Redox speciation and early diagenetic behavior of dissolved molybdenum in sulfidic muds

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ABSTRACT

In order to further elucidate the early diagenetic behavior of Mo, we examined the redox speciation of dissolved Mo in organic rich sediment from a back-barrier salt marsh environment in eastern Long Island (Flax Pond, NY). Total dissolved Mo (ΣMo) was ~80 nM in surface nonsulfidic porewater, dominantly as Mo (VI). ΣMo increased up to 150 nM at a depth of 3.5 cm with low sulfide content (ΣH_2S: 25–100 μM), and Mo (V) reached 20 nM. ΣMo decreased to ~70 nM at a depth of 7.5 cm in highly sulfidic deep sediment porewater (ΣH_2S: >100 μM) with Mo(V) accounting for ~10%. Mo(VI) dominated residual ΣMo, likely as MoS_4^{2-}. Averaged in situ Mo speciation patterns are complicated by mixed redox conditions created by biogenic structures and reworking. Serial anoxic incubation of surface sediments revealed reductive redox reaction progression without complications from transport and biogenic microenvironments: Mo(VI) dominated initially, followed by increases in ΣMo (dMo/dt ~7 nM/h) and production of Mo(V) under low sulfide conditions (ΣH_2S: 25–100 μM; Mo(V) as high as 160 nM). Mo(V) was subsequently lost rapidly from solution (dMo(V)/dt ~−5 nM/h) and residual ΣMo, presumably a mixture of Mo(VI) and a small percentage of Mo(IV), was gradually reestablished under highly sulfidic conditions (ΣH_2S >100 μM). Mo(V) is clearly produced as a transient dissolved intermediate during reductive redox reaction succession. Mo(V) may react with particles or disproportionate in the presence of polysulfides into Mo(IV), which likely rapidly adsorbs–precipitates as pyritic Mo–Fe–S, sulfidized organic complexes, or perhaps MoS_2. Mo(VI), which remains, at least temporarily in solution as thiomolybdate is removed more slowly. In contrast to reductive reactions, reoxidation of reduced sediment results in rapid release of Mo dominated by Mo(VI). Dynamic diagenetic cycling and the existence of Mo(V) as a dissolved reaction intermediate must be accounted for in models of Mo fixation and associated isotopic fractionation in sulfidic deposits.

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1. Introduction

Molybdenum (Mo) is the most abundant transition element in the ocean, and has an almost conservative behavior under oxygenated conditions (mean concentration ~107 nM) (e.g., Collier, 1985). However, Mo is removed from solution and enriched in anoxic, sulfidic sediments (e.g., Bertine and Turekian, 1973; Emerson and Huested, 1991; Crusius et al., 1996; Morford et al., 2009; Poulson-Brucker et al., 2009). Thus, Mo enrichment and its isotopic composition in sediments and sedimentary rocks have been used extensively as paleoceanographic indicators of reducing depositional conditions (e.g., Nijenhuis et al., 1998; Dean et al., 1999; Adelson et al., 2001; Wilde et al., 2004; Lyons et al., 2009; Scheiderich et al., 2010).

Mo(VI) may accumulate in oxic surface sediments in host phases such as Mn and Fe oxides, biomass, or in both organic and inorganic components of recycled sedimentary debris (e.g., Bertine and Turekian, 1973; Crusius et al., 1996; Sundby et al., 2004; Chappaz et al., 2008). Under reducing conditions dissolved Mo(VI) is regenerated during organic matter remineralization or reductive dissolution of Fe, Mn-oxides (Morford and Emerson, 1999; Adelson et al., 2001; Schlieker et al., 2001; Dalai et al., 2005; Brumsack, 2006). Further Mo reduction is generally thought to be necessary for Mo fixation, either in association with scavenging onto particles in euxinic water columns or during precipitation–adsorption processes within anoxic, sulfidic deposits (Emerson and Huested, 1991; Huerta-Diaz and Morse, 1992; Calvert and Pedersen, 1993; Crusius et al., 1996; François, 1988; Zheng et al., 2000). Under sulfidic conditions ($H_2S > 11 \pm 3$ μM or $\Sigma H_2S > 25$ μM at pH ~8, as defined by Helz et al., 1996 and Erickson and Helz, 2000), Mo(VI) can form a series of thiomolybdates, e.g., MoO_3S^{2-}, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$, and MoS_4^{2-}, which can be partially co-precipitated with or adsorbed onto Fe-sulfides, or become associated with organic material, the latter often

