Molybdenum speciation and burial pathway in weakly sulfidic environments: Insights from XAFS

Meghan Wagner^{a,b,*}, Anthony Chappaz^b, and Timothy W. Lyons^c

^aPresent address:

School of Natural Resources and Environment

University of Michigan

440 Church St.

Ann Arbor, Michigan 48109

USA

(megwagn@umich.edu)

^bDepartment of Earth and Atmospheric Sciences

Central Michigan University

Brooks Hall

Mount Pleasant, Michigan 48859

USA

(anthony.c@cmich.edu)

^cDepartment of Earth Sciences

University of California

Geology Building

Riverside, California 92521

USA

(timothy.lyons@ucr.edu)

*Corresponding author

Email: megwagn@umich.edu

Phone: +1 734 764 5618

Fax: +1 989 774 2142

Abstract

Sedimentary molybdenum (Mo) accumulation is a robust proxy for sulfidic conditions in both modern and ancient aquatic systems and has been used to infer changing marine redox chemistry throughout Earth's history. Accurate interpretation of any proxy requires a comprehensive understanding of its biogeochemical cycling, but knowledge gaps remain concerning the geochemical mechanism(s) leading to Mo burial in anoxic sediments. Better characterization of Mo speciation should provide mechanistic insight into sedimentary Mo accumulation, and therefore in this study we investigate Mo speciation from both modern (Castle Lake, USA) and ancient (Doushantuo Formation, China) environments using X-Ray Absorption Near Edge Structure (XANES) spectroscopy. By utilizing a series of laboratory-synthesized oxythiomolybdate complexes—many containing organic ligands—we expand the number of available standards to encompass a greater range of known Mo chemistry and test the linkage between Mo and total organic carbon (TOC). In weakly euxinic systems ($[\text{H}_2\text{S}_{(\text{aq})}] < 11 \mu\text{M}$), or where sulfide is restricted to pore waters, natural samples are best represented by a linear combination of MoO_3 , $\text{MoO}_x\text{S}_{4-x}^{2-}$ (intermediate thiomolybdates), and $[\text{MoO}_x(\text{cat})_{4-x}]^{2-}$ (cat = catechol, $x = 2$ or 3). These results suggest a revised model for how Mo accumulates in weakly sulfidic sediments, including a previously unrecognized role for organic matter in early sequestration of Mo and a de-emphasized importance for MoS_4^{2-} (tetrathiomolybdate).

Keywords: molybdenum, euxinia, speciation, XAFS

1. Introduction

Molybdenum (Mo) is well established as a reliable proxy of anoxic, sulfidic conditions in both modern and ancient sediments (e.g., Algeo and Maynard, 2004; Crusius et al., 1996; Reinhard et al., 2013; Scott and Lyons, 2012; Scott et al., 2008). More recently, Mo stable isotopes have emerged as a novel tool for exploring the history of oceanic redox conditions (e.g., Arnold et al., 2004; Dahl et al., 2011; Kendall et al., 2011; Kendall et al., 2015). Despite its wide application, a comprehensive understanding of the geochemical mechanism of sedimentary Mo accumulation is still lacking. Briefly, the current model of Mo geochemical cycling begins with molybdate (MoO_4^{2-}) as the dominant species in oxygenated waters. Molybdate displays conservative behavior in the ocean, having a concentration well above that of other transition metals at ~100 nM (Collier, 1985). Oxidic freshwater lake concentrations are typically on the order of 10^{-1} to 10^1 nM (Chappaz et al., 2008; Glass et al., 2013). Under oxidic conditions, Mo adsorbs to Fe and Mn oxyhydroxides in sediments (Chappaz et al., 2008; Shimmield and Price, 1986; Zheng et al., 2000). With the onset of sulfidic conditions, progressive substitution of O for S occurs, leading to the formation of multiple thiomolybdate intermediates ($\text{MoO}_x\text{S}_{4-x}^{2-}$). In modern marine systems, above a threshold sulfide concentration of ~11 μM (as $\text{H}_2\text{S}_{(\text{aq})}$), a “geochemical switch” is flipped, and complete conversion to tetrathiomolybdate (MoS_4^{2-}) occurs (Erickson and Helz, 2000; Helz et al., 1996). Fixation in sediments has previously been hypothesized to occur in association with iron-sulfur phases (Bostick et al., 2003; Helz et al., 1996), although recent work has proposed multiple co-occurring pathways involving Mo reduction and/or Mo association with Fe phases, organic matter, and/or polysulfide (Algeo and Lyons, 2006; Ardakani et al., 2016; Chappaz et al., 2014; Dahl et al., 2013; Dahl et al., 2017), highlighting substantial remaining knowledge gaps.

Observations of conservative behavior by Mo in the open ocean have additionally led to the idea that MoO_4^{2-} is an unreactive species. However, explorations of Mo chemistry—driven partly by interest in Mo-containing enzymes such as nitrogenase—have demonstrated otherwise. Molybdate readily and predictably undergoes reactions with chelating organic ligands having ionizable protons (Table 1). Complexation nearly always involves expansion of the coordination number from four to six, with a corresponding change in geometry from tetrahedral MoO_4^{2-} to octahedral complex ion. Moreover, the species formed depends on the relative concentrations of ligand versus MoO_4^{2-} and ambient pH.

The ability of MoO_4^{2-} to undergo ligand substitution is of paramount importance for Mo biochemistry. Molybdenum is taken up by cells as MoO_4^{2-} , after which it is incorporated into enzymes containing FeMo-co at the active site (bacterial nitrogenases) or into pterin-based enzymes (Schwarz et al., 2009). Molybdenum cofactors required for enzyme biosynthesis typically have a coordination number of five or six, with ligands coordinating through a combination of O, S, and N donor atoms. Interestingly, FeMo-co contains a homocitrate ligand, which coordinates bidentately through carboxylate and hydroxyl groups, similar to complexes described from experimental chemistry.

At present it is unknown whether similar Mo compounds containing organic ligands exist in reducing sediments. However, the experimental insights into Mo coordination chemistry described above, as well as widely observed correlations between Mo and total organic carbon concentrations in ancient and modern euxinic environments (Algeo and Lyons, 2006; Lyons et al., 2009), suggest the possibility. Improved characterization of Mo speciation in sediments should further elucidate the mechanism(s) controlling Mo accumulation, and therefore in this study we explore the local Mo coordination environment in both ancient and modern anoxic

sediments using X-Ray Absorption Near Edge Structure (XANES) spectroscopy. We use a series of laboratory-synthesized oxythiomolybdate complexes, many containing organic ligands, to expand the number of standards against which spectra of natural samples can be compared, providing new insight into Mo speciation and its burial pathway under weakly sulfidic conditions.

2. Methods and materials

2.1 Materials (natural samples)

2.1.1 Castle Lake (CAL)

Molybdenum geochemical cycling in Castle Lake was previously investigated by Glass et al. (2013). Castle Lake is a small, subalpine tarn lake located in northern California, USA, that experiences hypolimnetic dysoxia during summer. At the time of sediment sampling, O₂ concentration in bottom waters was 12-30 µM. Sediment samples analyzed for this study were taken from a core collected in 2009 at a water depth of 35 m. Molybdenum concentrations for samples CAL_0_5 (0.5 cm core depth), CAL_7_8 (7.5 cm core depth), and CAL_41_42 (41.5 cm core depth) are 28.5, 36.0, and 39.6 ppm, respectively (Glass et al., 2013). Pore water data coupled with reaction-transport modeling indicate onset of Fe-Mn oxyhydroxide dissolution at ~1 cm below the sediment-water interface, with Mo transport controlled by Fe oxyhydroxide dissolution (Glass et al., 2013).

2.1.2 Doushantuo Formation (HN)

The Doushantuo Formation is an Ediacaran-age succession of shallow- and deep-water sedimentary facies located in Nanhua Basin, South China. This unit has provided important

insight into Neoproterozoic oceanic redox conditions (e.g., Li et al., 2010; McFadden et al., 2008). Selected samples came from the inner shelf Jiulongwan section, where Fe speciation analysis indicates that euxinic conditions prevailed at the time of deposition. Molybdenum concentrations for samples HN23 and HN12 are 180.7 and 125.1 ppm, respectively (Li et al., 2010).

