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 $S_1^{2-}$) are produced, one bound to one fracture surface and the second to the opposite fracture surface. This monomer is reduced to $S_2^{2-}$ (monosulphide) during relaxation through oxidation of surface Fe$^{2+}$ ions to Fe$^{3+}$. 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 disulphide contributions at 162.6 eV and two surface state contributions at 162.0 and 161.3 eV. The monosulphide ($S_2^{2-}$) 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 disulphide ions. The Fe(2p 3/2 ) XPS spectrum includes three contributions, a bulk Fe$^{2+}$ emission near 707 eV and emissions from two Fe surface states. One surface state is interpreted to be Fe$^{2+}$ surface ions. Their coordination is changed from octahedral before fracture to square pyramidal after fracture. The consequent stabilization of the antibonding Fe d orbital yields unpaired electrons in the valence band resulting in multiplet peak structure in the Fe(2p 3/2 ) spectrum. Similarly, each surface Fe$^{3+}$ 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 Fe$^{2+}$ multiplet peaks centered near 708 eV and the surface Fe$^{3+}$ multiplets spanning the binding energies from 708.75 to about 712 eV.

INTRODUCTION

Mineral fracture surfaces are commonly exposed to natural solutions in sedimentary environments and during mining operations. Transport of sediment within fluvial and coastal marine sedimentary environments results in innumerable grain-grain collisions, and production of fracture surfaces through abrasion. Similarly, glaciation exposes fresh fracture surfaces to natural weathering solutions. Much of the Northern Hemisphere now is blanketed in glacially derived detritus. From an industrial perspective, fresh fracture surfaces are produced by milling in preparation for flotation. Pyrite is the most common of sulphide minerals, and the chemical state of its fracture surfaces is the focus of this study.

Fractured pyrite surfaces react with aerated solutions of sedimentary environments, generally to produce Fe-oxyhydroxides and sulphuric acid. Pyrite is an abundant mineral in mine wastes where it again reacts with aerated solutions to produce high concentrations of sulphuric acid observed in acidic mine waste waters. The chemical states of pyrite and other sulphide mineral fracture surfaces are vitally important to efficient separation of ore minerals from gangue (e.g., pyrite) during flotation. A complete understanding of natural weathering processes, mineral processing, and treatment of mine wastes necessarily begins with documentation of pristine fracture surfaces, thus motivating detailed study of such surfaces.

Recent interest in the nature of sulfur species at pristine pyrite surfaces is substantial. Hyland and Bancroft (1989) and Nesbitt and Muir (1994) noted a major disulphide contribution to the S(2p) X-ray photoelectron spectra (XPS) spectrum of a fractured, unreacted pyrite surface, but required a small contribution to both the low and high energy sides of the disulphide peak to properly fit the spectrum. Bronold et al. (1994) recognized a distinct peak on the low energy side of the disulphide peak and ascribed it to a surface disulphide species. Termes et al. (1987) and Buckley et al. (1988) documented the S(2p) spectrum of