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containing Fe and S (Helz et al., 1996; Vorlicek et al., 2004; Algeo and Lyons, 2006). The likely involvement of Mo(V) in Mo fixation has been proposed at various times but was never explicitly demonstrated (e.g., Szilágyi, 1967; Bertine, 1972; Vorlicek et al., 2004). As a transient intermediate, Mo(V) could directly react with organic matter, or be further reduced to Mo(IV) and precipitated as Mo–Fe–S pyrite surface associations, MoS_2, or scavenged by organic matter, particularly under sulfidic conditions in the presence of elemental S and polysulfides (Vorlicek et al., 2004). The reduction processes: $Mo(VI) \rightarrow Mo(V) \rightarrow Mo(IV)$, mediated by SO_4^{2-} reducing bacteria and directly producing MoS_2, were also reported under sulfidic conditions in the laboratory (Sugio et al., 1988; Tucker et al., 1997; 1998).

Although Mo enrichment and isotopic compositions in sediments have been used as diagnosis of reducing depositional conditions, limited information is available regarding dissolved Mo redox speciation and associated diagenetic reaction mechanisms. In this contribution, we measured Mo redox-speciation, using the analytical method recently developed by Wang et al. (2009), in porewater from a back-barrier salt marsh environment. The field study was complemented with manipulative laboratory experiments that allow us to infer speciation changes of dissolved Mo in response to different redox conditions in the absence of transport or bioturbation. We show that Mo(V) is produced during early diagenesis, that Mo concentrations and speciation are potentially highly dynamic in bioturbated deposits, and infer that Mo(V) is a likely significant intermediate in the anoxic removal of ΣMo from solution.

2. Materials and methods

2.1. Sediment porewater and surficial sediment sample collections

Sediment cores were collected at intertidal sites in Flax Pond (FP), Long Island during low tide, in June 2007. FP is connected to Long Island Sound through a single channel, is tidally exchanged with seawater, has a small drainage basin and therefore has no large input of water or nutrients from the uplands (Woodwell and Whitney, 1977). FP sediments are organic-rich (1–6% C_{org}; Mackin, 1986; Montluçon and Lee, 2001), and organic inputs to the sediments in FP include marsh detritus, terrigenous material, and plankton debris (Swider and Mackin, 1989; Wang and Lee, 1994). Dissolved Mn(II) and Fe(II) typically reach maxima, ~10 and 50–150 μM respectively, in the upper 0.5 to 1 cm and attenuate sharply by 2 cm (Swider and Mackin, 1989; Montluçon and Lee, 2001). Sulfate reduction rates in the upper few centimeters range from 0.1 to 5 mmol L^{-1} d^{-1} (Swider and Mackin, 1989; Mackin and Swider, 1989; Wang and Lee, 1994), typical of reactive nearshore deposits (Burdige, 2006). During the sampling period, the salinity of the overlying bottom water was ~28, the temperature was 21 °C, pH = 7.6 and DO was 50 μM for water close to the sediment surface. Reported sediment pH over the upper ~15 cm is 6.5–7 (Swider and Mackin, 1989; Zhu et al., 2006).

Core samples composed of sandy mud were collected with a hand-held acrylic box corer (165 cm^2 of cross-sectional area) and were extruded at 1 cm intervals (down to 7 cm depth) into 250 mL clean polypropylene bottles under nitrogen. The porewater was separated by centrifugation at 4000 rpm for 10 min. Supernatant samples were filtered through 0.2 μm Nuclepore membrane filters in plastic holders, and separated for different chemical redox species of Mo, Mo(V) and Mo(VI) immediately. The chemical speciation of Mo was quantified using the method of Wang et al. (2009). Filtered porewater was also collected in Teflon bottles and analyzed for dissolved sulfide (ΣH₂S) by standard spectrophotometric methods (Cline, 1969). The detection limit for ΣH₂S was ~10 μM. All sampling materials used in this study were prepared using trace metal clean techniques and all of the sample manipulations and separation procedures were carried out inside a nitrogen-filled glove bag (Bray et al., 1973; Troup et al., 1974). For the laboratory incubation experiments, we collected surficial (0–

1 cm) and deep (4–5 cm) sediments using a hand-held acrylic box corer.