2.2 Methods

2.2.1 Synthesis of Mo(VI) complexes and conversion to thiomolybdates (experimental samples)

Sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$); sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$); sodium chloride (NaCl); pH 6, 7, 8, and 9 buffers; and organic compounds were purchased from Fisher Scientific (Acros Organics). Solid sodium sulfide was rinsed with Milli-Q (18 M Ω) water prior to use in order to remove oxidation products. Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$) was purchased from Alfa Aesar. All reagents were used without further purification. Stock solutions were prepared with 80% v/v 0.1 M NaCl plus 20% v/v buffer as the diluent.

Complexes of Mo(VI) with citrate, malate, oxalate, catecholate, and tannic acid were prepared by combining appropriate volumes of stock solutions of MoO_4^{2-} and organic ligand, diluted to produce final concentrations of 0.1 mM and 3.75 mM, respectively. Complexation with catecholate and tannic acid occur instantaneously, evidenced by immediate color change of the solution from colorless to orange-red.

Substitution of oxo-, carboxylato-, and phenolato- ligands with sulfido- ligands was accomplished by adding aqueous sodium sulfide to complexes. Stock solutions of sodium sulfide were freshly prepared by dissolving a weighed amount into deoxygenated water. The pH was then adjusted to roughly 7-8 by addition of 1 M hydrochloric acid to prevent reactions from

becoming strongly basic. For complete conversion to MoS_4^{2-} , a tenfold molar excess of sulfide was added; for conversion to intermediate thiomolybdate species ($\text{MoO}_x\text{S}_{4-x}^{2-}$), a stoichiometric amount was added. Additional pH adjustment with 1 M hydrochloric acid and/or 1 M sodium hydroxide was occasionally necessary. Reaction progress was followed by UV-visible spectroscopy by monitoring the growth and disappearance of thiomolybdate peaks (Table 2), similar to the approach used by Erickson and Helz (2000).

Complexation of thiomolybdate species with Fe(II) was achieved by adding an appropriate volume of an aqueous stock solution of ammonium iron(II) sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$) (Muller et al., 1982). Upon addition, the solution became rose to purple-red in color. The Fe(II) reagent was purchased as the hexahydrate from Fisher Scientific (Acros Organics) and used without further purification.

2.2.2 X-ray Absorption Fine-Structure (XAFS) experiments

Detailed methods and a description of the XAFS experiment are given in Dahl et al. (2013). Here we provide only a summary and note specifics relevant to data collection for this study. Liquid samples (experimental samples, and inorganic standards $\text{Mo}^{\text{VI}}\text{O}_4^{2-}$ and $\text{Mo}^{\text{VI}}\text{S}_4^{2-}$) were loaded directly into 5-mm thick Teflon holders, while natural samples (powder for Doushantuo Formation and mud for Castle Lake) and solid inorganic standards ($\text{Mo}^{\text{IV}}\text{O}_2$, $\text{Mo}^{\text{VI}}\text{O}_3$, and $\text{Mo}^{\text{IV}}\text{S}_2$) were transferred into 2-mm thick Teflon holders. Solid inorganic standards were diluted with boron nitride before loading. All sample holders were then sealed with Kapton tape. Oxygen-sensitive samples were prepared at the synchrotron facilities within anaerobic chambers and were continuously maintained under anaerobic conditions. XAFS measurements for experimental samples and inorganic standards were performed at the Advanced Photon

Source (APS), Argonne National Laboratory, on beamline 13-BM-D using a Si(111) double crystal monochromator. Castle Lake samples were analyzed at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, on beamline X11-A using a Si(311) double crystal monochromator. Doushantuo Formation samples were analyzed at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, on beamline 4-1 using a Si(220) double crystal monochromator.

At each beamline, the incident beam intensity was detuned by ~20% to reject higher-order harmonic frequencies. Data were collected in the fluorescence mode using either a Canberra 13-element Ge detector (SSRL and NSLS) or a Canberra 16-element Ge detector (APS). A Mo(0) foil was measured simultaneously in the transmission mode as an internal standard for energy calibration, allowing comparison between samples and standards. Spectra were collected prior to the Mo K-edge (19800-19960 eV) at a resolution of 5 eV, across the edge (19960-20050 eV) at a resolution of 1 eV, and throughout the EXAFS region at a resolution of 0.05 Å⁻¹. Reference spectra were collected for Mo standards Mo^{VI}O₄²⁻_(aq), Mo^{VI}S₄²⁻_(aq), Mo^{VI}O_{3(s)}, Mo^{IV}O_{2(s)}, and Mo^{IV}S_{2(s)}. Standards were purchased from Fisher Scientific, Strem Chemicals, and Alfa Aesar and were used without further processing or purification. Spectra collected for experimental samples were treated as new XAFS standards.

Raw data were processed and analyzed using the Demeter (Athena and Artemis) software package (Ravel and Newville, 2005) for background removal and for XANES and EXAFS interpretation. For calibration, the first and fourth peaks in the first derivative spectrum of the Mo(0) foil were assigned 20000.0 and 20039.1 eV, respectively. At least four spectra per sample were merged to improve signal-to-noise ratio and enhance energy resolution. Uncertainty due to noise was <0.5% of the total absorption signal as estimated from ±1 standard deviation of

merged spectra. The position of the K-edge (E_K) and the maximum peak (E_M) in the XANES portion of the spectrum have previously been shown to be related to Mo oxidation state and ligand identity (Dahl et al., 2013). The energies at which these spectral features appear were determined via the Athena software for all samples using the first derivative of the spectrum (E_K) and the exported raw spectrum (E_M). Linear combination fits (LCF) for natural samples were performed over the interval -20 to +80 eV from the edge using ≤ 4 standards. The best fit for each sample was chosen as the one with the lowest R-factor (best goodness-of-fit).

The fitting domain for EXAFS interpretation of experimental samples (new Mo standards) was chosen to encompass the maximum range where all spectra were well defined ($k = 3\text{--}10 \text{ \AA}^{-1}$; $R = 1\text{--}4 \text{ \AA}$), ensuring that performance indices (R-factors) could be compared. The $\chi(k)$ function was Fourier transformed using k^2 weighting to perform model fits both on the raw absorption spectrum (k-space) and on Fourier transformed data (R-space). During the fitting process, the total amplitude (S_0^2) was allowed to vary between 0.8 and 1.1 but was fixed at the same value for all shells. Additionally, the energy shift (E_0) was constrained to within ± 10 eV, and the Debye-Waller terms (σ_i^2) were constrained to be $0 < \sigma_i^2 < 0.02 \text{ \AA}^2$. The best model fit for each experimental sample or standard was chosen as the one with the lowest R-factor (best goodness-of-fit). Several model fits required parameter values slightly outside the imposed constraints on S_0^2 , E_0 , and σ_i^2 to produce solutions having physically reasonable path lengths and lowest R-factors. However, these values are acceptable within calculated uncertainties. Additionally, these model fits may reflect the presence of multiple Mo species and should be viewed as probable reaction products until structures are independently confirmed by other methods.

3. Results

3.1 Reactivity of $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_x]^{n-}$ complexes in the presence of sulfide

Molybdenum(VI) complexes of the form $[\text{MoO}_2\text{L}_x]^{n-}$ (where L is a bi- or tridentate ligand, $x = 1$ or 2) are easily converted to thiomolybdate intermediates, and ultimately to MoS_4^{2-} , by addition of aqueous sulfide. The reaction is faster at lower pH, and successive ligand substitutions with S are progressively slower (e.g., the reaction of $[\text{MoO}_2(\text{mal})_2]^{2-}$ with sulfide, Figure 1), identical to the findings of Erickson and Helz (2000) for conversion of MoO_4^{2-} to MoS_4^{2-} . For example, at pH 6.24, the reaction went nearly to completion in less than three days. However, at pH 8.96, little to no MoS_4^{2-} was present after 12 days, and the dominant species was MoOS_3^{2-} . Tetrathiomolybdate (MoS_4^{2-}) did not react with organic ligands—an expected result given that substitution of organic ligands for S proceeds spontaneously.

