocean residence time and relatively invariant seawater concentrations of Mo. Systematic differences in sediment composition may play a role (Barling and Anbar 2004).

***Euxinic sediments.*** The Black Sea and the Cariaco Basin are both euxinic basins in which the sediment-water interface is overlain by anoxic, $H_2S$-bearing waters. The Black Sea is the classic "type euxinic" basin: At depths exceeding ~100 m, [$H_2S$] exceeds 100 μM. Mo concentrations fall sharply at these depths (Emerson and Huested 1991), and underlying sediments are enriched in Mo by 10–100 fold over average crust.

The most significant Mo isotope feature in these settings is their $\delta^{97/95}$Mo enrichment (Barling et al. 2001; Arnold et al. 2004): in Holocene, organic-rich sediments from both basins, $\delta^{97/95}$Mo is >1‰ heavier than in igneous rocks, molybdenites or ferromanganese sediments. Black Sea Unit I samples are more enriched in heavy isotopes than any other rocks analyzed to date.

Uniformity among these euxinic sediments is not as tight as in the case of ferromanganese crusts and nodules. For example. some variability is seen between Unit I and Unit II of the Black Sea, with Unit I enriched in $^{97}Mo/^{95}Mo$ by ~0.4‰. $\delta^{97/95}Mo$ in ~14,000 year old sediments from the Cariaco basin, which is second only to the Black Sea in its extent of modern anoxic-sulfidic water-column conditions, are comparable to Black Sea Unit II.

*Suboxic sediments.* Siebert et al. (2003) analyzed Mo isotopes in a limited number of samples from marine sediments accumulating under a range of water column conditions best described as "suboxic" or "dysoxic" (e.g., $O_2 < 5$ μmol kg$^{-1}$). Mo concentrations in these sediments are enriched over average crust by a factor of ~3–100, in some cases exceeding enrichments seen in Black Sea sediments (e.g., Chile Margin sediments). Isotopically, $\delta^{97/95}Mo$ in these sediments covers a large range, essentially filling the gap between igneous rocks and euxinic sediments. A rough correlation is suggested between Mo concentration and $\delta^{97/95}Mo$.

*Clastic and pelagic sediments.* Only a handful of clastic and pelagic samples have been analyzed for $\delta^{97/95}Mo$ (Siebert et al. 2003). Clastic sediments (two samples) are indistinguishable from igneous rocks in their Mo isotope compositions. Pelagic clays (two samples) show enrichment in Mo (3.4 and 185 ppm), and also a shift toward lighter $\delta^{97/95}Mo$ similar to ferromanganese sediments.

## Waters

*Seawater.* A half dozen analyses of Mo isotopes in the Pacific, Atlantic and Indian oceans, covering depths to ~3000 m (Barling et al. 2001, Siebert et al. 2003), reveal two important facts. First, there is no detectable $\delta^{97/95}Mo$ variation in the oceans with location or depth. Second, $\delta^{97/95}Mo$ in the oceans is similar to the heaviest of euxinic sediments, and is heavier than in igneous rocks or ferromanganese sediments by ~1.5‰ and ~2‰, respectively. A uniform isotopic composition in the oceans is consistent with the $10^5$–$10^6$ year ocean residence time. The explanation for the heavy isotopic composition is discussed further below.

*Low temperature hydrothermal fluids.* Warm fluids emerging from hydrothermal systems on the flanks of mid ocean ridges have recently emerged as a net source of Mo and other elements to the oceans (Wheat and Mottl 2000). Mo isotopes have recently been investigated (McManus et al. 2002). These fluids are found to be isotopically lighter than seawater, but heavier than igneous rocks. Mixing relationships point to an endmember hydrothermal fluid with $\delta^{97/95}Mo$ ~0.5‰.

*Suboxic porewaters.* As described above, $\delta^{97/95}Mo$ in suboxic sediments is intermediate between igneous rocks and euxinic sediments (and seawater). McManus et al. (2002) examined $\delta^{97/95}Mo$ in sediment porewaters from the Santa Monica basin (Fig. 7), a well-studied suboxic setting ($O_2 < 5$ μmol kg$^{-1}$). The upper ~25 cm were analyzed. Fe and Mn remobilization is seen in these fluids in association with a down-core redox gradient. $\delta^{97/95}Mo$ immediately below the sediment water interface is ~0.25‰ lighter than seawater, potentially reflecting release of light Mo associated with Mn oxides; elevated Mn and Mo concentrations are seen in fluids at these depths. The concentration of Mo is progressively depleted at depths >5 cm. In conjunction with this depletion, $\delta^{97/95}Mo$ is progressively $^{97}Mo$-enriched, ultimately reaching a value heavier than seawater by nearly 1‰—the heaviest Mo isotopic composition measured to date.