2.2. General description of the method for separating Mo(V)

Mo(V) was separated from water samples using the method of Wang et al. (2009). Mo(V) was first selectively complexed with tartrate solution under neutral conditions, and then the Mo(V)–tartrate complexes were removed by passing solutions through poly-prep columns with Amberlite XAD 7HP resins. Mo(V) was eluted off the column with acidic acetone and analyzed using GFAAS. The remaining Mo (represented as Mo(VI) in this research) was reduced to Mo(V) using stannous chloride solution, and analyzed according to the above steps for Mo(V). Total Mo (ΣMo) was obtained by summing concentrations of Mo obtained by these two steps. In order to check the speciation method for possible interferences from Mo(IV), MoS_2 was leached with $H_2SO_4 + H_2S$ under N_2, pH adjusted, and the solution analyzed as outlined (Wang et al., 2009). Approximately 6% of the Mo (IV) in solution was complexed by tartrate (e.g., 0.16 nM of a total 2.66 nM Mo(IV)), indicating minimal contribution from any dissolved Mo(IV) to the analytical determinations. All of the chemicals used were of analytical reagent grade or the highest purity available. Milli-Q water (18.2 MΩ, Millipore) and HPLC-grade absolute acetone were used throughout.

2.3. Anoxic incubation of oxidized surface sediment

Sediment incubations are often used to reveal biogeochemical behaviors during aerobic and/or anaerobic processes (e.g., Martens and Berner, 1974; Aller and Yingst, 1980; Elsgaard and Jørgensen, 1992; Kristensen et al., 1999; Hansen et al., 2000). In this study, anoxic incubation of initially oxic surface sediments was carried out by homogenizing surface sediments (collected at a depth of 0–1 cm in FP during low tide) under N_2 in a glove bag and distributing portions into a set of incubation bottles (200 mL wide-mouth HDPE). These bottles were sampled serially with time. All sediment-filled bottles were sealed with no gas space, and all sample bottles were buried in anoxic sediment to maintain anoxic conditions. The time series for sampling was: 0, 3, 12 and 24 h, 2, 3, 4, 6 and 7 d. Once a bottle was taken out of the incubation container, it was centrifuged at 4000 rpm for 10 min, supernatant removed into gas tight syringes, and filtered through inline 0.2 μm filters. Porewater was processed immediately and analyzed for total sulfide (ΣH₂S), Mo(V) and Mo(VI). All bottles, filters and sampling apparatus were maintained under nitrogen for at least 12 h before the experiments (Bray et al., 1973; Troup et al., 1974).

2.4. Oxidation of sulfidic sediment

Particle reworking and bioirrigation typically result in exposure of reduced sediment and reoxidation. Dissolved Mo speciation dynamics during reoxidation was examined in a simple oxidation experiment. Subsurface, reduced sediment (4–5 cm depth interval) was taken from a sandy mud core and ~219.5 g (dry weight equivalent) was immediately placed unamended into a 2 L plastic beaker. Two liters of seawater were added into the beaker, and the seawater–sediment slurry was vigorously aerated with a gas frit attached to an aquarium pump and stirred continuously with a Teflon coated magnetic stirring bar. Water samples (100 mL) were removed at 0 h, 3 h, 12 h, 24 h, 2 d, 3 d, 4 d, 6 d, and 7 d. The samples were immediately filtered through a 0.2 μm pore filter, and measured for S, Mn, Fe, Mo(V) and Mo(VI). All filters and water sampling apparatus were maintained under nitrogen for at least 12 h before sample handling (Bray et al., 1973; Troup et al., 1974).