3.2 Characterization of experimental samples

3.2.1 Known Mo(VI) complexes with organic ligands

Data from previous workers (Cruywagen et al., 1986; Cruywagen et al., 1997; Kustin and Liu, 1973) indicate that in the presence of excess ligand, the reaction of MoO_4^{2-} with malate, oxalate, and catecholate produces multiple complexes, with the formula $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ being prominent (where L = malate, oxalate, or catecholate). The complex formed by reaction of MoO_4^{2-} with tannic acid has also previously been reported, along with the results of EXAFS modeling (Kiboku and Yoshimura, 1958; Wichard et al., 2009). Finally, the reaction of MoO_4^{2-} with citrate has previously been proposed as $[\text{Mo}^{\text{VI}}\text{O}_3(\text{cit})]^{3-}$ (for citrate that is not fully deprotonated; Cruywagen et al., 1995), but our EXAFS data (Table 3, Figure S1) instead support the formulation $[\text{Mo}^{\text{VI}}\text{O}_2(\text{cit})]^-$. Such a complex would differ from others synthesized for this

study by incorporating a tridentate ligand that results in a coordination number of five, rather than six.

3.2.2 EXAFS (*Extended X-Ray Absorption Fine Structure*) modeling

Interatomic distances and fitting parameters for EXAFS modeling of experimental samples are given in Tables 3 and 4. XANES spectra and k- and R-space plots for experimental samples are available in the Supplementary Information (Figure S1). Complexes formed from the reaction of MoO_4^{2-} with organic ligands (malate, oxalate, catecholate, citrate, and tannic acid) were modeled as the most likely species based on available data (see previous section) except for the complex with citrate, which we found to be different from the results of Cruywagen et al. (1995). Experiments to replace oxo- ligands in $[\text{MoO}_2(\text{cit})]^-$ and $[\text{MoO}_2(\text{cat})_2]^{2-}$ with sulfido- ligands by adding two equivalents of sulfide produced different results. In the former case, sulfido- ligands appear to have completely displaced citrate, forming $[\text{MoO}_2\text{S}_2]^{2-}$ (Table 4). In the latter case, the best model fit comprised one Mo-S path; three shorter Mo-O paths; and two additional, longer Mo-O paths (Table 4). The Mo-S and shorter Mo-O lengths both imply double bonded, terminal ligands such as in MoO_3 and MoS_4^{2-} (Dahl et al., 2013). The longer Mo-O length is more similar to those found in $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$ type complexes (Table 3), implying that at least one catecholate ligand remained. The simple formula $[\text{MoO}_3\text{S}(\text{cat})]^{n-}$ derived from the model fit is chemically implausible, and it is more likely that a mixture of products ($\text{MoO}_x\text{S}_{4-x}^{2-}$ and $[\text{MoO}_x(\text{cat})_{4-x}]^{2-}$, $x = 2$ or 3) existed at the time of XAFS analysis. The reaction was allowed to stand overnight prior to analysis because preliminary experiments demonstrated that MoO_4^{2-} could be converted to $\text{MoO}_2\text{S}_2^{2-}$ within this amount of time, as confirmed by UV-visible spectroscopy. However, XAFS results suggest that it may not have gone to completion before

samples were measured. Given that linear combination fits indicated a significant component of this experimental sample in natural samples (see Section 3.3), we retained it as a new standard and simply refer to it hereafter as APS2.

Thiomolybdates are well known as good ligands for divalent first row transition metals (Coucovanis, 1998). The known complex $[\text{Fe}(\text{MoS}_4)_2]^{3-}$ was fitted with four Mo-S paths at $2.34 \pm 0.01 \text{ \AA}$ —longer than typical for tetrathiomolybdate (Dahl et al., 2013)—and one Fe-Mo path at $2.74 \pm 0.03 \text{ \AA}$. Lastly, the complex $[\text{Fe}(\text{MoO}_3\text{S})_2]^{3-}$ was fitted with three Mo-O paths at $1.73 \pm 0.01 \text{ \AA}$, one Mo-S path at $2.37 \pm 0.06 \text{ \AA}$, and 0.5 Fe-Mo path at $2.62 \pm 0.03 \text{ \AA}$. Originally, we intended to synthesize the complex $[\text{Fe}(\text{MoO}_2\text{S}_2)_2]^{3-}$; however, by the time the sample was measured at the beamline, the prepared reactant $\text{MoO}_2\text{S}_2^{2-}$ appears to have hydrolyzed to $\text{MoO}_3\text{S}^{2-}$. In preliminary experiments, $\text{MoO}_2\text{S}_2^{2-}$ could be reliably produced from MoO_4^{2-} by the addition of a stoichiometric amount of dissolved sulfide. However, thiomolybdate intermediates are known to hydrolyze (Clarke et al., 1987; Harmer and Sykes, 1980), and it is plausible that after $[\text{Fe}(\text{MoO}_2\text{S}_2)_2]^{3-}$ initially formed, it subsequently decomposed to $[\text{Fe}(\text{MoO}_3\text{S})_2]^{3-}$.

3.3 XANES (X-Ray Absorption Near Edge Spectroscopy) measurements

XANES spectra for natural samples (Figure 2) are qualitatively very similar to one another. Pre-edge features are visible $\sim 20,006 \text{ eV}$, approximately coinciding with the pre-edge features observed for MoO_3 and MoO_4^{2-} . However, pre-edge features for natural samples are less pronounced than those of MoO_3 and MoO_4^{2-} . A small pre-edge feature is also observed for MoS_4^{2-} , although it appears at lower energy ($\sim 20,002 \text{ eV}$). For our experiments, these pre-edge features indicate the presence of Mo=O for oxides (e.g., MoO_4^{2-}) or Mo=S for sulfides (e.g., MoS_4^{2-}). The pre-edge features are large for tetrahedral geometry and reduced or almost

nonexistent for octahedral geometry. Positions of the K-edge (E_K) and maximum peak (E_M) for MoO_3 , MoO_4^{2-} , and MoS_4^{2-} (Table 5) are also offset from natural samples in most cases (Figure 2). Together, these features suggest that none of these standards is the sole Mo species present in the natural samples. XANES spectra for MoO_2 and MoS_2 lack pre-edge features, and the positions of E_K and E_M are at lower energy than for natural samples, effectively ruling out these compounds as the Mo species in the Castle Lake and Doushantuo Formation samples.

Linear combination fitting (LCF) relies on a linear combination of standard spectra to fit the spectrum of an unknown mixture and can help to identify the components present and their relative amounts. Using our extended library of standards (inorganic Mo standards and experimental samples), linear combination fits (Figure 3) indicate a similar composition for modern Castle Lake and Neoproterozoic Doushantuo Formation samples (Table 6): all samples are well described by a combination of MoO_3 and APS2. Sample HN12 (Doushantuo Formation) could also be described as a combination of MoO_3 , APS2, and $[\text{Fe}(\text{MoO}_3\text{S})_2]^{3-}$, suggesting that Fe may also be associated with the preserved Mo species. Inclusion of other fitting standards produced physically unreasonable fits or higher R-factors.

4. Discussion

The spectral similarity of natural samples to APS2 supports earlier suggestions that sedimentary Mo exists in multiple phases (Chappaz et al., 2014; Helz et al., 1996) and that Mo is strongly associated with organic matter (Algeo and Lyons, 2006; Ardakani et al., 2016; Dahl et al., 2017; Glass et al., 2013; Helz et al., 1996; McManus et al., 2006). (For example, catecholate moieties associated with tannins in leaf litter have been shown to bind MoO_4^{2-} in soils, preventing its leaching (Wichard et al., 2009). Thus, catecholate is a reasonable proxy for

naturally-occurring organic ligands containing similar functional groups.) More specifically, similarity to APS2 suggests that Mo speciation in natural samples is a mixture of thiomolybdates and complexes containing organic ligands. It is possible to produce satisfactory fits to natural samples using only standards of the form $\text{MoO}_x\text{S}_{4-x}^{2-}$ (Table S1); however, inclusion of APS2 better reproduces the shape of the spectrum from about +15 to +80 eV from the edge and the position of the maximum peak.

