

Environmental Chemistry of Mercury in Sulfidogenic Sediments: A Key to Understanding the Ecological Impact of Mercury and Gold Mining

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Performance Report

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## Comparison of Accomplishments with Established Objectives

The proposed work comprised two objectives: (1) Study the kinetics of adsorption/desorption of Hg(II) to/from goethite ( $\alpha$ -FeOOH) and kaolinite as a function of chloride concentration and (2) determine the molecular speciation of Hg, Fe, and sulfur in slurries sampled during the progressive sulfidization of goethite to which Hg(II) is adsorbed. Due to the experimental difficulties (explained below), the first objective was not met. The second objective was achieved, as summarized below.

**Objective (1).** Stated more specifically, our objective was to study the adsorption of low, environmentally typical concentrations of Hg(II) on kaolinite, which were appreciably lower than those previously studied. Under these experimental conditions, however, adhesion of Hg(II) to containers precluded reliable analytical recovery of Hg. As a result, we could not quantify how much Hg adsorbed to kaolinite, or proceed with desorption and stability experiments. Dozens of trials were performed to overcome these difficulties, with no resolution.

**Objective (2).** The second objective addressed how sulfide would change the reactivity of Hg(II) adsorbed to goethite. Most sources of mercury (Hg) emit inorganic Hg-containing species to the environment, which do not cause appreciable ecological harm. Ecological harm occurs when inorganic Hg is converted to methylmercury by sulfate- and iron-reducing bacteria (SRB and FeRB). The effects of chemical processes involving oxidized and reduced forms of sulfur and iron on the reactivity of inorganic Hg, including its propensity to be methylated, are poorly understood.

Under abiotic conditions, using a laboratory flow reactor (Fig. A1 of Attachment 1), bisulfide ( $\text{HS}^-$ ) was added at 40 to 250  $\mu\text{M h}^{-1}$  to 5  $\text{g L}^{-1}$  goethite suspensions to which Hg(II) was adsorbed (30 to 100  $\text{nmol m}^{-2}$ ) at pH 7.5. Dissolved Hg initially decreases from  $10^3$  or  $10^4$  nM (depending on initial conditions) to  $10^{-1}$  nM (Fig. A2), during which the concentration of Hg(II) adsorbed to goethite decreased by 80% and metacinnabar ( $\beta$ -HgS) formed. These estimates are based on Hg L<sub>III</sub>-edge extended X-ray absorption fine structure (EXAFS) spectroscopic analysis (Fig. A3).

Interestingly, further sulfidation increased dissolved Hg concentrations by one to two orders of magnitude (0.5 nM to 10 or 30 nM) (Fig. A2), suggesting that byproducts of bisulfide oxidation and Fe(III) reduction, primarily polysulfide and potentially Fe(II), enhanced the dissolution of  $\beta$ -HgS or the desorption of Hg. Rapid accumulation of Fe(II) in the solid phase (up to 40  $\mu\text{mol g}^{-1}$ ) coincided with faster elevation of dissolved Hg concentrations (data not shown). Fe(II) served as a proxy for elemental sulfur [S(0)], as S(0) was the dominant bisulfide oxidation product coupled to Fe(III) reduction to Fe(II). The chemical form of sulfur was determined by sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy (Fig. A3). In one experiment, shown in Fig. A2, dissolved Hg concentrations tracked those of all sulfide species [S(-II)]. These results suggest that S(-II) reacted with S(0) to form polysulfide, the latter of which then caused the dissolution of  $\beta$ -HgS. Examination of interrelated processes involving S(-II) and Fe(III) revealed new modes of Hg solubilization previously not considered in Hg reactivity models.

## Work Products Produced

In addition to this performance report, a manuscript entitled *Transformations of mercury, iron, and sulfur during the reductive dissolution of iron oxyhydroxide by sulfide* is currently under revision for publication in *Geochimica et Cosmochimica Acta*. The anonymous and associate editor reviews were generally favorable, so we are confident that this manuscript will be accepted for publication in *GCA*. This manuscript also constituted the final chapter of Dr. Slowey's Ph.D. dissertation. The research funded by the MRERP was presented at the following professional conferences and public agency meetings (authors are A. J. Slowey and G. E. Brown, Jr. and the title is the same as the manuscript unless otherwise noted):

Oral presentation 2857, 16<sup>th</sup> V. M. Goldschmidt Conference. Melbourne, Australia. 2006.

