Reduction of Sb(V) by coupled biotic-abiotic processes under sulfidogenic conditions

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As the mining and use of antimony (Sb) continues to increase, environmental concerns involving the element have grown. Antimony(V) and (III) are the two most environmentally-relevant oxidation states, but little is known about the redox transitions between the two in natural systems. To better understand the behavior of antimony in anoxic environments, we examined the transformations of Sb(V) under sulfidogenic conditions in aqueous suspensions that contained 2 mM $KSb(OH)_6$, 50 mM Fe(III) (as ferrihydrite), 10 mM sulfate, and 10 mM lactate, and were inoculated with wetland sediment. Samples were collected over time to track changes in the concentrations of Sb, Fe(II), sulfate, and lactate, as well as the composition of the microbial community. We also examined the interaction of Sb(V) with pure Fe(II) mineral phases in aqueous suspensions containing 2 mM $KSb(OH)_6$ and 50 mM Fe(II) as either magnetite, siderite, vivianite, green rust, or mackinawite. X-ray absorption fine-structure spectroscopy was used to determine the valence state of Sb and its chemical speciation. Lactate was rapidly fermented to acetate and propionate, with the latter serving as the primary electron donor for dissimilatory sulfate reduction (DSR). The reduction of ferrihydrite was primarily abiotic, being driven by biogenic sulfide. Sb K-edge X-Ray absorption near edge structure (XANES) analysis showed reduction of Sb(V) to Sb(III) within 4 weeks, concurrent with DSR and the formation of FeS. Sb K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy analysis indicated that the reduced phase was a mixture of S- and O-coordinated Sb(III). We observed variable responses in the ability of specific Fe(II) minerals to reduce Sb(V). No reduction was observed with magnetite, siderite, vivianite, or green rust. In the presence of mackinawite, however, Sb(V) was reduced to amorphous Sb(III) sulfide. These results suggest that the reduction of Sb(V) is not likely under solely Fe(III)-reducing conditions, but is expected in sulfidogenic environments.