Submicron-scale isotopic variations within biogenic ZnS record the mechanism and kinetics of extracellular metal-sulfide biomineralization

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Spheroidal aggregates (1-5 um) of ZnS nanoparticles form by bacterial sulfate reduction (BSR) in a biofilm growing in an abandoned mine. Here we use microanalytical and molecular methods to constrain the potential of biofilm-dwelling sulfate reducing bacteria (SRB) to sequester aqueous metals as sulfides.

Flux calculations for the mine/biofilm system yield a BSR rate ~10^{-16} mol SO_4^{2-} $cell^{-1}$ day^{-1}. Given estimated cell densities, we predict precipitation of ~2 ug ZnS cm^{-3} day^{-1}. Ten cm^3 of SRB biofilm can produce several grams of ZnS in 5-20 yrs, consistent with measured wt% ZnS accumulated over ~35 years of biofilm growth.

NanoSIMS analyses revealed 10-20‰ $\Delta^{34}S$ across isotopically light ZnS spherules, consistent with a temporal record of changing BSR rate. This interpretation, however, required greater insight into the mechanism and stability of nanoparticle aggregation.

NanoSIMS and infrared spectroscopy also showed organically-bound nitrogen and amide absorptions diagnostic of polypeptides to be concentrated within spherules. We mechanically separated the biofilm into organic- and ZnS-rich fractions, and extracted and compared total proteins from each. The ZnS-rich fraction contained an increased concentration of ~30kD protein(s).

We also conducted aggregation experiments on synthesized nano-ZnS. Results showed that individual amino acids such as cysteine increased nanoparticle aggregation rate by ~4X. We infer that proteins play a previously unrecognized role in the formation of extracellular biogenic sulfide aggregates. These findings hold importance for understanding the mobility and stability of colloidal metal sulfides in the environment.