Although the current model for Mo geochemical cycling focuses on tetrahedral species such as MoO_4^{2-} and MoS_4^{2-} , Mo(VI) complexes frequently exhibit an octahedral geometry when organic ligands are present (see Section 1). Consistent with this chemistry, major components of the Doushantuo Formation and Castle Lake samples identified by LCF (Table 6) have six-fold coordination: MoO_3 and $[\text{MoO}_x(\text{cat})_{4-x}]^{2-}$ (from APS2). Although our LCF results consistently indicated MoO_3 as a component in natural samples, molybdate rarely occurs in nature and MoO_3 is better interpreted as evidence for a six-coordinate Mo species having organic ligands (Ardakani et al., 2016). Inclusion of this standard is probably an attempt by the Athena software to fit the pre-edge features in spectra of natural samples (Figure 2). These pre-edge features appear at slightly higher energy for natural samples and MoO_3 (~20,005-20,006 eV) compared to $[\text{MoO}_2(\text{cat})_2]^{2-}$ and APS2 (~20,002-20,003 eV). Molybdate (MoO_4^{2-}) also has a pre-edge peak at approximately the same energy as MoO_3 , but—consistent with tetrahedral geometry—its intensity is higher than that found for natural samples. Therefore, the lower intensity of the pre-edge peaks for natural samples—similar to MoO_3 —indicates the presence of a Mo species with a distorted octahedral geometry (Bare, 2005). Further investigation of Mo speciation and iterative measurement of additional Mo standards in future studies will help to identify a more appropriate set of standards.

The absence of MoS_4^{2-} in the Doushantuo Formation samples is somewhat unexpected given that Fe speciation analysis indicates sediments were deposited under euxinic conditions (Li et al., 2010), which could favor Mo species with only sulfur-containing ligands. However, Fe speciation cannot discriminate between weakly euxinic ($[\text{H}_2\text{S}_{(\text{aq})}] < 11 \mu\text{M}$) and strongly euxinic ($[\text{H}_2\text{S}_{(\text{aq})}] > 11 \mu\text{M}$) conditions, with the latter required for near-quantitative formation of MoS_4^{2-} (Erickson and Helz, 2000; Neubert et al., 2008); below the $11 \mu\text{M}$ threshold, thiomolybdate intermediates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) are favored. Therefore, our XAFS data suggest that $[\text{H}_2\text{S}_{(\text{aq})}]$ was locally less than $11 \mu\text{M}$, consistent with Mo isotope data for most of the Doushantuo Formation, including sample HN23 (Kendall et al., 2015). However, preservation of intermediate thiomolybdates over long timescales has not previously been suggested, and $[\text{MoO}_x\text{S}_{4-x}]^{2-}$ species are less stable than oxythiomolybdate endmembers MoO_4^{2-} and MoS_4^{2-} (Erickson and Helz, 2000). These points raise the question of whether the primary Mo signal has been lost through post-depositional oxidative weathering or geochemical alteration of the original Mo speciation.

Post-depositional oxidative weathering is unlikely because potentially weathered surfaces were removed from collected samples prior to analysis (Li et al., 2010), and a second core from the Doushantuo Formation confirmed negligible deleterious oxidative weathering in samples from the Jiulongwan outcrop section (Kendall et al., 2015). Alteration of the original Mo speciation is more difficult to assess. High Mo concentrations in samples HN12 and HN23 (see Section 2.1.2) indicate deposition under permanently euxinic, Mo-replete conditions (Scott and Lyons, 2012). However, Mo isotope measurements for sample HN23 ($\delta^{98}\text{Mo} = 1.01\text{‰}$, relative to NIST SRM 3134 standard) suggest weak euxinia and initial burial of intermediate thiomolybdates (Kendall et al., 2015), consistent with our XAFS results and supportive of at least partial preservation of the primary Mo signal. Molybdenum isotopes were not analyzed for

sample HN12, but one sample (HND 30.35) from approximately the same stratigraphic level of the Jiulongwan section (Li et al., 2010) has a $\delta^{98}\text{Mo}$ of -0.47‰ (relative to NIST SRM 3134 standard), which is possibly a post-depositional artifact (Kendall et al., 2015). Hence Mo isotopes are unhelpful in determining the original Mo species present in sample HN12 and whether Mo speciation has been altered over time.

We cannot, however, exclude the possibility that samples were partially oxidized after collection, whether at the beamline or elsewhere. APS2 makes up only 20-35% of Mo in the Doushantuo Formation samples (Table 6). Linear combination fitting using $[\text{MoO}_2\text{S}_2]^{2-}$ and $[\text{MoO}_2(\text{cat})_2]^{2-}$ indicates that $[\text{MoO}_2\text{S}_2]^{2-}$ comprises 81.1% of APS2, which translates to only 16.2-28.4% of Mo present as thiomolybdate intermediates. Most Mo is therefore associated with $[\text{MoO}_x(\text{cat})_{4-x}]^{2-}$ and MoO_3 (or something spectrally similar, as discussed above). Nevertheless, despite the possibility of oxidation artifacts, our results suggest that we have correctly identified the Mo species buried hundreds of millions of years ago, within the limits of available standards.

Weak euxinia may also explain why Doushantuo Formation samples chemically resemble those from Castle Lake. Castle Lake bottom waters contain oxygen, but during the summer season detectable sulfide concentrations ($\sim 2\ \mu\text{M}$) first appear at 0.5 cm below the sediment-water interface and steadily decrease downcore (Table S3). In addition to low pore water sulfide concentrations, seasonal changes in bottom water oxygen concentrations known to occur in Castle Lake (Glass et al., 2013) are also predicted to favor intermediate thiomolybdate species (Erickson and Helz, 2000). Natural samples investigated for this study therefore underscore that strongly euxinic conditions ($[\text{H}_2\text{S}_{(\text{aq})}] > 11\ \mu\text{M}$) are necessary for complete conversion to MoS_4^{2-} and that these conditions are not always satisfied in either ancient or modern environments. Additionally, $[\text{MoO}_x(\text{cat})_{4-x}]^{2-}$ in APS2 is consistent with the finding of Glass et al. (2013) that

most Mo in Castle Lake is associated with non-detrital particulate material (organic matter and Fe-Mn oxyhydroxides).

Our natural samples therefore suggest a geochemical model for Mo burial in weakly sulfidic environments (i.e., sedimentary pore waters and bottom waters) very similar to that proposed by Helz et al. (1996), and in contrast to recent work focusing on strongly euxinic systems (Helz et al., 2011; Helz et al., 2014). Importantly, where dissolved sulfide concentrations ($[H_2S_{(aq)}]$) are less than 11 μM , complexes of the form $[Mo^{VI}O_2L_x]^{n-}$ (where L is a bi- or tridentate ligand, $x = 1$ or 2) may be involved in early-stage Mo sequestration. We propose that these complexes first capture Mo when dissolved organic matter containing appropriate chemical functional groups reacts with MoO_4^{2-} , either in the water column or within sedimentary pore waters (Figure 4). Although water column formation is possible under the right conditions, sedimentary pore waters are a more likely location for complex formation because sufficiently high concentrations of reactive functional groups are needed, and dissolved organic matter concentrations are expected to be higher there (Burdige and Komada, 2015). Furthermore, short-chain organic acids comprise part of the dissolved organic matter pool in anoxic pore waters (Burdige and Komada, 2015), and some appear to be unavailable to iron and sulfate reducers due to complexation (Finke et al., 2007). Subsequently, in the presence of dissolved sulfide, $[Mo^{VI}O_2L_x]^{n-}$ complexes undergo conversion to intermediate thiomolybdates (Figure 4). In marine environments, this process may be kinetically inhibited because the substitution reaction occurs faster at lower pH (Figure 1). Doushantuo Formation samples imply that Mo species structurally similar to intermediate thiomolybdates can undergo long-term burial and preservation, potentially in association with Fe phases as suggested by sample HN12 (Table 6) and by previous workers (Helz et al., 1996; Helz et al., 2004). Importantly, our model does not

preclude other mechanisms of Mo fixation in highly sulfidic environments, where MoS_4^{2-} formation is favored and adsorption to Fe-S mineral phases (e.g., pyrite) may occur (Bostick et al., 2003; Chappaz et al., 2014; Freund et al., 2016; Helz et al., 2011). Additionally, thiolation of organic matter at low ($[\text{H}_2\text{S}_{(\text{aq})}]$) or in the presence of polysulfides, followed by complexation to Mo, could provide another pathway by which Mo is sequestered in sediments during early diagenesis. Abiotic thiol formation has been shown to occur in reducing sediments (Vairavamurthy and Mopper, 1987, 1989), and MoS_4^{2-} is capable of simultaneously binding to pyrite and thiols (Freund et al., 2016).

