Minerals and Microbes in a Euxinic Ecosystem

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Proterozoic ocean euxinia was widespread and affected evolution and geochemical cycling on a global scale for perhaps billions of years. On the modern Earth, euxinic ecosystems are isolated and relatively remote, such that important relationships among minerals, organic matter, and biological activity are yet not well understood. We describe a Proterozoic analog ecosystem in a terrestrial aquifer accessible via more than 25 km of cave passages. The passages lead from an energy-rich, microoxic zone at the water table surface to deeper conduits isolated from the cave atmosphere and filled with sulfidic (~800 mM) water – the euxinic zone. We have begun a system-wide investigation of the geochemistry and microbiology of the euxinic zone, including metagenomics and bulk and micron/nanometer scale mineralogy and geochemistry. Our initial investigations revealed that the ecosystem is ecologically coherent on a kilometer scale, microbiologically very diverse, and dominated by relatives of sulfur-cycling Proteobacteria and anaerobic, polymer-degrading Chloroflexi. Deltaproteobacteria sequences are especially abundant (20-30% of amplicon sequences) and many represent novel clades. Meter-scale, net-like biofilms that form in the euxinic water column and on conduit walls are widely but heterogeneously distributed. Although many taxa in the biofilms are related to anaerobic clades, the fractured and heterogeneous nature of the karst aquifer lead us to wonder whether the biofilms are indicators of energy made available by diffuse penetration of slightly more oxidized water, similar to the situation that would arise around oxygen oases in Proterozoic oceans. Consistent with this hypothesis, the biofilms contain high concentrations of S(0) and iron sulfides. The iron sulfides are embedded in organic matrices and include both pyrite and marcasite that co-occur as small grains within framboids and as larger euhedral crystals. NanoSIMS and δ^{56}Fe data also suggest that iron sulfides precipitating in the euxinic zone have multiple origins that strongly affect their crystal structure, trace metal composition, and isotopic signatures. Future work will investigate the potential role of oxygen in powering the biofilms using oxygen sensors with nanomolar detection limits, and on understanding the role of microbial metabolisms and organic matrices in determining iron sulfide mineral structures, trace metal contents, and isotopic signatures.

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