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Ultrastructure, aggregation-state, and crystal growth of biogenic nanocrystalline sphalerite and wurtzite

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ABSTRACT

In this study, we investigated the size, submicrometer-scale structure, and aggregation state of ZnS formed by sulfate-reducing bacteria (SRB) in a SRB-dominated biofilm growing on degraded wood in cold ($T \sim 8$ °C), circumneutral-pH (7.2–8.5) waters draining from an abandoned, carbonate-hosted Pb-Zn mine. High-resolution transmission electron microscope (HRTEM) data reveal that the earliest biologically induced precipitates are crystalline ZnS nanoparticles 1–5 nm in diameter. Although most nanocrystals have the sphalerite structure, nanocrystals of wurtzite are also present, consistent with a predicted size dependence for ZnS phase stability. Nearly all the nanocrystals are concentrated into 1–5 μm diameter spheroidal aggregates that display concentric banding patterns indicative of episodic precipitation and flocculation. Abundant disordered stacking sequences and faceted, porous crystal-aggregate morphologies are consistent with aggregation-driven growth of ZnS nanocrystals prior to and/or during spheroid formation. Spheroids are typically coated by organic polymers or associated with microbial cellular surfaces, and are concentrated roughly into layers within the biofilm.

Size, shape, structure, degree of crystallinity, and polymer associations will all impact ZnS solubility, aggregation and coarsening behavior, transport in groundwater, and potential for deposition by sedimentation. Results presented here reveal nanometer- to micrometer-scale attributes of biologically induced ZnS formation likely to be relevant to sequestration via bacterial sulfate reduction (BSR) of other potential contaminant metal(loid)s, such as Pb^{2+}, Cd^{2+}, As^{3+} and Hg^{2+}, into metal sulfides. The results highlight the importance of basic mineralogical information for accurate prediction and monitoring of long-term contaminant metal mobility and bioavailability in natural and constructed bioremediation systems. Our observations also provoke interesting questions regarding the role of size-dependent phase stability in biomineralization and provide new insights into the origin of submicrometer- to millimeter-scale petrographic features observed in low-temperature sedimentary sulfide ore deposits.