

**EXPERIMENTAL STUDY OF RADIOLYTIC OXIDATION OF PYRITE: IMPLICATIONS FOR MARS-RELEVANT CRUSTAL PROCESSES.** L. Lefticariu<sup>1</sup>, L. M. Pratt<sup>1</sup>, J. A. LaVerne<sup>2</sup>, <sup>1</sup>Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, (lleftica@indiana.edu), <sup>2</sup> Radiation Laboratory, University of Notre Dame, Notre Dame, IN 47405.

**Introduction:** Radiolytic dissociation of water produces a highly reactive combination of oxidizing (e.g.,  $\text{H}_2\text{O}_2$ , OH radicals, and  $\text{O}_2$ ) and reducing (e.g., H atoms and  $\text{H}_2$ ) species [1]. In subsurface environments, radiolysis can produce gradients of both electron acceptors and electron donors that are possible sources of metabolic energy [2]. Radiation-induced chemical reactions have particular significance in geologic environments where molecular oxygen derived from the atmosphere is a negligible input. Results from geochemical studies of unconformity-related uranium deposits indicate that radiolysis is considerably under recognized as a naturally occurring source of chemical energy for biotic and abiotic reactions. In particular, radiolysis of water coupled to oxidation of sulfide minerals [3] or elemental sulfur [4] can produce gradients of partially to fully oxidized sulfur species that might be suitable for microbial metabolism.

Recent data from Mars Exploration Rovers provide multiple lines of evidence indicating the extensive presence of sulfates on Mars's surface. Measurements by NASA's Mars Pathfinder and Viking landers showed that sulfur is a substantial component of soil dust and surface rocks [5]. Evidence of hydrated sulfate salt deposits in the Martian tropics comes from near-infrared spectral data on Mars Express [6]. In addition, sulfates have been identified in SNC meteorites, which contain salt minerals including sulfates, up to 1% by volume. These evidences taken together strongly suggest that sulfate minerals are on the Mars surface and within the upper lithosphere. Sulfate minerals are a potential archive of information on both the sulfur geochemical cycle and history of water on Mars.

On Earth,  $\text{H}_2\text{O}_2$  has been detected as a stable product of radiolysis in anoxic subsurface environments associated with uranium deposits. Although  $\text{H}_2\text{O}_2$  is generally regarded as of little or no geochemical significance on Earth, it is increasingly clear that the  $\text{H}_2\text{O}_2$  molecule plays a pivotal role in Martian atmospheric and soil chemistry. Trace-level concentrations of  $\text{H}_2\text{O}_2$  in Mars atmosphere have been measured recently using mid-infrared [6] and sub-millimeter spectroscopy [7] employing ground-based telescopes.

Traditional models for the oxidation of sulfide minerals in aerobic environments involve the presence of molecular oxygen and water, as the key oxidants for sulfides. In recent years, however, geochemists have increasingly recognized that radiolysis could be an

effective process in producing active oxidizing species on Mars and can play a pivotal role as a source of oxidants in deep vadose zones.

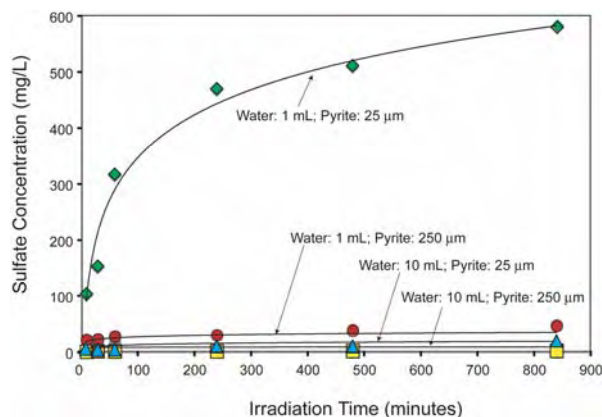
**Experimental Methods:** In order to evaluate the efficiency of radiolytic sulfide oxidation in the production of sulfate gradients and the stable isotope signatures of sulfur products, we performed a series of radiation experiments using Park City pyrite and DI water. Radiation experiments were carried out using a  $^{60}\text{Co}$  gamma source at the Radiation Laboratory of the University of Notre Dame. The dose rate was of 11.3 krad/min (113 Gy/min), as determined by the Fricke dosimeter. Water used in these experiments was deoxygenated to minimize competing reactions with  $\text{O}_2$ . These water/pyrite mixtures were degassed and flame sealed in quartz tubes of 2 cm diameter and 10 cm length. The tubes were irradiated from 1 to 14 hours. After irradiation, samples were analyzed for gaseous, aqueous, and solid species produced during radiolysis.