## Laboratory experiments

*Adsorption to Mn oxides.* The only thorough experimental study of Mo isotope fractionation to date focused on adsorption to Mn oxides (Barling and Anbar 2004). The intent of this study was to examine the possibility that Mo isotopes are fractionated during this process. In these experiments, Mo dissolved in aqueous solution of defined ionic strength at room temperature was exposed to synthetic δ-$MnO_2$. pH (6.5–8.5) and solution-solid contact
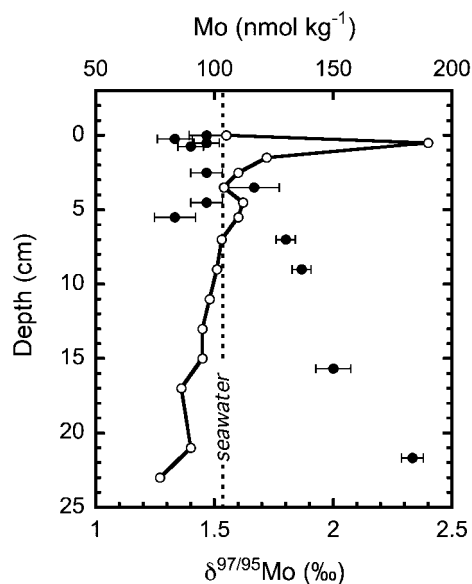
**Figure 7.** Mo concentrations ($\circ$) and isotopic compositions ($\bullet$) from reducing pore fluids in Santa Monica Basin (McManus et al. 2002). Dotted line indicates seawater values for both variables. The data can be fit by a 1-D reaction-diffusion model with a fractionation factor of ~1.005. The effective fractionation factor for Mo removal across the sediment-water interface is smaller, <1.0025 (see text).

time (2–96 hr) were varied so that the extent of total Mo adsorbed ranged from ~40% to >95% in the various experiments. Mo was extracted both from solutions and from Mn oxides for $\delta^{97/95}$Mo determination.

The major isotopic findings are summarized in Figure 8. A mean $\delta^{97/95}$Mo offset of ~1.8‰ was observed between dissolved and oxide-bound Mo in all experiments. The data do not fit the expectations of a Rayleigh model, as might be expected from irreversible adsorption. Instead, the data closely approximate closed system exchange between adsorbed and dissolved Mo, suggesting that Mo isotope fractionation in this system is an equilibrium process.

***Leaching.*** Mo isotope fractionation has also been investigated during mild HCl dissolution of one granite sample (Siebert et al. 2003). The goal of this experiment was to provide a crude indication of Mo isotope fractionation during rock weathering. After transfer of >50% of Mo to solution, no significant fractionation was detected between solution and the granite starting material.

## INTERPRETATIONS

Some of the above observations are particularly striking and provide a focus for efforts to interpret the Mo ocean isotope system. These observations include:

a.   The $\delta^{97/95}$Mo uniformity of the oceans

b.   The ~2‰ $\delta^{97/95}$Mo offset between seawater and ferromanganese oxide sediments, and the uniformity of $\delta^{97/95}$Mo in these sediments

c.   The 1.5–2.0‰ offset between $\delta^{97/95}$Mo in ferromanganese oxides and in euxinic sediments (and hence the similarity of $\delta^{97/95}$Mo in euxinic sediments and seawater).

d.   The apparent ~1.5‰ $\delta^{97/95}$Mo offset between seawater and igneous rocks.

Interpretations of these observations are discussed below.

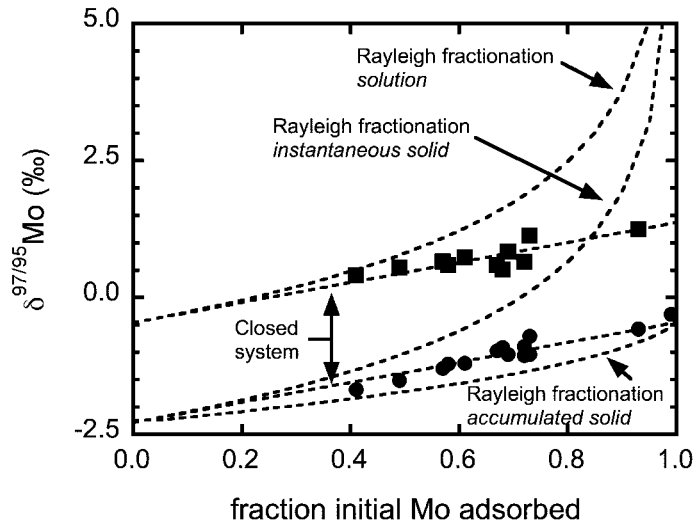**Figure 8.** Results of Mo adsorption experiments of Barling and Anbar (2004). Mo-bearing solutions were exposed to synthetic Mn oxides ($\delta$-MnO$_2$) for 2–96 hours at pH 6.5–8.5. Residual Mo in solution (■) was measured for all experiments. Mo adsorbed to oxide particle surfaces (●) was either measured or inferred from mass balance. Dissolved Mo was systematically heavier than adsorbed Mo with a fractionation factor of 1.0018 ± 0.0005. The data are consistent with closed system equilibrium, in which isotopes exchange continuously between surface and solution, but incompatible with an irreversible, Rayleigh-type process. Figure modified after Barling and Anbar (2004).

## Mo isotope fractionation in the oceans

The uniform isotopic composition of dissolved Mo in the oceans is readily understood in terms of the $10^5$–$10^6$ year Mo ocean residence time. For example, given an ocean mixing time of ~$10^3$ years, and assuming that the $\delta^{97/95}$Mo contrast of different Mo isotope sources is <5‰ (consistent with the range of values measured to date), Mo isotope variations between ocean basins or with depth should be <5‰/($10^5$/$10^3$) = 0.05‰. Such variations are smaller than present analytical uncertainties.

