

## **The interaction of pyrite {100} surfaces with O<sub>2</sub> and H<sub>2</sub>O: Fundamental oxidation mechanisms**

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### **ABSTRACT**

The interaction of gaseous O<sub>2</sub>, H<sub>2</sub>O, and their mixtures with clean {100} surfaces of pyrite (FeS<sub>2</sub>) were investigated in ultra-high vacuum using scanning tunneling microscopy and spectroscopy (STM-STS), ultraviolet photoelectron spectroscopy (UPS) and ab initio calculations. He I UPS spectra of O<sub>2</sub> exposed surfaces show that the density of states decreases at the top of the valence band but increases deeper in the valence band. These changes indicate oxidative consumption of low binding energy electrons occupying dangling bond surface states localized on surface Fe atoms, and the formation of Fe-O bonds. No such changes in the valence band spectra are observed for pyrite surfaces exposed to H<sub>2</sub>O. However, UPS spectra of surfaces exposed to mixtures of O<sub>2</sub> and H<sub>2</sub>O demonstrate that the combined gases more aggressively oxidize the surface compared to equivalent exposures of pure O<sub>2</sub>. Atomically resolved STM images of O<sub>2</sub> and O<sub>2</sub>-H<sub>2</sub>O exposed surfaces show discrete oxidation “patches” where reacted surface Fe sites have lost surface state density to the sorbed species. STS spectra show the removal of highest occupied and lowest unoccupied surface state density associated with dangling bond states consistent with the interaction of sorbates with surface Fe sites. Ab initio cluster calculations of adsorption energies and the interaction of O<sub>2</sub> and water species with the surface show that O<sub>2</sub> dissociatively sorbs and H<sub>2</sub>O molecularly sorbs to surface Fe. For the mixtures, the calculations indicate that H<sub>2</sub>O dissociatively sorbs when O<sub>2</sub> is present on the surface. Charge population analyses also show that the surface S sites become more electropositive in this environment which should allow for easier formation of S-O surface bonds, thus promoting the production of sulfate during oxidation.