Poster presentation, 8<sup>th</sup> International Conference on Mercury as a Global Pollutant. Madison, Wisconsin. 2006.

Poster presentation, 2<sup>nd</sup> Annual Meeting of the Stanford Environmental Molecular Science Institute, Stanford, CA. 2006.

Oral presentation, 4<sup>th</sup> Symposium of Kanazawa University. Kanazawa, Japan. 2006.

Oral presentation, San Francisco Bay mercury research coordination meeting, San Francisco Estuary Institute. Oakland, CA. 2006.

Poster presentation, 32<sup>nd</sup> Stanford Synchrotron Radiation Laboratory User Meeting. Menlo Park, CA. 2005.

Spectroscopic investigations of mercury-contaminated sediments: Adapating restoration goals to mechanistic reasearch. Division of Geochemistry presentation 82. Research, Education and Outreach in the NSF Environmental Molecular Science Institutes. 230<sup>th</sup> American Chemical Society National Meeting, Washington, D.C. 2005.

Accumulation, release and methylation of mercury in oxygen-depleted riparian zones: Preliminary results. Oral presentation, Technical workgroup meeting of the San Francisco Estuary Institute, Oakland, CA. 2005.

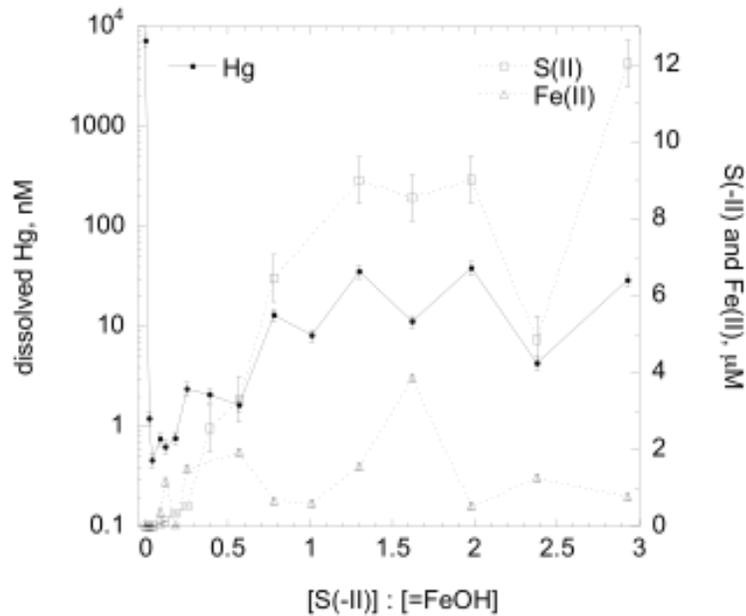
## Concluding Remarks

The insights gained during the research funded by the MRERP will guide several ongoing and future field investigations by Dr. Slowey in his current capacity as an employee with the Mineral Resources Division under the supervision of Dr. James Rytuba. A Mendenhall Fellowship proposal is also being prepared to extend the research covered by that summarized here.