But why is $\delta^{97/95}$Mo of seawater ~1.5‰ heavier than igneous rocks and ~2‰ heavier than Mo in ferromanganese sediments? A number of ideas related to Mo inputs can be quickly deemed unlikely, if not altogether ruled out. An obvious possibility is Mo isotope fractionation during weathering, because Mo probably enters the oceans largely via rivers. However, evidence from leaching experiments suggests weathering imparts a relatively minor isotopic effect (Siebert et al. 2003), and it seems likely that, because of the efficient transfer of Mo from minerals to solution during oxic weathering, mass balance would minimize the influence of any such effect on riverine Mo. Input of heavy Mo from hydrothermal sources cannot be completely eliminated as an alternative hypothesis, given the limited available data, but there is no indication that such sources are of sufficient volumetric importance, or sufficiently heavy in terms of $^{97}$Mo/$^{95}$Mo, to be the answer. Ancient euxinic sediments (e.g., Paleozoic black shales) clearly constitute a reservoir with appropriate isotopic composition, and the weathering of such sediments when they are exhumed on land or exposed to oxidizing conditions on the seafloor is probably not a trivial source of Mo to the oceans. However, Mo in such sediments is, itself, derived from ancient ocean Mo. Hence, such an Mo input cannot be the *primary* cause of heavy Mo isotope enrichment in the oceans.

It seems much more likely that Mo isotopes are fractionated within the ocean system during removal from seawater, as first proposed by Barling et al. (2001). This possibility is considered below with respect to Mo removal to ferromanganese oxides, euxinic sediments and suboxic sediments.

***Ferromanganese oxides.*** The ~2‰ $\delta^{97/95}$Mo offset between Mo associated with ferromanganese sediments and Mo in seawater is by far the largest Mo isotope variation observed to date. This offset is remarkably systematic, as documented above (Barling et al. 2001; Siebert et al. 2003). Combined with knowledge that Mo and Mn concentrations correlate in such sediments, these observations strongly suggest that there is a large, systematic fractionation of Mo isotopes, favoring removal of light isotopes from solution, when Mo is authigenically enriched in association with Mn oxides (Barling et al. 2001; Siebert et al. 2003).

The simplest hypothesis consistent with such observations is an equilibrium Mo isotope fractionation during adsorption of Mo onto the surfaces of Mn oxide particles (Barling et al. 2001; Siebert et al. 2003). Although the enrichment of light isotopes in Mn oxides is suggestive of a kinetic isotope effect (Barling et al. 2001), the similarity of $\delta^{97/95}$Mo in crusts, nodules and pelagic clays from different ocean basins indicates that this fractionation is largely independent of sedimentation rate. While not ruling out a kinetic effect, an equilibrium effect seems more likely. Recent examination of this fractionation in the laboratory supports this hypothesis (Barling and Anbar 2004).

Based on the $\delta^{97/95}$Mo offset between seawater and such sediments, a fractionation factor, $\alpha_{sw-MnO_x}$, of ~1.002 is inferred ($\delta^{97/95}$Mo$_a$ − $\delta^{97/95}$Mo$_b$ = $\Delta^{97/95}$Mo$_{a-b}$ ~ 1000 × ln($\alpha_{a-b}$)). This value is indistinguishable from $\alpha_{dissolved-adsorbed}$ = 1.0018 ± 0.0005 determined experimentally (Barling and Anbar 2004). Therefore, isotope fractionation during Mo adsorption is fully capable of creating the offset in $\delta^{97/95}$Mo between ferromanganese sediments and seawater.

The fractionation mechanism is not entirely clear. $MoO_4^{2-}$ may adsorb directly to Mn-oxide surfaces by an inner-sphere mechanism in which Mn–O–Mo bonds are formed (Barling and Anbar 2004):

$$\equiv MnOH + MoO_4^{2-} + 2H^+ \leftrightarrow \equiv MnHMoO_4 + H_2O$$
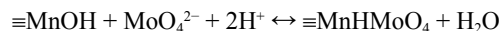
If so, equilibrium isotope exchange of the following sort is possible between dissolved and adsorbed species:

$$^{97}MoO_4^{2-} + \equiv MnH^{95}MoO_4 \leftrightarrow {}^{95}MoO_4^{2-} + \equiv MnH^{97}MoO_4$$
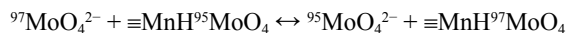
Alternatively, Siebert et al. (2003) proposed that adsorption may proceed via a minor species such as $Mo(OH)_6$. If so, then fractionation could be driven by the following exchange, in solution:

$$^{97}MoO_4^{2-} + {}^{95}Mo(OH)_6 \leftrightarrow {}^{95}MoO_4^{2-} + {}^{97}Mo(OH)_6$$
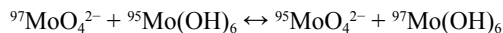
The coordination geometries of $MoO_4^{2-}$ and $Mo(OH)_6$ are tetrahedral and octahedral, respectively. Such differences may drive isotope fractionation (Anbar et al. 2000; Roe et al. 2003). While seawater speciation of Mo is dominated by $MoO_4^{2-}$, trace intermediates like $Mo(OH)_6$ may still play a role in isotope fractionation if they adsorb because, at equilibrium, the overall fractionation factor for $MoO_4^{2-} \leftrightarrow$ Mo-surface necessarily equals the product of the fractionation factors for $MoO_4^{2-} \leftrightarrow Mo(OH)_6$ and $Mo(OH)_6 \leftrightarrow$ Mo-surface regardless of the concentrations of the three species.