Nevertheless, the implications of this model (Figure 4) are twofold. First, initial formation of Mo complexes containing organic ligands could explain commonly-observed correlations between Mo and total organic carbon (Algeo and Maynard, 2004; Cruse and Lyons, 2004; Lyons et al., 2009; McManus et al., 2006; Tribovillard et al., 2004; Wilde et al., 2004), through (a) delivery to and burial in sediments of a Mo-organic matter complex and/or (b) concurrent burial of organic matter with Mo after dissolved pore water sulfide transforms the Mo-organic matter complex to thiomolybdates. Second, intermediate thiomolybdate species—not just tetrathiomolybdate—must be seriously considered as major contributors to total sedimentary Mo concentrations. An enhanced role for intermediate thiomolybdates at low sulfide concentrations additionally would carry implications for Mo isotope fractionation, similar to what has been observed in Black Sea sediments (Arnold et al., 2012; Neubert et al., 2008). However, the question of Mo speciation in (lithified) anoxic sediments will only be satisfactorily resolved with further XAFS measurements from a wider variety of ancient and modern samples. Our method nonetheless sheds essential new light on longstanding questions about Mo cycling

and paleoproxy calibration in marine and nonmarine depositional systems, and validates the overall utility of the approach.

5. Conclusions

Although MoO_4^{2-} behaves conservatively in the modern ocean, it is known to undergo ligand substitution reactions with chelating organic ligands to form species such as $[\text{MoO}_2\text{L}_2]^{2-}$ when sufficiently high concentrations are available (Table 1). The importance of these species in open ocean waters and sedimentary pore waters remains unknown, but linear combination fits of XANES spectra suggest that at least some Mo in weakly euxinic ($[\text{H}_2\text{S}_{(\text{aq})}] < 11 \mu\text{M}$) environments is initially buried as a complex with organic matter. Intermediate thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) were identified as additional species present in natural samples from the Doushantuo Formation and Castle Lake, and they appear to be more important than tetrathiomolybdate (MoS_4^{2-}) in locations having low sulfide concentrations and/or seasonally fluctuating redox conditions, with potential impacts for Mo isotopes. Sedimentary Mo enrichment is clearly associated with sulfidic conditions, but complexation with organic matter represents a previously unrecognized first step in the geochemical mechanism of Mo burial, necessitating further investigation of Mo geochemical cycling and related isotope systematics in order to fully exploit Mo as a paleoredox proxy.

Acknowledgements. The authors gratefully acknowledge support from the U.S. National Science Foundation (Award # EAR-1124327). Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund, awarded to A.C., for support of this research (ACS-PRF 54583-DNI2). Additional support was provided to T.W.L. and A.C. by the NASA Astrobiology Institute and the U.S. National Science Foundation (Award # EAR-

443 1503596), respectively. We also thank C. Li for the Doushantuo Formation samples. The
444 Advanced Photon Source, National Synchrotron Light Source, and Stanford Synchrotron
445 Radiation Lightsource are user facilities operated by the U.S. Department of Energy, Office of
446 Science. We thank M. Newville and T. Lanzirotti for providing beamline assistance at the APS
447 and J. Spreitzer for assisting with sample preparation and measurement.

448

REFERENCES

- Algeo, T.J. and Lyons, T.W. (2006) Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* 21.
- Algeo, T.J. and Maynard, J.B. (2004) Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chemical Geology* 206, 289-318.
- Ardakani, O.H., Chappaz, A., Sanei, H. and Mayer, B. (2016) Effect of thermal maturity on remobilization of molybdenum in black shales. *Earth Planet. Sci. Lett.* 449, 311-320.
- Arnold, G.L., Anbar, A.D., Barling, J. and Lyons, T.W. (2004) Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans. *Science* 304, 87-90.
- Arnold, G.L., Lyons, T.W., Gordon, G.W. and Anbar, A.D. (2012) Extreme change in sulfide concentrations in the Black Sea during the Little Ice Age reconstructed using molybdenum isotopes. *Geology* 40, 595-598.
- Bare, S.R. (2005) XANES Measurements and Interpretation, APS XAFS School, Argonne National Laboratory.
- Bellenger, J.-P., Arnaud-Neu, F., Asfari, Z., Myneni, S.C.B., Stiefel, E.I. and Kraepiel, A.M. (2007) Complexation of oxoanions and cationic metals by the biscatecholate siderophore azotochelin. *Journal of Biological Inorganic Chemistry* 12, 367-376.
- Bellenger, J.-P., Wichard, T., Kustka, A.B. and Kraepiel, A.M.L. (2008) Uptake of molybdenum and vanadium by a nitrogen-fixing soil bacterium using siderophores. *Nat. Geosci.* 1, 243-246.

470 Bostick, B.C., Fendorf, S. and Helz, G.R. (2003) Differential adsorption of molybdate and
 471 tetrathiomolybdate on pyrite (FeS₂). *Environmental Science and Technology* 37, 285-291.

472 Burdige, D.J. and Komada, T. (2015) Sediment Pore Waters, in: Hansell, D.A., Carlson, C.A.
 473 (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*, Second ed. Elsevier, New York,
 474 pp. 535-578.

475 Caldeira, M.M. and Gil, V.M.S. (1986) Complexes of Mo(VI) with lactic, thiolactic, and
 476 thiomalic acids studied by NMR spectroscopy. *Polyhedron* 5, 381-385.

477 Cavaleiro, A.M.V.S.V., Pedrosa De Jesus, J.D., Gil, V.M.S., Gillard, R.D. and Williams, P.A.
 478 (1990) Molybdenum(VI) complexation by amino acids part II. Species in aqueous solutions of
 479 (R)-cysteine and sodium molybdate or tungstate. *Inorganica Chimica Acta* 172, 25-33.

480 Chappaz, A., Gobeil, C. and Tessier, A. (2008) Geochemical and anthropogenic enrichments of
 481 Mo in sediments from perennially oxic and seasonally anoxic lakes in Eastern Canada.
 482 *Geochimica et Cosmochimica Acta* 72, 170-184.

483 Chappaz, A., Lyons, T.W., Gregory, D.D., Reinhard, C.T., Gill, B.C., Li, C. and Large, R.R.
 484 (2014) Does pyrite act as an important host for molybdenum in modern and ancient euxinic
 485 sediments? *Geochimica et Cosmochimica Acta* 126, 112-122.

486 Clarke, N.J., Laurie, S.H., Blandamer, M.J., Burgess, J. and Hakin, A. (1987) Kinetics of the
 487 formation and hydrolysis reactions of some thiomolybdate(VI) anions in aqueous solution.
 488 *Inorganica Chimica Acta* 130, 79-83.

