



Redox state of dissolved arsenic in sulfidic environments; a quandary.

G. Helz (1,2), C. Neuberger (2)

(1) Center for Marine and Environmental Research, Rudjer Bošković Institute, Croatia (helz@umd.edu). (2) Department of Chemistry and Biochemistry, University of Maryland, USA.

It is agreed that in anaerobic soils and sediments, dissolved arsenate is reduced to arsenite ($\text{As}[\text{OH}]_3^0/\text{AsO}[\text{OH}]_2^-$). It is further agreed that with the onset of sulfate reduction, arsenite is converted to thiolated species. Until recently, these latter species were believed to be As^{III} species such as $\text{AsS}[\text{SH}][\text{OH}]^-$ and $\text{As}_3\text{S}_4[\text{SH}]_2^-$. Recently, persuasive ion-chromatographic evidence has shown that these thiolated species are actually As^V species: $\text{H}_n\text{As}^V\text{O}_x\text{S}_{4-x}^{n-3}$. Counter-intuitively, sulfide apparently drives As^{III} to As^V with coupled reduction of As^{III} to As^0 . Here, we present new arsenic solubility measurements in sulfidic solutions in contact with As_2S_3 -alone and $\text{As}_2\text{S}_3\text{-S}^0$ (the latter solutions containing polysulfides as well as sulfide). Polysulfides fail to enhance solubilities, as expected if As^V thioarsenates are predominant dissolved species. Seemingly, the predominant oxidation state of As does not change as $\text{As}_2^{III}\text{S}_3$ (orpiment) dissolves. An additional problem arises when the protonation equilibria of thioarsenates are considered. Based on chemical principles and upon limited empirical observations, thioarsenates are expected to be either non-protonated or monoprotinated in mildly alkaline solutions. Solubilities of such species would have a greater pH dependence than observed in experiments with As_2S_3 . Further, our effort to reinterpret the data of Wilkin et al. (2003) in terms of As^V species also requires implausible assumptions about protonation equilibria. We can find no flaw in the ion-chromatographic results, but we are unable to reconcile them with other information about arsenic speciation in sulfidic solutions. Until this problem is resolved, predictions of arsenic behavior in highly reducing environments will be in doubt.