Mo adsorption chemistry offers few clues as to which mechanism is operative. Mo adsorption is found to increase at decreasing pH (Chan and Riley 1966; Barling and Anbar 2004). As pH decreases, oxide surfaces become positively charged, facilitating adsorption

of anions like $MoO_4^{2-}$ (Dzombak and Morel 1990; Stumm and Morgan 1996). However, $Mo(OH)_6$ becomes increasingly important at pH<5 due to protonation of oxygen atoms and a change from tetrahedral to octahedral coordination via the following reactions (Aveston et al. 1964; Busey and Keller 1964; Cruywagen and Rohwer 1975; Mitchell 1999):

$$MoO_4^{2-} + H^+ \leftrightarrow HMoO_4^-$$

$$HMoO_4^- + H^+ + 2H_2O \leftrightarrow Mo(OH)_6$$
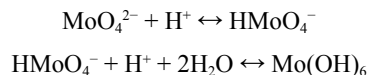
Therefore, the observed pH dependence of Mo adsorption is consistent with either mechanism.

Regardless of mechanism, it is likely that this isotope effect contributes substantially to the $\delta^{97/95}Mo$ offset between igneous rocks and seawater because of the importance of ferromanganese sediments for the ocean Mo budget. This possibility is discussed further below. This hypothesis is supported by the similarity of $\delta^{97/95}Mo$ in Mo-rich pelagic clays and ferromanganese sediments. It is likely that the Mo enrichment in these clays results from adsorption to authigenic Mn oxides. Further study of Mo isotopes in pelagic sediments is needed to validate this hypothesis.

***Euxinic sediments.*** The similarity of $\delta^{97/95}Mo$ in sediments accumulating in euxinic basins and seawater, to within <0.5‰, suggests that net fractionation when Mo is removed from the water column in strongly reducing depositional settings is small in comparison to the ~2‰ effect during uptake by Mn oxides. This observation may be a consequence of mass balance: Mo removal from aqueous systems when $[H_2S] > 100$ μM is nearly quantitative (Fig. 3), and a very large fraction is removed even when $[H_2S]$ is a tenth this value (Helz et al. 1996; Erickson and Helz 2000; Zheng et al. 2000a).

Evidence for this hypothesis can be found in the rough correlation between $\delta^{97/95}Mo$ and [Mo] in suboxic sediments (Siebert et al. 2003): Higher [Mo] is associated with $\delta^{97/95}Mo$ approaching the seawater value, as expected from mass balance in a closed reservoir (the reservoir is the diffusive zone beneath the sediment-water interface in suboxic settings; see following section).

Importantly, this hypothesis does not exclude the possibility of large equilibrium Mo isotope effects between equilibrating species in reducing systems or large kinetic isotope effects during unidirectional or incomplete reactions. The controlling factor on the magnitude of fractionation between sediments and dissolved Mo is *not* the existence or absence of such specific isotope effects, but rather the mass balance constraints in the water column or sediment pore waters. Indeed, specific isotope effects seem likely because speciation and redox transformations of the sort that occur in these settings commonly drive isotope fractionation. For example, equilibrium or kinetic isotope effects might well occur between $MoO_4^{2-}$ and $MoO_{4-x}S_x^{2-}$ because of the substantial differences in Mo bonding environments between such complexes.

The small offsets between sediments from Black Sea Unit I and from Black Sea Unit II and the Cariaco Basin and seawater may provide a hint that removal is not necessarily quantitative even in $H_2S$-rich systems, or that $[H_2S]$ was not as high as generally believed during deposition of these sediments. Alternatively, these offsets could reflect regional or basin-scale reservoir effects linked to riverine Mo fluxes (Arnold et al. 2004). For example, during the deposition of the analyzed Cariaco interval, glacial melt water influx to the Atlantic ocean was approximately three times greater than today's, affecting the seawater chemistry of the Gulf of Mexico (Bertine and Keene 1974; Fairbanks 1989). Similarly, during the deposition of Black Sea Unit II, sea level was lower than today and flow through the Bosphorus was more restricted (Hay 1988). Consequently, the relative importance of local riverine input was presumably greater, and $\delta^{97/95}Mo$ of the overlying water may have

deviated more from open ocean values relative to more recent intervals.

However, the most important observation regarding euxinic sediments is that $\delta^{97/95}$Mo in euxinic sediments is *not* strongly shifted from seawater, and therefore that $\delta^{97/95}$Mo in sediments accumulating at the bottom of euxinic basins is similar to that of the waters entering such basins even if there are large isotope effects during Mo removal to these sediments. Consequently, the contribution of fractionation during the removal of Mo to euxinic sediments to global-scale Mo isotope fractionation is likely to be small in comparison to the effect during removal to ferromanganese sediments (Barling et al. 2001; Siebert et al. 2003; Arnold et al. 2004).