489 Collier, R.W. (1985) Molybdenum in the Northeast Pacific Ocean. *Limnology and*
 490 *Oceanography* 30, 1351-1354.

491 Coucouvanis, D. (1998) Syntheses, structures, and reactions of binary and tertiary thiomolybdate
 492 complexes containing the (O)Mo(S_x) and (S)Mo(S_x) functional groups (x = 1, 2, 4). *Advances in*
 493 *Inorganic Chemistry* 45, 1-73.

494 Cruse, A.M. and Lyons, T.W. (2004) Trace metal records of regional paleoenvironmental
 495 variability in Pennsylvanian (Upper Carboniferous) black shales. *Chemical Geology* 206, 319-
 496 345.

497 Crusius, J., Calvert, S., Pedersen, T. and Sage, D. (1996) Rhenium and molybdenum enrichments
 498 in sediments as indicators of oxic, suboxic, and sulfidic conditions of deposition. *Earth Planet.*
 499 *Sci. Lett.* 145, 65-78.

500 Cruywagen, J.J., Heyns, J.B. and van de Water, R.F. (1986) A potentiometric,
 501 spectrophotometric, and calorimetric investigation of molybdenum(VI)-oxalate complex
 502 formation. *Journal of the Chemical Society Dalton Transactions* 1986, 1857-1862.

503 Cruywagen, J.J., Heyns, J.B.B. and Rohwer, E.A. (1993a) Molybdenum(VI) complex formation.
 504 Part 6. Reactions with aspartate in 1.0 mol dm⁻³ sodium chloride medium at 25°C. *Journal of the*
 505 *Chemical Society, Dalton Transactions*, 1713-1717.

506 Cruywagen, J.J., Kruger, L. and Rohwer, E.A. (1993b) Molybdenum(VI) and tungsten(VI)
 507 complex formation. Part 5. The reaction with lactate in 1.0 mol dm⁻³ sodium chloride medium.
 508 *Journal of the Chemical Society, Dalton Transactions*, 105-109.

509 Cruywagen, J.J. and Rohwer, E.A. (1995) Equilibria and thermodynamic quantities for the
 510 reactions of molybdenum(VI) and tungsten(VI) with mandelate (α -hydroxybenzeneacetate).
 511 Journal of the Chemical Society, Dalton Transactions, 3433-3438.

512 Cruywagen, J.J., Rohwer, E.A. and van de Water, R.F. (1997) Molybdenum(VI) complex
 513 formation. Equilibria and thermodynamic quantities for the reactions with malate. Polyhedron
 514 16, 243-251.

515 Cruywagen, J.J., Rohwer, E.A. and Wessels, G.F.S. (1995) Molybdenum(VI) complex
 516 formation-8. Equilibria and thermodynamic quantities for the reactions with citrate. Polyhedron
 517 14, 3481-3493.

518 Dahl, T.W., Canfield, D.E., Rosing, M.T., Frei, R.E., Gordon, G.W., Knoll, A.H. and Anbar,
 519 A.D. (2011) Molybdenum evidence for expansive sulfidic water masses in ~ 750 Ma oceans.
 520 Earth Planet. Sci. Lett. 311, 264-274.

521 Dahl, T.W., Chappaz, A., Fitts, J.P. and Lyons, T.W. (2013) Molybdenum reduction in a sulfidic
 522 lake: Evidence from X-ray absorption fine-structure spectroscopy and implications for the Mo
 523 paleoproxy. Geochimica et Cosmochimica Acta 103, 213-231.

524 Dahl, T.W., Chappaz, A., Hoek, J., McKenzie, C.J., Svane, S. and Canfield, D.E. (2017)
 525 Evidence of molybdenum association with particulate organic matter under sulfidic conditions.
 526 Geobiology 15, 311-323.

527 Erickson, B.E. and Helz, G.R. (2000) Molybdenum (VI) speciation in sulfidic waters: Stability
 528 and lability of thiomolybdates. Geochimica et Cosmochimica Acta 64, 1149-1158.

529 Finke, N., Vandieken, V. and Jørgensen, B.B. (2007) Acetate, lactate, propionate, and
 530 isobutyrate as electron donors for iron and sulfate reduction in Arctic marine sediments,
 531 Svalbard. *FEMS Microbiology Ecology* 59, 10-22.

532 Freund, C., Wishard, A., Brenner, R., Sobel, M., Mizelle, J., Kim, A., Meyer, D.A. and Morford,
 533 J.L. (2016) The effect of a thiol-containing organic molecule on molybdenum adsorption onto
 534 pyrite. *Geochimica et Cosmochimica Acta* 174, 222-235.

535 Glass, J.B., Chappaz, A., Eustis, B., Heyvaert, A.C., Waetjen, D.P., Hartnett, H.E. and Anbar,
 536 A.D. (2013) Molybdenum geochemistry in a seasonally dysoxic Mo-limited lacustrine
 537 ecosystem. *Geochimica et Cosmochimica Acta* 114, 204-219.

538 Harmer, M.A. and Sykes, A.G. (1980) Kinetics of the interconversion of sulfido- and
 539 oxomolybdate(VI) species $\text{MoO}_x\text{S}_{4-x}^{2-}$ in aqueous solutions. *Inorganic Chemistry* 19, 2881-2885.

540 Helz, G.R., Bura-Nakić, E., Mikac, N. and Ciglencčki, I. (2011) New model for molybdenum
 541 behavior in euxinic waters. *Chemical Geology* 284, 323-332.

542 Helz, G.R., Erickson, B.E. and Vorlicek, T.P. (2014) Stabilities of thiomolybdate complexes of
 543 iron; implications for retention of essential trace elements (Fe, Cu, Mo) in sulfidic waters.
 544 *Metallomics* 6, 1131-1140.

545 Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R.A.D., Garner, C.D.
 546 and Vaughan, D.J. (1996) Mechanism of molybdenum removal from the sea and its
 547 concentration in black shales: EXAFS evidence. *Geochimica et Cosmochimica Acta* 60, 3631-
 548 3642.

549 Helz, G.R., Vorliceck, T.P. and Kahn, M.D. (2004) Molybdenum Scavenging by Iron
 550 Monosulfide. *Environmental Science & Technology* 38, 4263-4268.

551 Honig, D.S. and Kustin, K. (1973) Relaxation spectra of molybdate-ethylenediaminetetraacetic
 552 acid complexes. *Journal of the American Chemical Society* 95, 5525-5528.

553 Kendall, B., Gordon, G.W., Poulton, S.W. and Anbar, A.D. (2011) Molybdenum isotope
 554 constraints on the extent of late Paleoproterozoic ocean euxinia. *Earth Planet. Sci. Lett.* 307, 450-
 555 460.

556 Kendall, B., Komiya, T., Lyons, T.W., Bates, S.M., Gordon, G.W., Romaniello, S.J., Jiang, G.,
 557 Creaser, R.A., Xiao, S., McFadden, K., Sawaki, Y., Tahata, M., Shu, D., Han, J., Li, Y., Chu, X.
 558 and Anbar, A.D. (2015) Uranium and molybdenum isotope evidence for an episode of
 559 widespread ocean oxygenation during the late Ediacaran Period. *Geochimica et Cosmochimica*
 560 *Acta* 156, 173-193.

561 Kiboku, M. and Yoshimura, C. (1958) Photometric determination of uranium, vanadium,
 562 molybdenum and tungsten with tannic acid. *Japan Analyst* 7, 488-491.

563 Kustin, K. and Liu, S.-T. (1973) Kinetics and complex formation of molybdate with catechol.
 564 *Journal of the American Chemical Society* 95, 2487-2491.

565 Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L. and Chu, X. (2010) A stratified
 566 redox model for the Ediacaran ocean. *Science* 328, 80-83.

567 Lyons, T.W., Anbar, A.D., Severmann, S., Scott, C. and Gill, B.C. (2009) Tracking Euxinia in
 568 the Ancient Ocean: A Multiproxy Perspective and Proterozoic Case Study, Annual Review of
 569 Earth and Planetary Sciences. Annual Reviews, Palo Alto, pp. 507-534.