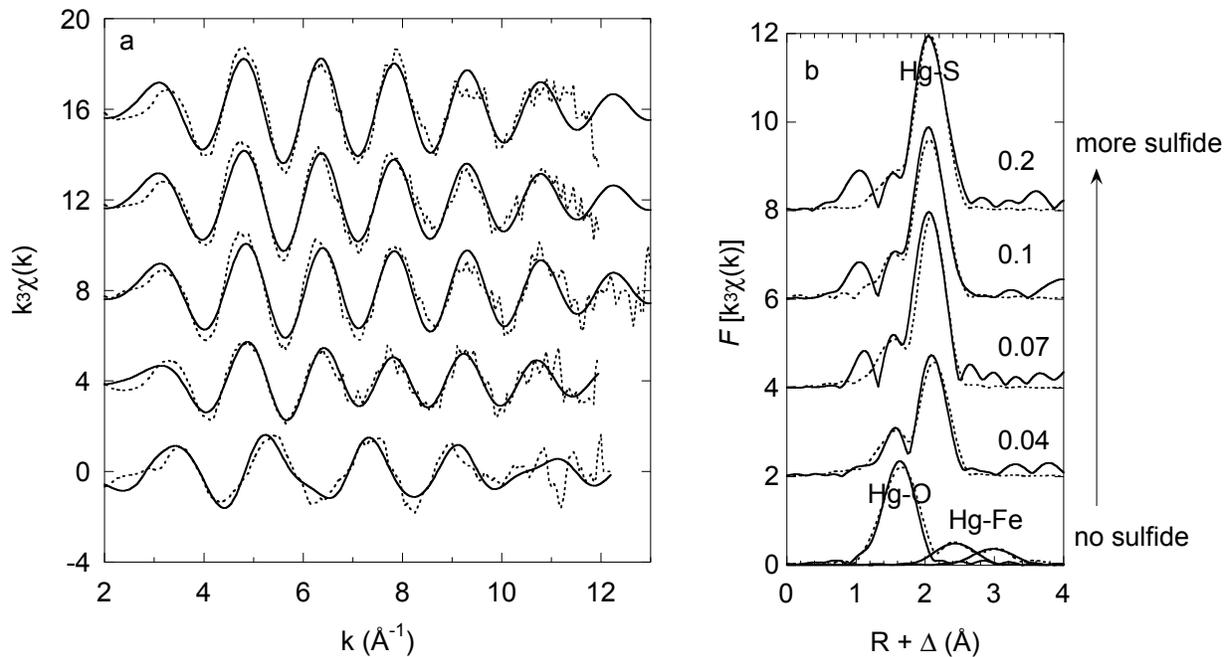
## Attachment 1. Figures



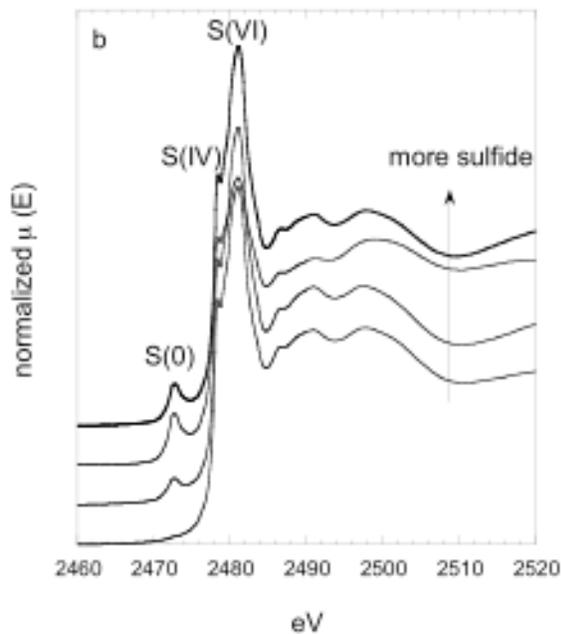
**Figure A1.** Sulfidation experimental apparatus.



**Figure A2.** Dissolved Hg, S(-II), and Fe(II) as a function of sulfide loading during experiment (a):  $1.9 \mu\text{M S(-II) h}^{-1} \text{ m}^{-2}$  applied to  $5 \text{ g L}^{-1}$  goethite with  $30 \text{ nmol adsorbed Hg m}^{-2}$  at pH 7.5. Error bars for Hg data represent the maximum variability of replicate sample analyses (approx. 20% of all samples), while those for S(-II) and Fe(II) are  $1 \sigma$  of triplicate analyses of a subset of samples (approx. 10%).



**Figure A3.** Hg L<sub>III</sub>-edge EXAFS (a) and radial structure functions (b) for one sulfidation experiment. Dotted lines are the experimental data and solid lines are the theoretical fits.



**Figure A4.** Sulfur K-edge XANES for solids sampled during a sulfidation experiment, including sulfide loadings, from bottom to top, of 0.01, 0.03, 0.04, 0.07, 0.10, and 0.20. Spectra were offset for clarity.