***Suboxic systems.*** The observations of Siebert et al. (2003) and McManus et al. (2002) in suboxic sediments and porewaters, respectively, are complementary. Siebert et al. (2003) found that $\delta^{97/95}$Mo in such sediments is lighter than in seawater (Fig. 6), while McManus et al. (2002) found that $\delta^{97/95}$Mo in porewaters were heavier than in seawater (Fig. 7). These data demonstrate that light isotopes are preferentially removed from porewaters to sediments in such settings. The isotope effect is not small: using a 1-D reaction-diffusion model, McManus et al. (2002) determined $\alpha \sim 1.005$ (reported here on a $^{97}$Mo/$^{95}$Mo basis), and hence is larger than that occurring during adsorption to Mn oxides.

The mechanism of Mo removal in suboxic systems is unclear, and so the fundamental nature of this fractionation requires further study. However, the effect may be understood in terms of a two layer diffusion-reaction model in which a reaction zone in the sediment (where Mo is chemically removed) is separated from seawater by a purely diffusive zone in which there is no chemical reaction (Brandes and Devol 1997). The presence of a diffusive zone is likely because Mo removal presumably occurs in sulfidic porewaters that lie a finite distance *L* below the sediment-water interface (Wang and van Cappellen 1996; Zheng et al. 2000a). If H$_2$S is present in the reactive zone such that Mo is removed below this depth, then Mo isotope fractionation in the diffusive zone may be driven by isotope effects in the reactive zone.

An important consequence of such a model is that the effect of such sedimentary systems on the ocean Mo isotope budget is *not* represented by $\alpha$, but rather by the relative fluxes of the isotopes across the sediment-water interface. This "effective" fractionation factor, $\alpha_{eff,}$ is likely to be smaller than $\alpha$ (Bender 1990; Brandes and Devol 1997) because the diffusive zone acts as a barrier to isotope exchange with overlying waters, approximating a closed system.

These considerations can be illustrated by adapting the mathematical treatment of Brandes and Devol (1997) for O$_2$ and N$_2$ to the case of Mo (Emerson and Breckel personal communication). Following this treatment, at steady state:

$$0 = \phi D \frac{d^2[Mo]}{dz^2} \ \text{ for } z < L$$

$$0 = \phi D \frac{d^2[Mo]}{dz^2} - \phi k[Mo] \ \text{ for } z > L$$

where: [Mo] is the concentration of Mo in porewaters; $\phi$ is the porosity; $D$ is the molecular diffusion coefficient for Mo (presumably diffusing as MoO$_4^{2-}$); and $k$ is the reaction rate constant for Mo removal (a first order reaction is assumed). For present purposes, advection is discounted. These equations can be solved subject to the boundary conditions $[Mo]_{z=0} = [Mo]_{sw}$ and $[Mo]_{z=\infty} = 0$ ("sw" denotes seawater). It is also assumed that where the layers meet, at $z = L$, [Mo] and d[Mo]/d$z$ are identical in both layers. Since we are interested in isotopic fluxes ($F$) across the sediment-water interface, we apply Fick's first law and solve for d[Mo]/d$z$ at $z = 0$:

$$F_{z=0} = -\phi D \left( \frac{d[Mo]}{dz} \right)_{z=0} = \phi D [Mo]_{sw} \left( \frac{\sqrt{\dfrac{k}{D}}}{1 + L\sqrt{\dfrac{k}{D}}} \right)$$

Analogous expressions can be derived for $^{95}Mo$ and $^{97}Mo$ in terms of $^{95}k$ and $^{97}k$, where $^{97}k = \alpha^{95}k$. $D$ is assumed identical for all isotopes. The relative isotope fluxes are therefore:

$$\frac{^{97}F}{^{95}F} = \frac{[^{97}Mo]_{sw}}{[^{95}Mo]_{sw}} \sqrt{\alpha} \left( \frac{1 + L\sqrt{\dfrac{^{95}k}{D}}}{1 + L\sqrt{\dfrac{\alpha^{95}k}{D}}} \right) = R_{sw}\alpha_{eff}$$

where $\alpha = {^{97}k}/{^{95}k}$ and $R_{sw} = [^{97}Mo]_{sw}/[^{95}Mo]_{sw}$. It is apparent that if $L = 0$, $\alpha_{eff} = \sqrt{(^{97}k/^{95}k)} = \sqrt{\alpha}$ (Bender 1990). If $L$ is >0 then the effective fractionation between the sediments and the bottom water is less than $\sqrt{\alpha}$. Therefore, $\alpha_{eff} < \sqrt{(1.005)} < 1.0025$; this magnitude is comparable to the fractionation during Mo adsorption by Mn oxides ($\alpha_{sw-MnO_x}$).

Based on these considerations, the importance of fractionation in suboxic sedimentary systems for the global ocean Mo isotope budget is probably modest. This conclusion follows from the magnitude of $\alpha_{eff}$ relative to $\alpha_{sw-MnO_x}$ and the relatively modest importance of suboxic sediments as compared to Mn oxides for the global ocean Mo elemental budget (Morford and Emerson 1999; Emerson and Breckel personal communication). However, this prediction must be assessed by further studies in open ocean reducing sediments.