570 McFadden, K.A., Huang, J., Chu, X., Jiang, G., Kaufman, A.J., Zhou, C., Yuan, X. and Xiao, S.
 571 (2008) Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation.
 572 Proceedings of the National Academy of Sciences 105, 3197-3202.

573 McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E., Klinkhammer,
 574 G.P. and Holm, C. (2006) Molybdenum and uranium geochemistry in continental margin
 575 sediments: Paleoproxy potential. Geochimica et Cosmochimica Acta 70, 4643-4662.

576 Müller, A., Diemann, E. and Heidborn, U. (1969) Übergangsmetallchalkogenverbindungen.
 577 Darstellung, Eigenschaften, IR-Spektren und röntgenographische Untersuchungen von
 578 Trithiomolybdaten und -wolframaten. Zeitschrift für anorganische und allgemeine Chemie 371,
 579 136-148.

580 Muller, A., Hellmann, W., Schneider, J., Schimanski, U., Demmer, U., Trautwein, A. and
 581 Bender, U. (1982) Some new aspects of the coordination chemistry of thiometalato ligands.
 582 Inorganica Chimica Acta 65, L41-L42.

583 Natansohn, S., Krugler, J.I., Lester, J.E., Chagnon, M.S. and Finocchiaro, R.S. (1980) Stability
 584 constants of complexes of molybdate and tungstate ions with *o*-hydroxy aromatic ligands.
 585 Journal of Physical Chemistry 84, 2972-2980.

586 Neubert, N., Nägler, T.F. and Böttcher, M.E. (2008) Sulfidity controls molybdenum isotope
587 fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* 36, 775-
588 778.

589 Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
590 ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12, 537-541.

591 Reid, R.S., Clark, R.J. and Quagrain, E.K. (2007) Accurate UV-visible spectral analysis of
592 thiomolybdates. *Canadian Journal of Chemistry* 85, 1083-1089.

593 Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker,
594 A., Konhauser, K.O. and Lyons, T.W. (2013) Proterozoic ocean redox and biogeochemical
595 stasis. *Proceedings of the National Academy of Sciences* 110, 5357-5362.

596 Schwarz, G., Mendel, R.R. and Ribbe, M.W. (2009) Molybdenum cofactors, enzymes and
597 pathways. *Nature* 460, 839-847.

598 Scott, C. and Lyons, T.W. (2012) Contrasting molybdenum cycling and isotopic properties in
599 euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies.
600 *Chemical Geology* 324-325, 19-27.

601 Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X. and Anbar, A.D. (2008)
602 Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452, 456-459.

603 Shimmiel, G.B. and Price, N.B. (1986) The behaviour of molybdenum and manganese during
604 early sediment diagenesis--offshore Baja California, Mexico. *Marine Chemistry* 19, 261-280.

605 Tribovillard, N., Riboulleau, A., Lyons, T. and Baudin, F. (2004) Enhanced trapping of
 606 molybdenum by sulfurized marine organic matter of marine origin in Mesozoic limestones and
 607 shales. *Chemical Geology* 213, 385-401.

608 Vairavamurthy, A. and Mopper, K. (1987) Geochemical formation of organosulphur compounds
 609 (thiols) by addition of H₂S to sedimentary organic matter. *Nature* 329, 623-625.

610 Vairavamurthy, A. and Mopper, K. (1989) Mechanistic Studies of Organosulfur (Thiol)
 611 Formation in Coastal Marine Sediments, Biogenic Sulfur in the Environment. American
 612 Chemical Society, pp. 231-242.

613 Wichard, T., Mishra, B., Myneni, S.C.B., Bellenger, J.-P. and Kraepiel, A.M.L. (2009) Storage
 614 and bioavailability of molybdenum in soils increased by organic matter complexation. *Nature*
 615 *Geosci* 2, 625-629.

616 Wilde, P., Lyons, T.W. and Quinby-Hunt, M.S. (2004) Organic carbon proxies in black shales:
 617 molybdenum. *Chemical Geology* 206, 167-176.

618 Zheng, Y., Anderson, R.F., van Geen, A. and Kuwabara, J. (2000) Authigenic molybdenum
 619 formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin.
 620 *Geochimica et Cosmochimica Acta* 64, 4165-4178.

621
 622

TABLES

Table 1. Examples of known Mo(VI) complexes containing organic ligands. Complexes have no known previously reported EXAFS modeling data, except for $[\text{MoO}_2(\text{tan})_x]^{2-}$.

Ligand	Proposed Product ^a	Reference
Ethylenediaminetetraacetate (EDTA)	$[\text{MoO}_3(\eta^2\text{-EDTA})\text{H}]^{3-}$	(Honig and Kustin, 1973)
Lactate (lac)	$[\text{MoO}_2(\text{lac})_2]^{2-}$	(Cruywagen et al., 1993b)
Azotochelin (azo)	$[\text{MoO}_2(\text{azo})]^{3-}$	(Bellenger et al., 2007; Bellenger et al., 2008)
Cysteine (cys)	$[\text{MoO}_3(\text{cys})]^{2-}$	(Cavaleiro et al., 1990)
Aspartate (asp)	$[\text{MoO}_3(\text{asp})]^{2-}$	(Cruywagen et al., 1993a)
Mandelate (man)	$[\text{MoO}_2(\text{man})_2]^{2-}$	(Cruywagen and Rohwer, 1995)
Oxalate (ox)	$[\text{MoO}_2(\text{ox})_2]^{2-}$	(Cruywagen et al., 1986)
Malate (mal)	$[\text{MoO}_2(\text{mal})_2]^{2-}$	(Cruywagen et al., 1997)
Citrate (cit)	$[\text{MoO}_2(\text{cit})]^-$	(Cruywagen et al., 1995)
Catecholate (cat)	$[\text{MoO}_2(\text{cat})_2]^{2-}$	(Kustin and Liu, 1973)
Tannic acid (tan)	$[\text{MoO}_2(\text{tan})_x]^{2-}$	(Kiboku and Yoshimura, 1958; Wichard et al., 2009)
Thiomalate (malS)	$[\text{MoO}_2(\text{malS})_2]^{2-}$	(Caldeira and Gil, 1986)
Thiolactate (lacS)	$[\text{MoO}_2(\text{lacS})_2]^{2-}$	(Caldeira and Gil, 1986)
Various <i>o</i> -hydroxy aromatic ligands (hydroxyAr)	$[\text{MoO}_2(\text{hydroxyAr})]^{2-}$	(Natansohn et al., 1980)

^aMultiple species are possible depending on reaction pH and relative concentrations of reactants. See references for more information.

633 Table 2. Absorption wavelengths for oxythiomolybdate species.
634

Species	(Reid et al., 2007)		(Erickson and Helz, 2000)		(Müller et al., 1969)	
	$\lambda_{\max}$	ε	$\lambda_{\max}$	ε	$\lambda_{\max}$	ε
MoO_4^{2-}	207	10100 ± 200			208	8400
					231	2800
$\text{MoO}_3\text{S}^{2-}$	290	8600 ± 50	290	7390	288	8000
			314	2900	314	3000
$\text{MoO}_2\text{S}_2^{2-}$	286	4300 ± 50	290	3940 ± 40	288	3000
	321	8470 ± 60	322	6740 ± 60	318	6000
	395	3790 ± 30	394	3230 ± 50	394	3000
MoOS_3^{2-}	312	7330 ± 40	312	7500 ± 40	313	6600
	396	9550 ± 80	396	9030 ± 80	392	8700
	461	1860 ± 20	462	2080 ± 10	465	2300
MoS_4^{2-}	317	17300 ± 300	318	16480 ± 190	317	18000
	468	12800 ± 200	468	11870 ± 150	467	13000

635

636

637 Table 3. Experimental samples: Mo(VI) complexes with O-containing ligands. Fit in R space from R = 1-4 Å. Values with no reported
638 uncertainty were set parameters. Wichard et al. (2009) also report EXAFS modeling data for the Mo-tannic acid complex. The
639 designation “xs” refers to excess reagent.

