

IRON SULFIDE-ARSENITE INTERACTIONS: ADSORPTION BEHAVIOR ONTO IRON MONOSULFIDES AND CONTROLS ON ARSENIC ACCUMULATION IN PYRITE

R. T. Wilkin, U. S. Environmental Protection Agency, National Risk Management Research Laboratory, Office of Research and Development, Ada, OK 74820
(wilkin.rick@epa.gov)

INTRODUCTION

Because arsenic in ground water and surface water poses a risk to ecosystem and human health, more detailed information is needed on the factors that govern arsenic fate and transport in the environment.

Arsenic mobility in natural systems is often linked to iron and sulfur cycling at redox boundaries, apparently due to co-precipitation reactions of arsenic with poorly crystalline iron (oxy)hydroxides, iron monosulfides, and pyrite (e.g., Edenborn et al., 1986; Moore et al., 1988). The mobility of arsenic under anoxic, sulfate-reducing conditions is expected to be governed by interactions between arsenite or thioarsenite species with amorphous or crystalline iron sulfides. Iron sulfide minerals are especially common components of soil/sedimentary environments, and reactions at the surfaces of iron sulfides play pivotal roles in metal retention, mobility, and bioavailability (Huerta-Diaz and Morse, 1992). Although essential for predicting the fate of arsenic in anoxic environments, details of reaction mechanisms, geochemical pathways, and the limiting factors that govern metal uptake by iron sulfides (iron monosulfides and iron disulfides) are incompletely understood. The kinetic nature of these interactions are currently being investigated at EPA's Subsurface Protection and Remediation Division where on-going studies evaluate the effects of pyrite nucleation rate and growth rate on the uptake of metals and metalloids.

METHODS

Strategy - In low-temperature sedimentary environments the concentration distribution of dissolved sulfide and ferrous iron is typically governed by the solubility of the iron monosulfide mackinawite, i.e.,



with $\log K_{\text{sp}} = -3.1$ (Berner, 1970; Wilkin and Barnes, 1997). Figure 1 shows the equilibrium solubility of mackinawite at pH 6 and 7 in terms of the concentrations of ferrous iron and total dissolved sulfide ($\text{H}_2\text{S} + \text{HS}^-$). Two general regions are apparent on this diagram: 1) ferrous iron excess region; and, 2) sulfide excess region. Region I (iron excess) is typical of environments where rates of

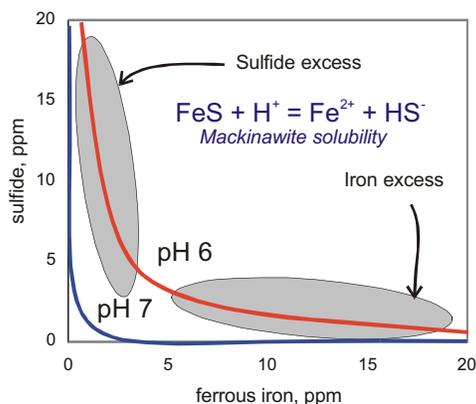


Figure 1. Equilibrium concentrations of ferrous iron and sulfide (total dissolved sulfide, H_2S) at pH 6 and 7 assuming saturation with mackinawite (Benning et al., 2000). Activity coefficients are set equal to 1. Note that solubility decreases as pH rises, and that when concentrations of either iron or sulfide are low the other is necessarily high.

sulfate reduction are low and/or reactive iron is available. Region II (sulfide excess) is typical of environments where all reactive iron has been consumed by precipitation of iron sulfide and H_2S accumulates. Experiments were designed to evaluate sorption of As(III) onto iron monosulfide at near-neutral pH in systems with an excess of ferrous iron or bisulfide.

Methods - Precipitated iron monosulfide (mackinawite) grains were prepared by addition of ferrous ammonium sulfate solution to NaHS at controlled pH. This procedure was carried out using deoxygenated, deionized water under a N_2/H_2 atmosphere (Wilkin and Barnes, 1996). Aliquots of the resulting suspension were then added to buffered sodium arsenite solutions containing variable amounts of ferrous iron and bisulfide at near-neutral pH.

In batch experiments, a solid/solution ratio of about 0.01 to 5 mg/mL was used. Arsenite was added to give initial solution concentrations from 0.1 to 30 ppm As. The arsenite solution was kept in contact with the mackinawite particles for up to 150 h and periodically agitated. After reaction, the supernatants were filtered, diluted, acidified, and analyzed using ICP-OES or ICP-MS. In experiments with $\text{HS}^-/\text{Fe(II)} > 0.1$, sulfide was oxidized prior to As determinations to prevent precipitation of As_2S_3 or elemental sulfur at low pH. Aliquots of NaOH were added to samples to raise pH to 11, then 30% H_2O_2 was added to oxidize sulfide prior to acidification with HNO_3 .

