

**INTERACTION OF RADIOLYTICALLY PRODUCED OXIDANTS WITH THE PYRITE SURFACE: A CRYSTAL TRUNCATION ROD (CTR) STUDY.** L. Lefticariu<sup>1</sup>, L. M. Pratt<sup>1</sup>, P. J. Eng<sup>2</sup>, S. K. Gose<sup>2</sup>, and D. L. Bish<sup>1</sup>, <sup>1</sup>Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, (lleftica@indiana.edu), <sup>2</sup>GSECARS, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL-60439, US).

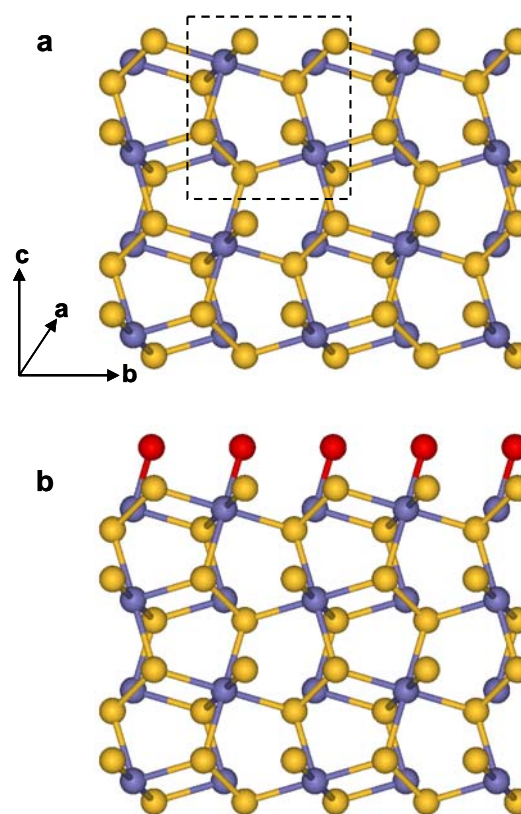
**Introduction:** Data collected by Viking, Pathfinder, and the Mars Exploration Rovers and analyses of Martian meteorites strongly suggest that sulfate minerals might be widespread not only on the Mars surface but also within the upper lithosphere. The present Martian thermal conditions, specially the lack of liquid water, preclude the alteration of sulfide minerals in the Martian soil. Sulfide oxidation can occur in the deep subsurface, where liquid water is likely to be present [1]. In order for oxidation of sulfide minerals to occur, a Martian oxidant must be present. We suggest radiolysis as effective mechanism for production of oxidizing species that are effective oxidants for sulfide minerals [2]. Interactions of radiolytically produced oxidants with mineral surfaces can play a significant role in geological environments where oxygen is a negligible input. In particular, the interaction of oxidizing species with sulfide minerals is the first stage in development of sulfur species which can be transferred into aqueous solution.

Many studies have been dedicated to understand the mechanisms and rates of aqueous pyrite oxidation using a plethora of methods including surface-sensitive, synchrotron-based methods [3], [4]. However, no theoretical or experimental studies have been undertaken to date to understand the interaction of radiolytically produced oxidants and sulfide mineral surfaces or the nature of the pyrite surfaces under radiolytically produced oxidation conditions.

**Experimental Methods:** To investigate the interaction of radiolytically produced oxidants with the pyrite surface, crystal truncation rod (CTR) diffraction data have been collected at Advanced Photon Source (APS) Argonne National Laboratories. Previous studies have shown that CTR diffraction is a powerful method in elucidating the chemical speciation of the aqueous solid interface [5], [6], [7]. Experiments were performed using single crystal cubes of natural pyrite (Logrono, Spain) that were cut to approximately 1-cm square. Both natural and polished (001) faces were used. The crystals were cleaned in 10 mM nitric acid, and multiply rinsed with DDI water. Measurements were performed at the University of Chicago GSECARS 13-ID beam line. X-rays from the first harmonic of an APS undulator "A" are monochromatized to 10 keV using a double-crystal Si (111) monochromator. Diffraction data were collected under

aqueous conditions using the kappa-geometry diffractometer in trajectory scanning mode. Initial data were collected from an acid-cleaned, dry pyrite surface to provide a baseline substrate structure necessary for interpreting spectra following surface reactions. Additional measurements were made on cleaned and polished pyrite surfaces that were exposed to water in a radiation environment to determine the surface effects of radiolytically produced oxidants.

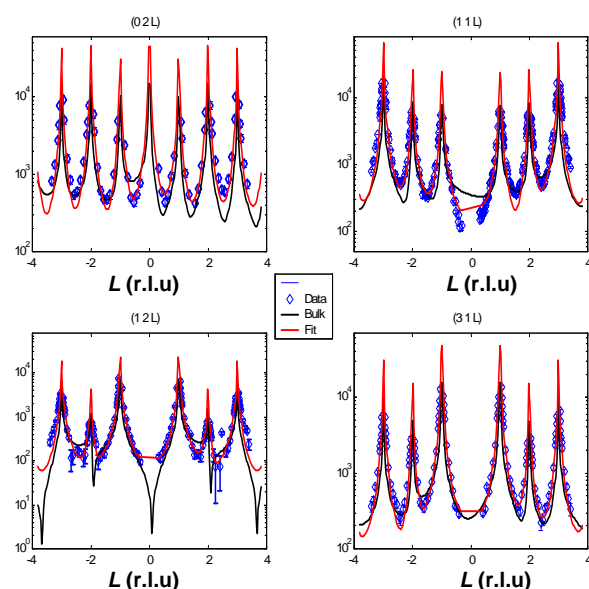
**Results:** One of the surprising results is the natural growth face of pyrite after cleaning produced a very smooth and ordered surface with near perfect alignment between the optical and crystallographic surfaces.



**Figure1: Preliminary models for pyrite (001) surface. (a) shows the bulk model with S termination and (b) shows the model with Oxygen from the hydroxyl layer on the single S-terminated surface, which is derived from the best fit model.**

Whereas surfaces prepared by diamond and CMP polishing were very rough and disordered – unsuitable for CTR measurements.

After performing an optical and crystallographic alignment on the diffractometer CTR scattering measurements were performed using a photon counting scintillation detector. Ten unique CTRs were collected by rocking the sample through each rod (H, K) at different L's integrating the intensities and averaging symmetry equivalents. A preliminary model was built and data fit to this model using the ROD analysis program [8]. The preliminary model that gives the best fit suggests a sulfur terminated layer (Figure 1a). The addition of a partially occupied hydroxyl layer (Oxygen) (Figure 1b) further improved the fit. Figure 2 shows the best fit to the data along with the CTR profile for the bulk termination.



**Figure 2:** Experimental and best fit theoretically calculated structure factors as a function of the perpendicular momentum transfer for the pyrite (001) surface. Theoretical curves for both the bulk terminated surface (black) and best fit surface model (red) CTRs are shown.

**Preliminary conclusions:** Based on our first dataset it was interesting to discover that the natural growth surface produce such a high quality surface providing an ideal platform for further study. Figure 1 shows that the outer termination is the sulfur bond. This termination will dictate in many cases the reactivity of pyrite surface toward radiolytically produced oxidants.

Since sulfur is a hydrophobic element, the presence of radicals produced during radiolysis is essential for pyrite oxidation. If oxidants formed during water cleavage are available, they may be involved in (1) sulfide oxidation or (2) competing reactions with other substrates.

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