Multiple Reaction Pathways during Radiolytic Oxidation of Pyrite

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Passage of ionizing radiation through groundwater produces a complex mixture of short-lived ions, free radicals, and excited molecules that participate in a wide range of chemical reactions and accelerate water-rock interaction. Radiolysis of groundwater in contact with sulfide minerals or elemental sulfur can produce plumes of partially to fully oxidized sulfur species, thereby stimulating microbial metabolism in unexpected subsurface environments. In order to study fractionation of sulfur isotopes during radiolysis, initial experiments were performed using sealed quartz tubes that contained pyrite and millimolar solutions of hydrogen peroxide (H_2O_2) that were reacted at temperatures from 4 to 150^{o}C over time periods of days to week. Mineralogical, chemical, and stable isotopic date from H_2O_2 experiments reveal multiple pathways for pyrite oxidation and distinct assemblages of products at difference temperatures. Sulfur isotopic signatures of oxidized products are enriched in ^{32}S by 0.5 to 2‰ compared to source sulfate.

Radiation experiments were carried out using a ^{60}Co gamma source at the Radiation Laboratory of the University of Notre Dame. Sealed quartz tubes that contained pyrite and deoxygenated DI water were irradiated from 1 to 14 hours with a dose rate of 11.3 krad/min (113 Gy/min). Initial experiments produced oxidized sulfur as gaseous (e.g., SO_2) and aqueous (e.g, SO_4) species at concentrations directly correlated to the volume of water and total irradiation dose.

Radiolysis proves to be an effective mechanism for the production of oxidizing species in geologically long-lived oxidizing systems. Iron sulfide minerals are decomposed and iron oxide/hydroxide minerals and sulfate ions are produced. Recognizing geochemical signatures of radiolytic oxidation is particularly important for understanding biotic and abiotic reaction pathways in environments where molecular oxygen is negligible and for assessing potential sources of chemical energy for microbial metabolism in the deep subsurface of Earth and Mars.

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