Comparison of biogenic and abiogenic sphalerite (ZnS) nanoparticles: Redox reactivity and surface photocatalysis

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Microbial reduction of sulfate is the major source of sulfide in low-temperature geochemical settings, and thus, an important mechanism for metal sulfide formation (e.g., FeS, ZnS, PbS, CdS) in seawater, critical zones, and stream, lacustrine, estuarine, and marine sediments. Intriguingly, recent studies have revealed that a significant portion of biogenic sulfides initially occur and/or remain as nanominerals (down to a few nm) in nature, indicating that these sulfides may have distinctively high reactivity (in terms of redox reactions, dissolution, and surface adsorption and catalysis) due to their small size. To systematically explore the physicochemical properties of nanosulfides produced by sulfate-reducing bacteria, we have prepared sphalerite (ZnS) nanominerals via both biological pathways and abiotic synthesis, and have developed procedures to investigate and compare their oxidative dissolution behavior under various solution conditions. Using a probe (APF), we are also testing their photocatalysis efficiency, in terms of promoting $OH^{\cdot}$ formation by reacting with H_2O/O_2 under UV illumination. The ultimate goal of this study is to understand how the physicochemical properties of biogenic nanosulfides may contribute to defining the mineral's fate, transformation, and interaction with surrounding components in the environment.

Specifically, we inoculate the Zn-amended metal toxicity medium (MTM) with 1% *Desulfovibrio desulfuricans* inoculum and incubate the mixture for 48 hr to yield biogenic ZnS, and we adopted a surfactant-based method to produce abiogenic ZnS nanoparticles. X-ray powder diffraction analysis (XRD), transmission electron micrographs (TEM), and selected area electron diffraction analysis (SAED) of the abiogenic and biogenic ZnS show that both products are composed of sphalerite nanocrystals with a uniform size of ~ 5 -10 nm. Preliminary dissolution results also confirmed that the methods used to remove residue cellular components in biogenic ZnS and surfactant in abiogenic ZnS are effective. The potential results of this study may have implication for a myriad of geological and environmental processes as well as for materials science and biomedical applications.