

Hydroxyl Radical Production from Abiotic Oxidation of Pyrite under Neutral Conditions: Effect of Low-molecule-weight Organic Acids

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Oxidation of pyrite under neutral conditions controls iron and sulfur cycling and electron conduction in marsh sediment [1, 2], wherein the low-molecule-weight organic acids (LOA) widely exist in pore waters. Hydroxyl radicals produced from pyrite oxidation by O₂ can lead to the oxidation of organics and redox sensitive elements. In this study, the abiotic oxidation of pyrite by O₂ under neutral conditions were investigated for production of hydroxyl radicals (•OH) in the presence of LOA. Batch experiments were conducted at 50 g/L pyrite and 20 mM benzoate acid and the pH was controlled by buffers. We found that the cumulative •OH concentrations reached 7.5 μM at pH 7 within 420 min in the absence of LOA, while increased to 14.8, 12.0 and 11.2 μM in the presence of 1 mM EDTA, citrate and oxalate, respectively. With the citrate concentrations increased from 0.5 to 5.0 mM, the cumulative •OH concentrations increased from 10.3 to 27.3 μM at pH 7. With the pH increased from 6.0 to 8.0, in the absence of LOA the cumulative •OH concentrations decreased from 23.3 to 2.1 μM, while in the presence of 3.0 mM citrate the concentrations decreased from 135.0 to 8.8 μM. Abundant dissolved Fe(III) species were observed in the presence of LOA. The results of FT-IR and EXAFS showed that ferrihydrite as the main Fe(III) minerals existed in oxidized pyrite surface in the absence and presence of citrate. The reaction of H₂O₂ with Fe(II)-LOA contributed to •OH production in the presence of LOA. We conclude that the LOA chelated with Fe(II), limited the precipitation of Fe(III) and increased the rate of H₂O₂ production from O₂ reduction by Fe(II) and pyrite, thus facilitated •OH production from pyrite oxidation under neutral conditions. The •OH may further oxidize the LOA or other organics, which affects the cycling of carbon and the transformation of substance.

[1] Luther et al. (1992) *Mar. Chem.* **23**, 295-309. [2] Nielsen et al. (2010) *Nature* **463**, 1071-1074.