

Electrochemical investigation of arsenic redox chemistry on pyrite

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Pyrite is known to attenuate dissolved arsenite, As(III), concentrations in anoxic environments via a surface-catalyzed reduction and precipitation of an “arsenopyrite-like” solid containing As(0) [1]. However, the exact role of the pyrite surface in the reduction mechanism is unknown. In this study, the redox behavior of As(III/V) on a pyrite microelectrode was described using amperometric techniques. As(V) was found to be redox inactive over the Eh-pH conditions of the study. However, two peaks present in cyclic voltammograms for a pyrite μ -electrode + As(III) were ascribed to: 1) As(III) reduction to a surface-bound As(0) species, and 2) the reverse oxidation reaction. Interestingly, As(III) redox reactions on pyrite occur at similar potentials to those on a platinum electrode, suggesting similar reaction kinetics/mechanism. Our results also show that the peak potential for As(III) reduction is pH dependent, suggesting that the reaction mechanism involves sorbed H⁺ on the pyrite surface.

Batch reactions of pyrite with As(III) were conducted under a range of Eh-pH conditions. Anodic stripping voltammetry and X-ray photoelectron spectroscopy (XPS) of the reacted pyrite confirm the presence of reduced As(0) on the surface of pyrite consistent with the voltammetric results. Thus, in this study we have linked fundamental electrochemical analyses with spectroscopy of surface redox products in order to better understand potential mechanism of As(III) reduction in anoxic environments.

[1] Bostick and Fendorf (2003) *Geochimica et Cosmochimica Acta*. **67(5)**: 909-921.