

Sulfur and iron surface states on fractured pyrite surfaces

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ABSTRACT

Pyrite has a poor {001} cleavage. Unlike most other minerals with a rocksalt-type structure, pyrite typically fractures conchoidally, demonstrating that parting surfaces are not constrained to the {001} crystallographic plane. Cleavage along {001} require rupture of only Fe-S bonds, but pyrite consists of both Fe-S and S-S bonds. Analysis of bond energies indicates that S-S bonds are the weaker bonds and they are likely to be ruptured when pyrite is fractured. With each ruptured S-S bond, two mononuclear species (formally S¹⁻) are produced, one bound to one fracture surface and the second to the opposite fracture surface. This monomer is reduced to S²⁻ (monosulfide) during relaxation through oxidation of surface Fe²⁺ ions to Fe³⁺. These surface relaxation processes explain the surface states observed in S(2p) and Fe(2p_{3/2}) X-ray photoelectron spectra (XPS) of pyrite. The S(2p) XPS spectrum is interpreted to include bulk disulfide contributions at 162.6 eV and two surface state contributions at 162.0 and 161.3 eV. The monosulfide (S²⁻) emission is near 161.3 eV, as observed in S(2p) spectra of pyrrhotite, and the 162 eV peak is interpreted to result from the surface-most sulfur atom of surface disulfide ions. The Fe(2p_{3/2}) XPS spectrum includes three contributions, a bulk Fe²⁺ emission near 707 eV and emissions from two Fe surface states. One surface state is interpreted to be Fe²⁺ surface ions. Their coordination is changed from octahedral before fracture to square pyramidal after fracture. The consequent stabilization of the antibonding Fe d_z orbital yields unpaired electrons in the valence band resulting in multiplet peak structure in the Fe(2p_{3/2}) spectrum. Similarly, each surface Fe³⁺ ion, having contributed a non-bonding 3d electron to the valence band (bonding orbital), contains unpaired 3d electrons, resulting in multiplet splitting of its Fe(2p_{3/2}) signal. The high-energy tail observed in the Fe(2p_{3/2}) spectrum of pyrite is the product of emissions from both surface states with Fe²⁺ multiplet peaks centered near 708 eV and the surface Fe³⁺ multiplets spanning the binding energies from 708.75 to about 712 eV.