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The effect of a thiol-containing organic molecule on molybdenum adsorption onto pyrite

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Abstract

The effect of a small thiol-containing organic molecule on the adsorption of Mo to pyrite was investigated through the use of equilibration experiments with molybdate (MoO_4^{2-}), tetrathiomolybdate (MoS_4^{2-}), and 2-mercaptopropionic acid (2MPA). MoO_4^{2-}, MoS_4^{2-}, and 2MPA individually adsorb to pyrite through the formation of specific interactions with the mineral surface. In select combination experiments, 2MPA effectively out-competes MoO_4^{2-} for pyrite surface sites, which is indicative of the relatively weaker MoO_4^{2-}-pyrite interactions. Results suggest that the presence of 2MPA on the pyrite surface would inhibit MoO_4^{2-} access to catalytic mineral surface sites for the transformation of MoO_4^{2-} to MoS_4^{2-}. In contrast, thiols are not expected to be an obstacle to Mo uptake once the "switch point", or the critical H_2S concentration required for the formation of MoS_4^{2-}, has been surpassed. This is due to the stronger adsorption of MoS_4^{2-} to the pyrite surface. EXAFS results support weak specific interactions with little change to the MoO_4^{2-} environment upon adsorption to pyrite. In contrast, larger changes to the Mo–S internuclear distances during MoS_4^{2-} adsorption to pyrite support a more substantial structural change upon adsorption. MoS_4^{2-} is able to bind to both the pyrite surface and a thiol-containing organic molecule to form a ternary structure on the pyrite surface, and may provide for a molecular-level connection between Mo and thiol-containing organic molecules. Mo(VI) is reduced to Mo(IV) during MoS_4^{2-} adsorption to pyrite as a result of ligand-induced reduction, thereby confirming that the thiolated form of Mo is necessary for Mo reduction.

1. INTRODUCTION

Molybdenum (Mo) concentrations in marine sediments have been interpreted to yield information about bottom water oxygen (Zheng et al., 2000), bottom water hydrogen sulfide (Zheng et al., 2000; Scott and Lyons, 2012), pore water hydrogen sulfide (Scott and Lyons, 2012), or general changes in reducing conditions in sediments and/or overlying waters (e.g., Calvert and Pedersen, 1993; Crusius et al., 1996; Piper and Isaacs, 1996; Zheng et al., 2000; Adelson et al., 2001; Tribovillard et al., 2006; Algeo and Lyons, 2006). The correlations between Mo concentrations and organic carbon content in sediments suggest Mo might be a proxy for organic carbon in oxygen-deficient environments (Lyons et al., 2003; Cruse and Lyons, 2004; Wilde et al., 2004; McManus et al., 2006; Algeo and Lyons, 2006; Anbar et al., 2007; Chappaz et al., 2014). Mo enrichment has also been found to be positively correlated with the amount of sulfurized organic matter, suggesting that organic–Mo interactions may be key in Mo sequestration and/or accumulation under sulfidic

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conditions on geologic timescales (Lyons et al., 2003; Tribovillard et al., 2004; Cruse and Lyons, 2004; Wilde et al., 2004). However, it has been problematic to quantitatively use Mo concentrations in black shales as a proxy for the original organic carbon concentration (Wilde et al., 2004). Cruse and Lyons (2004) suggest that variable Mo concentrations in black shales could be due to either Fe cycling, which keeps sulfide concentrations below the level required for Mo sequestration, or the concentration and type of organic matter that accumulates in a particular area. Understanding the interplay among Mo, other metals, such as Mn and Fe (e.g., Goldberg et al., 1996; Chappaz et al., 2008; Scholz et al., 2013), and organic matter, which can also deliver Mo to the sediment–water interface (Nameroff et al., 2002), may be necessary for understanding the geochemical cycling and accumulation pathways for Mo in marine sediments.