RESULTS

Results indicate contrasting behavior in the iron- and sulfide-excess regions plotted in Figure 1. Arsenite sorption onto iron monosulfide surfaces is complete at low concentrations in the iron-excess region (Figure 2). Saturation of available surface sites appears to occur at higher

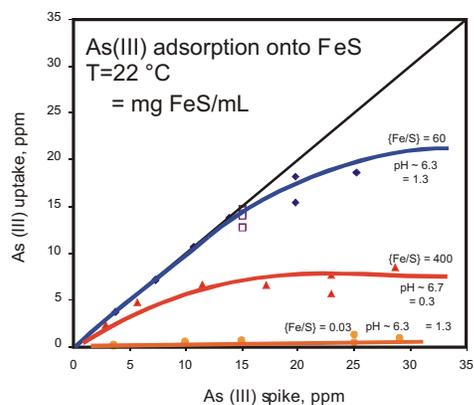


Figure 2. Uptake of As(III) from solution by mackinawite as a function of initial As(III) concentration in solution and particle loading.

arsenic spikes and lower surface densities. In contrast, when free hydrogen sulfide or bisulfide is present, little adsorption occurs and arsenic remains in solution (Figure 2).

The lack of sorption at low Fe/S apparently is related to the presence of the thioarsenite species (Figure 3). Stability relations and stoichiometries of thioarsenite species are poorly understood. Thermodynamic data for monomeric, dimeric, and trimeric thioarsenite species have been estimated from orpiment solubility studies, but these data are highly uncertain (see Spycher and Reed, 1989; Clarke and Helz, 2000). For the present experiments at generally low total arsenic concentrations, we assume that monomeric species dominate, however, more research is needed to confirm this assumed stoichiometry. The experimental results and geochemical modeling suggest that AsS_2^- is particle unreactive compared to $\text{H}_3\text{AsO}_3(\text{aq})$. The important implication is that in environments where iron monosulfide precipitates accumulate, arsenic uptake will occur preferentially in systems where reactive iron is available as compared to regions where free sulfide is present at levels greater than about 0.1 mM.

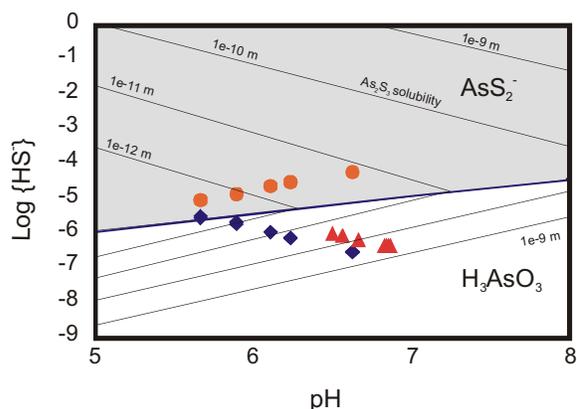


Figure 3. Experimental data plotted on predominance area diagram for As(III). Symbols correspond to those in Figure 2. Contours show equilibrium solubility of orpiment; all experiments were supersaturated with respect to As_2S_3 . Orpiment nucleation is kinetically inhibited at near-neutral pH (e.g. Webster, 1990). Thermodynamic data for arsenic species from Ferguson and Gavis (1972) and Clarke and Helz (2000).

We were unable to synthesize orpiment from supersaturated solution at near-neutral pH. Because arsenic sulfide precipitation is kinetically favored only at low pH, arsenic geochemical behavior is unlike that of the d-transition metal elements (e.g., Fe, Cd, Pb, Zn). For these metals, the solubility of sulfide precipitates decreases with increasing pH and precipitation rates are fast. This means that standard methods to evaluate exposure to toxic metals (i.e., SEM/AVS) in anoxic systems may be inappropriate for arsenic. Arsenic bioavailability will be under predicted using the SEM/AVS method.

Transformation studies are currently underway to examine the effect of pyrite nucleation and growth rate on As uptake. We are also currently expanding the use of chromatographic separations (IC-HG-AFS) to speciate arsenic in sulfide-bearing solutions and constrain thioarsenite stoichiometry.

ACKNOWLEDGEMENTS

Robert Ford and Robert Puls are thanked for discussions on arsenic fate and transport processes. Disclaimer: Although the research described in this poster has been funded wholly or in part by the U. S. EPA, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency; no official endorsement may be inferred.

REFERENCES

- Benning, L., Wilkin, R., Barnes, H. (2000). *Chemical Geology*, 167: 25-51.
- Berner, R. (1970). *American Journal of Science*, 268, p. 1-23.
- Clarke, M. B. and Helz, G. H. (2000). *Environmental Science and Technology*, 34: 1477-1482.
- Edenborn, H. M., Belzile, N., Mucci, A., Lebel, J., and Silverberg, N. (1986). *Biogeochemistry*, 2, p. 359-376.
- Ferguson, J. and Gavis, J. (1972). *Water Research*, 6: 1259-1274.
- Huerta-Diaz, M. and Morse, J. (1992). *Geochimica et Cosmochimica Acta*, 56: 2681-2702.
- Moore, J.N., Ficklin, W.H. and Johns, C. (1988). *Environmental Science and Technology*, 22: 432-437.
- Spycher, N. F. and Reed, M. H. (1989). *Geochimica et Cosmochimica Acta*, 53: 2185-2194.
- Webster, J. (1990). *Geochimica et Cosmochimica Acta*, 54: 1009-1017.
- Wilkin, R. T. and Barnes, H. L. (1996). *Geochimica et Cosmochimica Acta*, 60: 4167-4179.
- Wilkin, R. T. and Barnes, H. L. (1997). *American Journal of Science*, 297, p. 620-650.