**Mo isotope mass balance in the oceans**

The preceding considerations point to a first order model in which Mo entering the oceans primarily from continental sources undergoes fractionation during removal to Mn oxides, resulting in an isotopically heavy reservoir of Mo dissolved in seawater. This model is somewhat analogous to the Ca isotope system (DePaolo 2004), wherein $\delta^{44/40}Ca$ of seawater is offset approximately +1.5‰ relative to riverine sources because of a fractionation during carbonate deposition. Within such a framework for Mo, euxinic and suboxic sediments are seen as having only a minor impact on the isotope budget, and Mn oxides and euxinic sediments would be seen to have complementary isotopic compositions—one light and the other heavy—relative to the input (Fig. 9).

The model depicted in Figure 9 can be tested by a simple mass balance calculation (Barling et al. 2001, Siebert et al. 2003):

$$\delta^{97/95}Mo_{input} = f_{ox} \times \delta^{97/95}Mo_{ox} + f_{eux} \times \delta^{97/95}Mo_{eux}$$

where the subscripts *input*, *ox* and *eux* denote the riverine input and oxic and euxinic sediments, respectively, and $f_{ox}$ and $f_{eux}$ denote the fraction of total Mo removed to each sediment type ($f_{ox} + f_{eux} = 1$). If the isotopic compositions presented above are representative of the major Mo sources
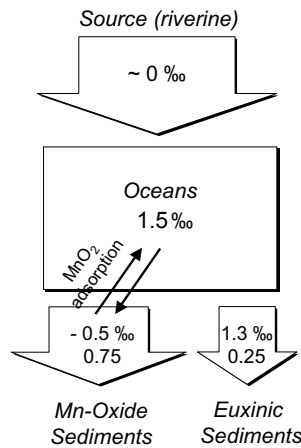
**Figure 9.** A schematic depiction of the apparent Mo isotope budget in the modern oceans, neglecting suboxic sediments. Mean isotopic values for inputs and outputs are indicated, along with the fractional importance of each sediment type for Mo removal. See text for details.

and sinks, then to a first approximation the global ocean Mo isotope budget can be expressed in terms of an input of ~0‰ and outputs to oxic and euxinic sinks with isotopic compositions of approximately −0.5‰ and 1.3‰, respectively. Using these mean values and the range of literature estimates of $f_{ox}$ and $f_{eux}$ in the modern oceans (Bertine and Turekian 1973; Emerson and Huested 1991; Morford and Emerson 1999), the predicted range of $\delta^{97/95}Mo_{input}$ matches reasonably well with measurements of Mo in igneous rocks, used here as a proxy for riverine input (Fig. 6). This agreement implies that the oxic and euxinic observations to date provide a first-order representation of Mo sources to, and sinks from, the oceans, and that the simple model in Figure 9 is a reasonable first-order description of the Mo isotope system in the oceans. Similar conclusions were reached by both Barling et al. (2001) and Siebert et al. (2003).

Conversely (Siebert et al. 2003; Arnold et al. 2004), mean $\delta^{97/95}Mo_{input}$, $\delta^{97/95}Mo_{ox}$ and $\delta^{97/95}Mo_{eux}$ data can be used to derive $f_{ox} \sim 0.75$ and $f_{eux} \sim 0.25$ (Fig. 9). These may be the best constraints to date on the relative magnitudes of these sedimentary sinks.

Nevertheless, it is important to stress that uncertainties persist in our understanding of the Mo ocean budget, particularly as regards Mo removal to suboxic sediments. The Mo isotope system may ultimately prove useful in reducing such uncertainties.

## POTENTIAL APPLICATIONS

Although understanding of Mo stable isotope systematics is still evolving, some paleoceanographic applications are already coming into focus. It is not too early to explore these applications, nor to speculate on other possibilities.

### Mo stable isotopes and global ocean paleoredox

The Mo isotope system is being developed in particular for investigations of global ocean paleoredox because of the strong redox sensitivities of the Mo elemental and isotopic budgets (Barling et al. 2001; Siebert et al. 2003; Arnold et al. 2004). Large variations in ocean oxygenation may have occurred repeatedly during Earth history. During the Pleistocene, the coupling of $p$CO$_2$, the ocean "carbon pump" and oxygen concentrations could have caused variations in ocean redox and the rate of organic carbon burial on glacial-interglacial timescales (e.g., Sarmiento and Toggweiler 1984). Globally-extensive deposits of carbonaceous shales are indicative of so-called "Ocean Anoxic Events" in the Cretaceous (e.g., Bralower et al. 1994), and similar deposits occur repeatedly in the Paleozoic (e.g., Wignall and Twitchett 1996). In the mid-Proterozoic, sulfur isotopes and other data are taken to indicate widespread anoxia or euxinia under the low $p$O$_2$ atmosphere of the period (Canfield 1998). This condition may have persisted for hundreds of millions of years, with evolutionary consequences (Anbar and Knoll 2002). The Archean oceans are generally believed to have been essentially anoxic, albeit not euxinic (Holland 1984).

There are many established or exploratory sedimentary paleoredox proxies, such as sedimentary iron chemistry (Canfield et al. 1996; Raiswell and Canfield 1998), S isotopes (e.g., Lyons 1997) and various elemental ratios (e.g., Algeo and Maynard 2003; Calvert et al. 2001; Crusius et al. 1996; Dean et al. 1997; Dean et al. 1999; Lyons et al. 2003; Sageman et al. 2003; Werne et al. 2002; Yarincik et al. 2000; Zheng et al. 2000b). However, these proxies provide information only about oxygenation of the *local* overlying water column. As outlined below, the Mo stable isotope system could provide a means of assessing the extent of ocean anoxia on *regional* or *global* scale (Barling et al. 2001; Siebert et al. 2003; Arnold et al. 2004). Hence, this non-traditional isotope system is likely to attract wide interest.