Mo exists in the aqueous phase under oxic conditions and near-neutral pH as molybdate (MoO_4^{2-}) and is found conservatively in oxic ocean waters at ~105 nM (Collier, 1985; Emerson and Huested, 1991). Removal of Mo from pore waters and accumulation in the solid phase occurs via diffusion across the sediment–water interface under anoxic and sulfidic conditions (e.g., Shaw et al., 1994; Emerson and Huested, 1991; Crusius et al., 1996; Morford and Emerson, 1999; Zheng et al., 2000; Little et al., 2015), although an additional source of Mo to pore waters occurs when manganese and/or iron oxides are reduced and release previously sorbed Mo (Shaw et al., 1994; Emerson and Huested, 1991; Morford et al., 2007; Scholz et al., 2013). Mo accumulates most rapidly in the solid phase when sulfide concentrations are high (Sundby et al., 2004), with ~0.1 μM sulfide necessary to begin Mo–Fe–S precipitation and ~100 μM sulfide required for Mo precipitation without Fe (Zheng et al., 2000). Previous research has suggested Mo association with pyrite in marine sediments (FeS_2; Huerta-Diaz and Morse, 1992; Bostick et al., 2003; Tribovillard et al., 2008). More recent literature has deemphasized the role of pyrite as the primary host phase (Chappaz et al., 2014). Although Chappaz et al. (2014) found that Mo was enriched 1.3 to 8 times in pyrite grains ranging from 8 to 75 μm or larger, pyrite grains constituted a relatively small fraction of the sample (0.5–5.8%). The larger percentage of the surrounding matrix, even with the relatively lower Mo concentration, resulted in the matrix having a larger contribution to the bulk Mo concentration, thereby deemphasizing the importance of pyrite for Mo fixation (Chappaz et al., 2014). However, this work assumed that the Mo in the matrix was not associated with a nanocrystalline form of pyrite, which may not be correct. It is possible that nanocrystalline pyrite hosts similar Mo enrichments that contributes to, or accounts for, the matrix Mo concentration. Therefore pyrite may still be extremely important for Mo fixation.

The nature of Mo adsorption on the molecular level also influences Mo isotopic fractionation (e.g., Kashiwabara et al., 2009, 2011; Wasylenki et al., 2011), but the mechanism of Mo accumulation in sediments is not well understood. One hypothesis suggests a conversion from molybdate (MoO_4^{2-}) to thiomolybdate ($MoO_{4-x}S_x{}^{2-}$, $x = 1$–4) could lead to adsorption onto solid phase Fe sulfides and/or humic-SH compounds (Helz et al., 1996; Erickson and Helz, 2000; Vorlicek and Helz, 2002). The conversion to thiomolybdate can be catalyzed by the presence of Brønsted acids (Erickson and Helz, 2000), including solid-phase aluminum oxyhydroxides (Vorlicek and Helz, 2002), which would explain Mo removal from pore waters rather than Mo removal from the water column. The role of mineral adsorption has been investigated, with comparisons of molybdate and tetrathiomolybdate adsorption onto goethite, iron monosulfide and pyrite suggesting that tetrathiomolybdate is generally more strongly adsorbed to surfaces relative to molybdate (Bostick et al., 2003; Helz et al., 2004; Xu et al., 2006). Experimental research has shown that tetrathiomolybdate forms strong, irreversible inner-sphere Mo–Fe–S cubane-type clusters on pyrite, whereas molybdate forms labile surface complexes that are reversible and result in the easy release of Mo (Bostick et al., 2003). Inner-sphere Mo complexation to mineral surfaces has been connected with octahedral coordination with the surface, whereas outer-sphere complexes have been associated with tetrahedral coordination with the mineral surface (Kashiwabara et al., 2009, 2011). These results suggest that the conversion to tetrathiomolybdate might drive the permanent sequestration of Mo, whereas adsorption of molybdate is reversible and could lead to diagenetic loss of Mo. Further experimental work discusses the importance of not only H_2S but also zero-valent sulfur in the reduction of Mo(VI) to Mo(IV or V) polysulfide anion intermediates that more easily form cuboidal-type Mo–Fe–S structures on pyrite (Bostick et al., 2003; Vorlicek et al., 2004). Recent analyses of euxinic lake sediments support a mechanism that includes Mo(VI) reduction through reactions with S(0) and scavenging of reactive Mo-polysulfide species to the solid phase (Dahl et al., 2013). Adsorption to pyrite surfaces can be further complicated with the presence of S-deficient defect sites that tend to be more reactive relative to disulfide sites that tend to be less reactive (Guevremont et al., 1997; 1998a,b,c). Other literature instead emphasizes the role of pH and the formation of nanoscale Fe(II)–Mo(VI) sulfide minerals (Helz et al., 2011).

Experimental work has been more limited regarding Mo–organic interactions, which could be important both in pore waters and in sediments. Pore waters from organic-rich sediments suggest a strong association of dissolved Mo with dissolved organic matter (DOM) (Malcolm, 1985; Alberic et al., 2000). The formation of an aqueous Mo–organic complex can affect both the rate of diffusion of Mo through pore waters and its ability to interact with mineral surfaces. Mineral surfaces can also be coated with organic material (e.g., Hedges and Keil, 1995; Keil and Cowie, 1999; Wagai and Mayer, 2007). The adsorption of organic material onto minerals can modify the solid surface by providing functional groups oriented outward into solution that can function as new adsorption sites or can stabilize adjacent surface sites (e.g., Davis and Leckie, 1978). Additional research using activated carbon suggest that covalent bonds form between Mo and functional groups of organics, such as carboxylic