

Thioarsenite formation and oxidative transformation in sulfidic waters: an experimental study

PENG HO¹, ROBERT FORD² AND RICHARD WILKIN²

¹National Academy of Sciences

²U.S. Environmental Protection Agency

Presenting Author: pengho0826@gmail.com

The transformation of arsenic oxyanions to thioanions in sulfidic groundwater plays an important role in controlling environmental mobility and toxicity of arsenic. We examined the crossover in arsenic speciation from oxyanionic to thioanionic forms in arsenite-sulfide model solutions (arsenite: $10^{-5.0}$ M; sulfide: $10^{-6.3}$ – $10^{-3.5}$ M) at pH 4.5, 5.5 and 7. We also investigated the transformation of thioarsenites as the model solutions (arsenite: $10^{-5.0}$ M; sulfide: $10^{-3.9}$ M, pH 5.5) were aged (0.2–28 d) in open containers exposed to air and closed containers within an oxygen-free glovebox. Arsenic species were quantified using a new anion-exchange chromatography method with sample/eluent pH matching [1] connected to an inductively coupled plasma mass spectrometer. At all pH conditions, the fractional abundance of arsenite decreased with increasing H_2S , indicating thioarsenite species developed progressively with increasing H_2S at the expense of arsenite. With increasing pH, the observed crossover from arsenite- to thioarsenic-dominated speciation shifted to slightly lower H_2S . In sulfide-rich model solutions, trithioarsenite dominated from pH 4.5 to 7.0. The crossover trends from our experiments were compared with predictions derived from experimental data [2] and thermodynamic models [3][4]. Comparable crossover trends between our experiments and Eary's data [2] at pH 4.5 and 5.5 suggest the need to re-examine the thioarsenic stability constants in existing thermodynamic models. The aging experiments showed that arsenite was the predominant species throughout aging of the model solutions under air exposure while trithioarsenite was predominant during the first 7 d; after 14 d arsenite became dominant in solutions stored in the glovebox. Observations from the aging experiments included: 1) arsenic speciation for samples aged for 0.2 d showed the reaction between arsenite and sulfide was not yet at a stable condition; 2) the fractional abundance of trithioarsenite decreased throughout aging and arsenite increased, suggesting that the transition from trithioarsenite to arsenite was due to the loss of H_2S .

[1] Wilkin et al. (2019), *Environ. Sci. Technol.* 53, 11684–116931.

[2] Eary (1992), *Geochim. Cosmochim. Acta* 56, 2267–2280.

[3] Nordstrom and Archer (2003), In *Arsenic in Ground Water*, 1–25. Kluwer.

[4] Helz and Tossell (2008), *Geochim. Cosmochim. Acta* 72, 4457–4468.