

Molybdenum Adsorption Mechanisms on Pyrite

Benjamin Bostick¹, Scott Fendorf (fendorf@stanford.edu)¹ & George Helz (gh17@umail.umd.edu)²

¹ Stanford University, Dept. of Geol. and Environ. Sci., Building 320, Room 118, Stanford CA 94305-2115, USA

² University of Maryland, Dept. of Chem. and Biochem., College Park, MD 20742-2021, USA

Introduction

Molybdenum has many biologically important functions, such as being present in nitrate reductase and in nitrogenase. Under oxic and suboxic conditions, molybdate is most stable. Molybdate adsorbs weakly to most minerals (Goldberg et al., 1996; Rietre et al., 1999), causing most molybdenum to remain in solution. In contrast, molybdenum forms thiomolybdate species and partitions strongly into the solid phase under sulfidic conditions (Emerson and Husted, 1991; Amrhein et al., 1993; Crusius et al., 1996). The strong affinity of molybdenum for sulfidic sediments and soils may be due to the formation of molybdenum sulphides. However, molybdenum trisulphide is typically too soluble to explain Mo sorption behaviour, and molybdenum disulphide formation is kinetically slow (Helz et al., 1996). Adsorption processes may be responsible for Mo adsorption in these systems. To test this hypothesis, this research examines the affinity of molybdenum for pyrite, an important metal sulphide. Information gleaned from this research will provide insight into Mo bio-availability and transport.

Methods

Batch studies were used to provide a macroscopic description of molybdate and thiomolybdate adsorption on synthetic pyrite. Adsorption was studied as a function of concentration, suspension density, pH and ionic strength. While these studies are useful, spectroscopic techniques are also needed to determine the mechanism of Mo sorption. Therefore, x-ray absorption fine-structure (XAFS) spectroscopy and Raman spectroscopy were used to determine the molecular-scale interactions of molybdenum with pyrite. Spectra were obtained for a range of molybdenum and sulphide concentrations, including conditions under which both molybdate and thiomolybdate were the thermodynamically stable species. However, analysis of adsorbed samples was immediate to prevent oxidation and prevent conversion between molybdate and thiomolybdate species. Results and Conclusions: Adsorption of molybdate and thiomolybdate was appreciable under all of the conditions of the study, although molybdate adsorbed to a lesser extent than thiomolybdate. Adsorption was rapid and reversible, suggesting

that adsorption was occurring and not surface precipitation. The extent of Mo adsorption varied strongly with pH. Sulphide addition decreased retention markedly, suggesting that sulphide competes for the same surface sites. XAFS analysis indicated that the co-ordination sphere of molybdate and thiomolybdate are not disrupted over short reaction periods. The Mo-O distance (1.73 Å) remained unaltered from solution species. Molybdate formed inner-sphere complexes, indicated by the presence of Mo-Fe distances near 2.8 Å. The spectrum of thiomolybdate was complicated by photo-oxidation in the x-ray beam, although data were still readily interpretable. Thiomolybdate contained Mo-S distances that were slightly elongated relative to thiomolybdate solutions. Thiomolybdate also contained Mo-Fe distances of near 2.8 Å, indicating that they are adsorbed as bidentate-mono-nuclear surface complexes. Under no circumstances were Mo-Mo distances discernible in the XAFS spectra; this implies that molybdenum sulphide precipitation is not the primary means of Mo sorption. Sulphide addition did not result in significant differences in XAFS spectra. Evidently, the pyrite surface did not catalyse the rate of sulphide substitution for adsorbed molybdate to thiomolybdate. Combined, these data indicate that molybdenum adsorbs to pyrite as inner-sphere complexes in a process that occurs differently than occurs for oxide minerals.

Goldberg S, Furstenu DW & Mao GW, *Soil Sci. Soc. Am. J.*, **60**, 425-432, (1996).

Rietre RPJJ, Hiemstra T & van Riemsdijk WH, *Geochim. Cosmochim. Acta*, **63**, 3009-3015, (1999).

Emerson SR & Husted SS, *Mar. Chem.*, **34**, 177-196, (1991).

Amrhein C, Mosher PA & Brown AD, *Soil Sci.*, **155**, 249-255, (1993).

Crusius J, Calvert S, Pedersen T & Sage D, *Earth Planet. Sci. Lett.*, **145**, 65-78, (1996).

Helz GR, Miller CV, Charnock JM, Mosselmans JF, Patrick RAD, Garner CD & Vaughan DJ, *Geochim. Cosmochim. Acta*, **60**, 3631-3642, (1996).