***Conceptual basis.*** The foundation of this type of application can be illustrated straightforwardly by modification of the mass balance equation above. If it is assumed that

Mo isotope fractionation in the oceans results from an equilibrium isotope effect between dissolved and Mn oxide-associated Mo (Barling et al. 2001; Siebert et al. 2003; Arnold et al. 2004; Barling and Anbar 2004), then $\delta^{97/95}Mo_{sw} - \delta^{97/95}Mo_{ox} \sim 1000 \times \ln(\alpha_{sw\text{-}MnO_x})$. Additionally, it seems reasonable that $\delta^{97/95}Mo_{eux}$ approximates $\delta^{97/95}Mo_{sw}$, at least in settings similar to the Black Sea and Cariaco Basin. Using these relationships and assuming $f_{ox} + f_{eux} = 1$ (i.e., neglecting suboxic sediments), we obtain:

$$\delta^{97/95}Mo_{eux} = \delta^{97/95}Mo_{input} + 1000\ln(\alpha_{sw\text{-}MnO_x}) \times f_{ox}$$

An analogous expression can be derived for $\delta^{97/95}Mo_{ox}$ in terms of $\alpha_{sw\text{-}MnO_x}$, $\delta^{97/95}Mo_{input}$ and $f_{ox}$ (or $f_{eux}$). Such a model illustrates that changes in ocean redox, which affect the relative proportions of $f_{eux}$ and $f_{ox}$, should result in changes in the isotopic composition of hydrogenous Mo in both euxinic and Mn-oxide sediments. Hence, measurements of $\delta^{97/95}Mo_{eux}$ or $\delta^{97/95}Mo_{ox}$ could yield information about changes in ocean redox through time.

It must be recognized that this model is highly idealized, particularly in the neglect of suboxic sedimentary environments and in the underlying assumption that $\delta^{97/95}Mo_{eux} \sim \delta^{97/95}Mo_{sw}$, and hence should not be applied with too much quantitative rigor. Nevertheless, based on present knowledge it seems inescapable that an expansion of euxinic environments should lead to a decrease in the extent of Mo isotope fractionation in the oceans, and vice-versa and that this should be reflected in sedimentary Mo. This conclusion follows from the observation that Mo isotope fractionation is much smaller during removal to euxinic sediments as compared to either Mn oxides or suboxic sediments.

The Mo isotope record should be an especially effective global redox proxy because of the long Mo ocean residence time relative to the ~1000 year timescale for ocean mixing. The residence time would decrease along with Mo concentrations during periods of greatly decreased oxygenation, but $\delta^{97/95}Mo_{sw}$ could be reasonably well-mixed unless ocean mixing times were substantially slower than today, or Mo concentrations decreased by more than a factor of ~50. For this reason, the Mo isotope system has the potential to provide paleoredox information on a global-scale.

A disadvantage of the long Mo ocean residence time is that it hinders the application of this system to ocean redox variations on timescales shorter than ~$10^6$ years—timescales of particular paleoclimatological interest. Substantial improvements in analytical precision will be required to detect the small $\delta^{97/95}Mo$ variations that may exist on such scales.

Initial efforts to apply the Mo isotope system have targeted sediments deposited under oxic conditions (marine ferromanganese crusts) as well as sediments deposited under reducing conditions (black shales). Results of these studies are summarized below.

*$\delta^{97/95}Mo_{ox}$ in Cenozoic ferromanganese crusts.* Siebert et al. (2003) applied the ocean Mo isotope mass balance concept to the interpretation of $\delta^{97/95}Mo$ in 60 million year records from Atlantic and Pacific ferromanganese crusts. The isotopic uniformity of this record, summarized above and in Figure 6, is taken to reflect invariance of $\delta^{97/95}Mo_{sw}$ at the sampled resolution of 1–3 million years. This interpretation assumes that $\alpha_{sw\text{-}MnO_x}$ is relatively insensitive to temperature, pH or the details of Mn-oxide mineralogy, which seems reasonable based on available data.

When analytical uncertainties are propagated through a mass balance model, $f_{ox} : f_{eux}$ is inferred to have varied less than 10% from modern values (~0.75 : 0.25, based on the mean $\delta^{97/95}Mo$ of each sediment type) (Siebert et al. 2003). This conclusion is not unreasonable. Although larger ocean redox perturbations are possible during this time in association with glacial $pCO_2$ drawdown, their duration does not approach the ~$10^6$ year timescale of crust sampling and the Mo residence.

***$\delta^{97/95}Mo_{eux}$ in mid-Proterozoic black shales.*** Arnold et al. (2004) investigated $\delta^{97/95}Mo_{eux}$ in black shales from ~1.6 and ~1.3 billion years ago in the McArthur and Tawallah Basins of Northern Australia to assess the anoxic ocean hypothesis of Canfield (1998). It is critical to note that the application of $\delta^{97/95}Mo$ in black shales for this purpose requires independent knowledge of local water column redox conditions because such sediments are not produced exclusively under euxinic water column conditions (Sageman et al. 2003). In the case of the McArthur and Tawallah basin samples, recent examination of sedimentary iron chemistry and sulfur isotopes indicates a water column that was at least locally euxinic (Shen et al. 2002, 2003).

