

## Molecular Characterization of the Hydrated Pyrite (001) Surface by Ambient Pressure XPS

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Pyrite (FeS<sub>2</sub>) is a common sulphide mineral in anaerobic sediments as well as igneous and metamorphic rocks. The oxidation of pyrite generates acidity, dissolved iron and other metals that can have severe environmental impacts. We currently lack an experimentally verified model for the molecular structure and speciation of pyrite surfaces, limiting our ability to understand and predict surface adsorption and redox reactions.

Pyrite lacks a natural cleavage surface, is easily oxidized, and is very difficult to synthesize as macroscopic crystals. Consequently, it is uncertain whether studies performed on fractured or powdered bulk crystals represent natural termination surfaces. We have developed a chemical-mechanical approach for treating pyrite (001) surfaces of natural pyrite crystals generating terraced surfaces free from sulfur or iron oxidation products.

We used ambient pressure X-ray photoelectron spectroscopy (XPS) with synchrotron soft-X-ray excitation to characterize the chemical state of S and Fe on pristine (001) surfaces, and the chemical and electrochemical trends upon exposure to partial pressures of water (up to 1 mTorr) and oxygen (up to 1  $\mu$ Torr).

The S<sup>2-</sup> species observed in prior studies is absent from pristine surfaces prepared here, indicating it to be an artifact of fracturing or sputtering. When generated, it is preferentially oxidized by O<sub>2</sub>. The data confirm the FeS<sub>2</sub> (001) surface to be terminated solely by Fe<sup>2+</sup> and S<sub>2</sub><sup>-</sup> groups and constrain the stoichiometry.

We measured a water sorption isotherm at room temperature, achieving sub-monolayer coverage up to 1 mTorr. Molecular oxygen physisorbs to wet pyrite causing shifts in the surface valence band levels without any oxidation at room temperature over 12 hours. Surface oxidation requires elevated temperature or higher water activity presently not achievable *in situ*. The data confirm the role for water for initiating pyrite oxidation and suggest chemical and electrochemical models for this step.