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Microbially‑mediated aerobic oxidation of trace element-bearing pyrite in neutral-pH sandstone aquifer sediments

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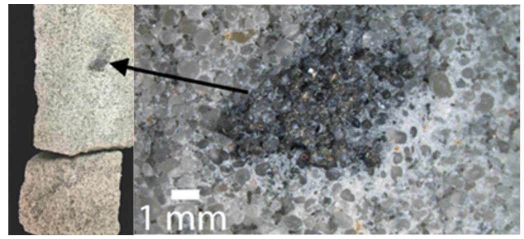
Oxidation of pyrite in the terrestrial subsurface is commonly associated with lowering of groundwater pH and release of constituent trace elements to solution. Although the central role of microbial activity in pyrite oxidation is well understood in acid mine/rock drainage and other low-pH (e.g. pH < 2) environments, the role of microorganisms in mediating pyrite oxidation under circumneutral pH conditions is not well understood. We report here on the potential for aerobic microbial metabolism to promote circumneutral pH oxidation of trace element-bearing pyrite in Cambrian-age sandstones from Trempealeau County, WI (USA). Microbial activity accelerated ca. 2-5 fold the rate and extent of sulfate release (a direct measure of pyrite oxidation) from reduced pyrite-bearing sediments. pH values dropped to 3 in biotic microcosms which contained limited carbonate (dolomite) buffering capacity. The overall surface area-specific rate constant for pyrite oxidation inferred from batch reaction modeling of these microcosms was 25-fold higher than for the corresponding abiotic reactors. Calcium and magnesium were proportionally released to solution with sulfate as a result of carbonate and/or Ca-aluminosilicate dissolution by acid generated from pyrite oxidation. When the amount of acid from pyrite oxidation exceeded the system buffering capacity, metals were selectively released from the geological material. No significant release of trace metals took place in abiotic reactors, which showed much lower rates of pyrite oxidation. These findings suggest that groundwaters in contact with pyrite-containing geological formations contain microorganisms capable of accelerating the oxidation of native pyrite in those formations. Analysis of microbial community composition in the microcosms by 16S rRNA gene amplicon sequencing showed enrichment in organisms related to taxa associated with chemolithotrophic metabolism from background levels (< 2%) to up to 40% of total sequence reads. A reactive transport modeling exercise demonstrated how microbial acceleration of pyrite oxidation rate could have a crucial, near-term (< 10 years) impact on pH decline and trace element release in response to influx of oxygenated groundwater into previously reduced geological strata. Our results have key implications for controls on the onset of low-pH conditions and associated changes in groundwater quality in drinking water wells located within pyrite-bearing geological formations.



Disseminated pyrite grains in sandstone aquifer sediments are subject to microbially-accelerated reaction with dissolved oxygen, leading to more rapid decline in pH and release of trace elements to solution compared to abiotic reaction pathways.