Reactants	Proposed Product ^a	Mo-O			S_0^2	E_0 (eV)	Mean R-factor
		n	r (Å)	σ^2			
MoO ₄ ²⁻ + xs oxalate (ox) pH = 7.03	[MoO ₂ (ox) ₂] ²⁻	2	1.64 ± 0.01	0.002	1.13 ± 0.06	-10.00	0.02 ± 0.00
		4	2.13 ± 0.01	0.002			
MoO ₄ ²⁻ + xs malate (mal) pH = 6.89	[MoO ₂ (mal) ₂] ²⁻	2	1.70 ± 0.01	0.001 ± 0.002	1.08 ± 0.33	10.00	0.09 ± 0.00
		2	1.98 ± 0.03	0.008 ± 0.002			
		2	2.28 ± 0.04	0.012			
MoO ₄ ²⁻ + xs citrate (cit) pH = 6.96	[MoO ₂ (cit)] ⁻	2	1.69 ± 0.01	0.003	1.10 ± 0.14	2.00	0.14 ± 0.00
		2	2.27 ± 0.02	0.003			
		1	1.95 ± 0.03	0.003			
MoO ₄ ²⁻ + xs catecholate (cat) pH = 6.87	[MoO ₂ (cat) ₂] ²⁻	2	1.69 ± 0.02	0.003	0.93 ± 0.21	7.52 ± 3.62	0.18 ± 0.00
		4	2.06 ± 0.03	0.009 ± 0.003			
MoO ₄ ²⁻ + xs tannic acid (tan) pH = 7.06	[MoO ₂ (tan) _x] ²⁻ , x = 1 or 2	2	1.69 ± 0.02	0.003	1.09 ± 0.20	6.09 ± 4.75	0.22 ± 0.00
		4	2.07 ± 0.04	0.015			
MoO ₄ ²⁻ + tannic acid (tan) Wichard et al. (2009)	[MoO ₂ (tan) _x] ²⁻ , x = 1 or 2	2.24 ± 0.15	1.73 ± 0.01	0.0032			
		3.46 ± 0.38	2.05 ± 0.01	0.0080			

640 ^aMultiple species are possible depending on reaction pH and relative concentrations of reactants. Only the species modeled in EXAFS, or the most important
641 species at oceanic pH, is listed here. See references in Table 1 for more details.

Table 4. Experimental samples: Mo(VI) complexes with mixed ligands. Fit in R space from R = 1-4 Å, except for [Fe(MoS₄)₂]³⁻ which was fit from R = 1.35-4 Å. Values with no reported uncertainty were set parameters. No known previously reported EXAFS modeling data exist for these complexes. The designation “xs” refers to excess reagent.

Reactants	Proposed Product(s)	Mo-O			Mo-S			Mo-Fe			S_0^2	E_0 (eV)	Mean R-factor
		n	r (Å)	σ^2	n	r (Å)	σ^2	n	r (Å)	σ^2			
MoO ₄ ²⁻ + xs citrate + 2HS ⁻ pH = 6.66	[MoO ₂ S ₂] ²⁻	2	1.72 ± 0.01	0.003	2	2.19 ± 0.02	0.013				1.10 ± 0.08	9.75 ± 0.04	0.07 ± 0.00
MoO ₄ ²⁻ + xs catecholate + 2HS ⁻ pH = 7.13	MoO _x S _{4-x} ²⁻ and [MoO _x (cat) _{4-x}] ²⁻ , x = 2 or 3 (APS2)	3	1.72 ± 0.01	0.003	1	2.23 ± 0.05	0.020				0.98 ± 0.08	9.01 ± 2.51	0.03 ± 0.00
		2	2.15 ± 0.02	0.004 ± 0.003									
(NH ₄) ₂ Fe(SO ₄) ₂ + 2 [MoS ₄] ²⁻ pH = 8	[Fe(MoS ₄) ₂] ³⁻				4	2.34 ± 0.01	0.017	1	2.74 ± 0.03	0.008 ± 0.004	1.00 ± 0.11	10.00	0.10 ± 0.00
(NH ₄) ₂ Fe(SO ₄) ₂ + 2 [MoO ₃ S] ²⁻ pH = 7.09	[Fe(MoO ₃ S) ₂] ³⁻	3	1.73 ± 0.01	0.002	1	2.37 ± 0.06	0.020	0.5	2.62 ± 0.03	0.003	1.14 ± 0.08	10.00	0.05 ± 0.00

648 Table 5. K-edge (E_K) and maximum peak (E_M) energies for natural and experimental samples
649 and standards. Energies given as distance from the Mo absorption edge (20,000 eV).
650

Sample	E_K (eV)	E_M (eV)	$E_M - E_K$ (eV)
<i>Natural samples</i>			
CAL_0_5	15.1	38.1	23.0
CAL_7_8	15.5	37.1	21.6
CAL_41_42	16.0	37.2	21.2
HN12	16.7	38.7	22.0
HN23	17.0	38.3	21.2
<i>Experimental samples</i>			
[MoO ₂ (cit)] ⁻	11.4	31.1	19.7
[MoO ₂ (mal) ₂] ²⁻	11.3	31.4	20.0
[MoO ₂ (ox) ₂] ²⁻	10.2	30.6	20.4
[MoO ₂ (cat) ₂] ²⁻	11.4	29.9	18.5
[MoO ₂ (tan) _x] ²⁻	10.0	30.5	20.4
[MoO ₂ S ₂] ²⁻	13.0	39.9	27.0
APS2	14.0	35.0	21.0
[Fe(MoS ₄) ₂] ³⁻	7	37.1	30.1
[Fe(MoO ₃ S) ₂] ³⁻	13.4	40.3	27.0
<i>Standards</i>			
MoO ₂	10.5	32.5	22.0
MoO ₃	14.4	39.4	25.0
MoO ₄ ²⁻	17.4	42.7	25.3
MoS ₂	6.0	30	24.0
MoS ₄ ²⁻	7	44.2	37.2

651
652
653 Table 6. Linear combination fitting (LCF) results.
654

	CAL_0_5	CAL_7_8	CAL_41_42	HN12	HN12	HN23
<i>Standard</i>						
MoO ₃	0.43	0.31	0.38	0.69	0.68	0.65
APS2	0.57	0.69	0.62	0.20	0.32	0.35
[Fe(MoO ₃ S) ₂] ³⁻				0.11		
R-factor	0.005	0.004	0.004	0.005	0.005	0.012

655

FIGURE CAPTIONS

Figure 1. UV-visible spectra following the conversion of $[\text{MoO}_2(\text{mal})_2]^{2-}$ to thiomolybdates ($\text{MoO}_x\text{S}_{4-x}^{2-}$) upon addition of excess sulfide. Reaction rate is faster at lower pH. A similar dependence of kinetics on pH was also found for other complexes of the form $[\text{MoO}_2\text{L}_x]^{n-}$ (where L is a bi- or tridentate ligand, $x = 1$ or 2). Wavelengths of absorption maxima (λ_{max}) are given in Table 2.

Figure 2. Molybdenum K-edge XANES spectra for natural samples and inorganic standards. Solid black dots denote values of E_M (maximum peak) and E_K (K-edge position) given in Table 5.

Figure 3. XANES analysis of Mo speciation in natural samples using linear combination fits (LCF) of standard spectra. See Table 6 for relative amounts of standards present. Sample HN12 could also be fit satisfactorily without $[\text{Fe}(\text{MoO}_3\text{S})_2]^{3-}$. Residuals (green lines) are the spectral portions not adequately described by the fits, and that must be added to the fits to produce the original XANES spectra. Dashed horizontal line provides a reference baseline for spectra and residuals.

Figure 4. Proposed model for Mo burial in (A) anoxic (i.e., sulfide is restricted to pore waters) and (B) euxinic settings, where $[\text{H}_2\text{S}_{(\text{aq})}] < 11 \mu\text{M}$. Dashed arrows represent diffusion of Mo species into sedimentary pore water. Octahedral Mo species represents a generic Mo-dissolved organic matter (DOM) complex with two bidentate ligands. SWI, sediment-water interface.

A. **B.**