As seen in Figure 6, mean $\delta^{97/95}Mo$ in these ancient sediments is significantly offset from that of modern seawater and from mean $\delta^{97/95}Mo$ of recent euxinic sediments. The offset is in the direction of less fractionation of Mo isotopes in the oceans (closer to the likely $\delta^{97/95}Mo_{input}$), as would be expected if removal of Mo to euxinic sediments expanded at the expense of removal to oxic (and suboxic) sediments. The result is consistent with the hypothesis of expanded ocean anoxia, and consequent increase in the areal extent of euxinic depositional settings, during this time. A similar, albeit smaller, offset is seen in repeated measurements of a Devonian black shale sample (USGS SDO-1; Fig. 6). This shift could be interpreted as consistent with somewhat expanded euxinic deposition during this time—an interpretation consistent with other evidence of expanded Paleozoic ocean anoxia in inland basins. While further work is needed, these initial results are promising.

## Other potential applications

Although current efforts are focused on global ocean paleoredox, the Mo stable isotope system should also prove useful in other oceanographic and environmental applications and in geobiological research. Such possibilities, while as yet unexplored, are previewed briefly below.

***Local water column paleoredox.*** The offset between recent euxinic and suboxic sediments (Fig. 6) suggests that such data could provide an additional tool to differentiate between euxinic and suboxic conditions in ancient sediments. Such application requires independent constraint on $\delta^{97/95}Mo_{sw}$, as might be obtained from analyses of coeval Mn oxide sediments.

***Paleoweathering intensity.*** Large variations in weathering rates may have occurred at various times in Earth history in association with changes in climate or terrestrial vegetation (e.g., Walker et al. 1981; Raymo 1991; Algeo and Scheckler 1998; Kump et al. 2000; Ravizza et al. 2001). Radiogenic isotope systems have been widely used to investigate such changes, especially $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$, because of contrasts between the isotopic compositions in seawater and crustal (weathering) sources. The same logic might apply to $^{97}Mo/^{95}Mo$. Changes in the flux of Mo to the oceans, or in the isotopic composition of riverine Mo due to changing weathering sources, should impact the ocean Mo isotope budget. In the case of flux changes the perturbation to $\delta^{97/95}Mo_{sw}$ will be transient (Siebert et al. 2003), recovering on the ~$10^6$ year timescale of the Mo ocean residence time. Changes in riverine $\delta^{97/95}Mo$ could result in longer lived shifts in $\delta^{97/95}Mo_{sw}$.

***Mechanisms of Mo environmental chemistry.*** Many of the chemical reactions that shape the distribution of Mo in the environment are still not well understood, as seen above in discussions of Mo adsorption to Mn oxides and removal in reducing systems. It is likely that different reaction pathways will impart different isotope effects. Hence, coupling of laboratory and well-constrained field studies should provide new insights into Mo environmental chemistry. Theoretical modeling of Mo isotope effects would also be useful in this context, as is proving true for Fe isotopes (Schauble et al. 2001).

***Mo biological uptake and processing.*** As an essential trace nutrient, Mo uptake and incorporation into enzymes is tightly controlled at the cellular level via selective "pumps" and

"chaperone" proteins. There are considerable uncertainties about the mechanisms involved, and their response to changes in Mo availability and other environmental variables. Mo isotope fractionation is likely during key steps in this biochemistry, which involve potentially significant changes in Mo coordination. For example, while Mo is present in solution in tetrahedral coordination as $MoO_4^{2-}$, it is bound to high-affinity uptake proteins in octahedral coordination. Such coordination differences and associated bond cleavage can drive isotope fractionation, as has been suggested experimentally and theoretically for Fe (Matthews et al. 2001; Schauble et al. 2001; Roe et al. 2003). Hence, the Mo isotope system could provide a useful new tool to examine how organisms extract this element from the environment and manipulate it internally (Williams and Frausto da Silva 2002).

## CONCLUSIONS

This chapter summarizes the results of the first wave of examinations of Mo stable isotopes in nature. These efforts reveal large, systematic variations in Mo isotope compositions in the ocean system that are apparently associated with the redox-sensitive marine geochemistry of this element. Laboratory studies of fractionation mechanisms, while limited in number, converge with predictions from natural observations. Combined with the relative simplicity of the Mo ocean budget and the likely preservation of oceanographically-interpretable Mo isotope signatures in both black shales and ferromanganese oxides, applications of this isotope system for paleoredox research are already apparent. Further work is needed to validate such applications, and to develop a framework to quantitatively relate $\delta^{97/95}$Mo variations in sedimentary records to changes in $\delta^{97/95}$Mo$_{sw}$ and hence in the relative importance of oxic and anoxic sedimentary reservoirs through time. Better constraints on the modern Mo element budget, which would permit more robust "calibration" of the Mo isotope budget, would be extremely helpful in this regard. However, even in advance of such refinements, the available data make clear that the Mo isotope system is poised to be among the more immediately useful of the emerging "non-traditional" stable isotope systems.

## ACKNOWLEDGMENTS

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