Evidence for Mo, organic molecule, and mineral interactions

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Introduction

Molybdenum (Mo) is relatively conservative in oxic seawater but is removed to the solid phase under sulfidic conditions. Investigators have been encouraged to use Mo solid phase concentrations or accumulation rates to infer past changes in reducing conditions in sediments and/or overlying waters. However, difficulties in fully using Mo as a proxy derive from a lack of information regarding the controlling factors for the removal of Mo from the aqueous phase to the solid phase. A commonly accepted hypothesis involves the thiolation of molybdate to a form that is more easily scavenged by particles[1,2]. A subsequent hypothesis instead suggests that the precipitation of a nanoscale Fe(II)-Mo(VI) sulfide mineral dictates Mo removal from the aqueous phase[3]. However, persuasive correlations between Mo concentrations and sulfurized organic matter hint at a role for organic molecules in Mo fixation and preservation in sediments[4].

We seek to clarify the influence of organic matter on Mo sequestration by determining the role of organic molecules, either aqueous or bound to solid surfaces, in the transition of Mo between the aqueous and solid phases. Simple organic molecules and single minerals are used as analogs for more complex humic material and heterogenous sediments, respectively, present in the environment.

Results

Initial results suggest that the nature of the organic molecule and the type of functional groups are important for aqueous molybdate-organic interactions. Molybdate preferentially complexes with organic molecules that have two phenolic functional groups on adjacent carbons as seen using ^{1}H and ^{13}C NMR. Analysis of molybdate with either 1,2-dihydroxybenzene or 2-mercaptopropionic acid using UV/Vis and ESMS supports the formation of a 1:2 Mo:organic complex.

Molybdate adsorption to aluminum oxide or pyrite is pH dependent with greater adsorption under acidic conditions. All adsorption experiments are consistent with a one-site adsorption surface as modelled with a Langmuir isotherm. The addition of 2-mercaptopropionic acid possibly inhibits the adsorption of molybdate to pyrite, although it is still uncertain whether the thiol competitively occupies pyrite adsorption sites or complexes molybdate, thereby making it incapable of adsorbing to the solid surface. Ultimately, the results of this research should clarify the influence of organic matter on Mo sequestration in modern sediments.

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Redox reactions affecting arsenic at iron-(oxyhydr)oxide mineral surfaces

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For the last few decades, a great deal of attention has been focused on better understanding and predicting the fate of arsenic in the environment. Indeed, due to natural as well as anthropogenic inputs, this element has been recognized as a pollutant in several countries, with major impacts on human health. One of the main conclusions drawn from the numerous studies conducted on natural and laboratory systems is that nanometer-sized iron-(oxyhydr)oxide minerals play a key role in the scavenging of arsenic in water, soils and sediments via sorption reactions. In addition, redox transformations of arsenic have been shown to greatly influence its mobility and toxicity, with As(III) species generally more mobile and toxic than As(V) species. Despite this extensive knowledge base, important questions remain about the detailed mechanisms of particular As oxidation and reduction reactions in complex heterogeneous media, and about the ultimate fate of this element in the presence of various electron donors and acceptors [1-4].

In the present communication, we will review important pathways for arsenic redox transformations that can be driven by either abiotic or abiotic processes. Examples will be chosen from recent studies using synchrotron-based X-ray absorption specoscopy (XANES, EXAFS) to monitor the redox state of arsenic in natural and laboratory systems. Focus will first be given to redox transformations that are usually slow at room temperature, but which can be catalyzed by chemical and physical factors. Particular attention will be paid to the complex interplay between Fe(II)/Fe(III) and As(III)/As(V) redox couples in the presence or absence of oxygen, and the role of photocatalysis in redox reactions [1-4]. Regarding these processes, classical artifacts involving catalysis of redox reactions during exposure to synchrotron radiation will be discussed as possible indicators of light-induced reactions.

In addition, examples of biotic redox transformations able to contribute to As sequestration by oxidized [5-7] or reduced iron-containing minerals [8] will be discussed in relation to the differing affinities of As(III) and As(V) species for specific mineral surfaces [9].

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