Fate of S^0 in a Sulfidic Aquifer

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The Frasassi Cave system (Italy) is intersected by a cold and perennially sulfidic (~500 μM) aquifer that mixes with oxygenated meteoric water in the upper 3-10 meters. Bulk [O_2] is typically <0.2 to 25 μM. The mixing zone therefore presents an ideal setting to study dark sulfur cycling under oxygen-limiting conditions, and is a potential analog to environments that produced economically important sulfur deposits in the past via partial sulfide oxidation in the subsurface. Conspicuous white mats dominated by non-vacuolate, freshwater *Beggiatoa* colonize sediment surfaces in the mixing zone streams and pools. *In situ* microsensor profiles showed that the mats consume O_2 and sulfide but do not produce acid, suggesting they incompletely oxidize H_2S to S^0. However, in the anoxic sediment below the mats we observed a strong pH decrease with depth. Elemental S concentrations in the mats are >20% by mass, while underlying organic-rich sediments contain <5% S^0.

In order to identify microbial populations potentially responsible for acid production and S^0 consumption in the absence of significant O_2, we analyzed the sediments using Illumina high-throughput sequencing with universal 16S rRNA primers. Up to half of the total OTUs belonged to only 3 clades: Sulfurovumales (ε), "Thiobacillus baregensis" (β), and *Desulfocapsa thiozymogenes* (δ), plus smaller populations of anaerobic heterotrophs related to *Cytophaga* and *Anaerophaga*. Both Sulfurovumales and close relatives of "T. baregensis" are though to be autotrophic sulfur oxidizers that can access zero-valent sulfur in the environment[1,2]. The presence of large populations of putative S^0 oxidizers in anoxic sediment below dense sulfide-oxidizing *Beggiatoa* mats is surprising, and suggests either inactive populations or an unexpected role for Sulfurovumales and "T. baregensis" in S^0 reduction. In culture, *D. thiozymogenes* carries out autotrophic S^0 disproportionation. Fe analyses and field observations indicate active Fe redox cycling, which could enhance the energetic yield for S^0 disproportionation via sulfide scavenging. Overall our data suggest that S^0 disproportionation is the primary sink for S^0 generated in the Frasassi aquifer mixing zone microbial mats.

[1] Pjevac et al. 2014, [2] Ito et al. 2004