**Results and Discussion:** Radiolysis of water generates a wide spectrum of radical and molecular products. Within a few picoseconds of the initial energy radiation event water decomposition produces hydroxyl radicals ( $\text{OH}\bullet$ ), solvated electrons ( $e_{\text{aq}}^-$ ), and hydronium ions ( $\text{H}_3\text{O}^+$ ). The excited water molecule can produce superoxide radical anion ( $\text{O}_2^{\bullet-}$ ), hydroperoxyl radical ( $\text{HO}_2\bullet$ ), hydrogen radicals ( $\text{H}\bullet$ ) and water [1]. Upon continuous irradiation, steady-state concentration of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ , and smaller amounts of dioxygen ( $\text{O}_2$ ) result and no further water decomposition occurs.  $\text{H}_2\text{O}_2$  is the main molecular oxidizing species produced during radiolysis, and not  $\text{O}_2$ . It is usually assumed that the primary mechanism for  $\text{H}_2\text{O}_2$  formation is the fast combination reaction of hydroxyl ( $\text{OH}\bullet$ ) radicals [8].

**Products of radiolytic oxidation of pyrite.** Molecular hydrogen was the dominant gas collected at the end of pyrite-water irradiation experiment. Molecular oxygen was more than an order of magnitude lower than the  $\text{H}_2$ . The  $\gamma$  radiolysis of liquid water in closed systems leads to a low, constant  $\text{H}_2$  concentration due to back reactions [8]. The initial experiments showed that the radiation chemical yield of molecular hydrogen increases with increase in the total irradiation dose. For the same total irradiation dose, the yield of  $\text{H}_2$  increases with decrease in the initial amount of water.

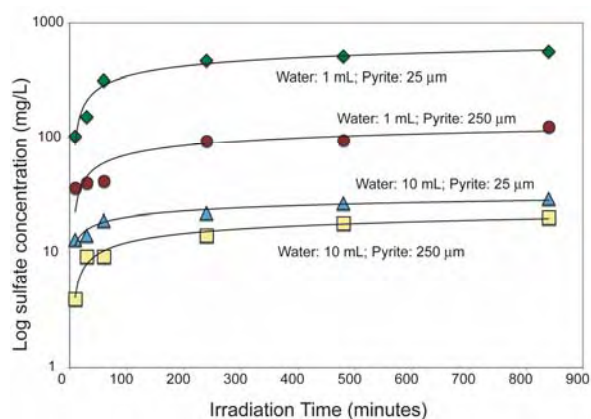
The dominant sulfur products collected during the

initial experiments were aqueous sulfate and trace amounts of gaseous sulfur dioxide. Sulfate was the only aqueous sulfur species detected by ion chromatography methods in the final solution.



**Figure 1.** Variations in yield of aqueous sulfate for small (25  $\mu\text{m}$ ) and large (250  $\mu\text{m}$ ) grain size pyrite as a function of irradiation time.

Regardless of the pyrite grain size and the water/pyrite ratio, the yield of aqueous sulfate directly correlates with total irradiation dose and inversely correlates with pyrite grain size (Fig.1). Unexpectedly, the yield of aqueous sulfate inversely correlates with water/pyrite ratio (Fig.2). Thus, higher yields of aqueous sulfate were obtained in experiments with small water/pyrite ratio compared to those with high water/pyrite ratio.



**Figure 2.** Log yields of aqueous sulfate as a function of irradiation time.

These preliminary results suggest that the chemical interactions during radiolysis of pyrite with  $\gamma$ -rays re-

sult in the generation of both reduced (e.g.,  $\text{H}_2$ ) and oxidized (e.g., aqueous sulfate) products. Variations in yield of radiolytic products correlate in a complex manner with irradiation dose, pyrite grain size, and water/pyrite ratios. The increased sulfate yield from small pyrite particles is attributed to an increase in probability of interaction between radiolytically produced oxidants and pyrite surface. The reactions occurring on a surface usually include several steps such as diffusion of the reacting molecules to the surface, adsorption on the surface (the reactive sites), reaction on the surface, desorption of products, and diffusion of the desorbed products. Further studies will specifically examine the surface interaction between radiolytically produced oxidants and pyrite oxidation using synchrotron-based methods. These further studies will also examine the effect of pH on the aqueous sulfate speciation for different experimental conditions.

**Conclusions:** Recognition that crustal radiolysis is an efficient mechanism in the production of oxidizing species in geologically long-lived oxidizing systems has profound implications for assessing microbial metabolism in the deep subsurface on Earth and Mars. Radiolytic processes are effective in producing hydrogen and sulfate gradients even in water-limited environments, such as predicted for Mars.

**References:** [1] Garrett B. C. et al., 2004, *Chem. Rev.*, **105**, 355-390. [2] Indiana Princeton Tennessee Astrobiology Initiative: <http://www.indiana.edu/~deeplife/research.html>. [3] Fayek, M., et al., 1997, *Appl. Geochem.* **12**, 549-565. [4] Carlson, R. W. et al., 2002, *Icarus* **157**, 456-463. [5] Bibring et al., 2005, *Science* **307**, 1576-1581. [6] Squyres et al, 2004, *Science*, **306**, 1698-1703. [7] Encrenaz et al, 2004, *Icarus* **170**, 424-429. [8] Clancy et al., 2004, *Icarus* **168**, 116-121. [9] Pastina B., and LaVerne, J.A., 20001, *J. Phys. Chem.*, **105**, 9316-9321.