



Binding of oxygen on vacuum fractured pyrite surfaces: Reactivity of iron and sulfur surface sites

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ABSTRACT

Synchrotron radiation excited photoelectron spectroscopy (SXPS) has been used to study the interaction of oxygen with vacuum fractured pyrite surfaces. Especially valence band spectra obtained with 30 eV photon energy were analyzed to provide a mechanism of the incipient steps of pyrite oxidation. These spectra are far more sensitive to the oxidation than sulfur or iron core level spectra. It is shown that oxygen is adsorbed on Fe(II) surface sites restoring the octahedral coordination of the Fe(II) sites. This process leads to the removal of two surface states in the valence band which are located at the low and high binding energy sides of the outer valence band, respectively. The existence of these surface states which have been proposed by calculations is experimentally proven. Furthermore, it is shown, that the sulfur sites are more reactive than expected. Sulfite like species are already formed after the lowest oxygen exposure of 10 L. This oxidation occurs at sulfur sites neighboring the Fe(II) surface sites. Oxidation of the S^{2-} surface sites which were considered as the most reactive species in former studies is second. No iron(III) oxides are formed during oxygen exposure, supporting the assumption that water plays an important role in the oxidation mechanism of pyrite surfaces.

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1. Introduction

1.1. General

Pyrite (FeS_2) is the most abundant sulfide mineral. Although often considered as the unwanted companion of the more valuable sulfides of lead, nickel and copper, it is the main component in sulfide mine wastes where it undergoes weathering processes. The resulting sulfuric acid and iron oxyhydroxides are responsible for the production of acid mine drainage which contaminates soil and surface water.

Furthermore, the surface properties of pyrite are important when separating it from other sulfide minerals by froth flotation and during separation from coal. In these processes the pyrite surface is modified by the addition of organic adsorbents (e.g. xanthates) as well as the conditions of the aqueous slurry (pH value, electrochemical potential).

Minimizing acid mine drainage and optimizing recovery of metals from sulfides require a detailed understanding of the redox chemistry of pyrite not only on a macroscopic but also on a microscopic scale especially at the surface.

Determined efforts to address these problems have been made in the last 25 years introducing modern surface science techniques such as synchrotron radiation excited photoelectron spectroscopy into mineralogy.

There is now a general agreement that pyrite shows a conchoidal fracture producing not only Fe and S surface sites caused by the fracture of Fe–S bonds but also S^{2-} and Fe(III) sites which are produced by the rupture of S–S bonds followed by a charge transfer from Fe(II) to the resulting S^- species. This process forms a monosulfide S^{2-} and a Fe(III) site [1]. These findings based on experiments (mainly photoelectron spectroscopic studies) have been confirmed by DFT calculations [2] and are summarized in Fig. 1. In addition, reactivity studies of the pyrite mineral have been reviewed by Murphy and Strongin in 2009 [3] and they summarize, with great effect, how a combination of different surface science techniques with and without lateral resolution provides a detailed understanding of the pristine pyrite surface and its reactivity.

Kendelewicz et al. [4] studied a pyrite surface after dosing with oxygen and water. They realized that only a relatively high dose of pure oxygen (10^7 L, $1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$) leads to an oxidation of sulfur and iron states at the surface. These findings are in contrast to STM investigations made by Rosso et al. [5] who studied the influence of the adsorption of very small amounts of oxygen. The latter proposed a dissociative adsorption of oxygen on the Fe surface sites of a regular pyrite (100) surface. However, they did not consider the existence

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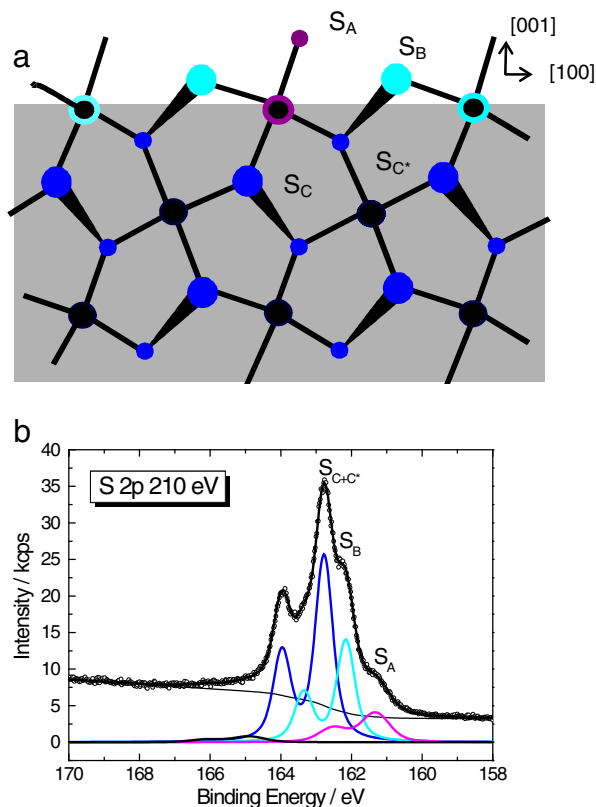


Fig. 1. Characterization of the pristine fractured FeS_2 surface. a) Structural model, different sulfur surface sites are indicated by different colors. Fe surface sites are marked by colored rings. b) Fitted S 2p spectrum. Signals from different surface sites are distinguished by the same colors as in a).

of S^{2-} and Fe(III) surface species. Other species, particularly S^0 (elemental sulfur) and S_n^{2-} species have been observed at modified pyrite surfaces using synchrotron based scanning photoelectron microscopy [6] but the pyrite surface on which they were observed was sputtered prior to exposure to oxygen and water. As Chandra and Gerson [6] state, and is known from former studies [7,8], this sample preparation leads to destruction of pyrite surfaces forming pyrrhotite (FeS) like phases which only contain S^{2-} (and $\text{S}_0/\text{S}_n^{2-}$). The results of the dosing experiments by Chandra and Gerson [6] are therefore not adaptable to a non-sputtered FeS_2 (100) surface.

1.2. Interpretation of valence band (VB) spectra of pyrite

In a previous work [9] where the energy dependence of the signal intensities was exploited, the major contributions of the valence band spectra of pyrite fracture surfaces were identified and the experimental results were consistent with theoretical calculations provided by Eyert et al. [10]. In general the pyrite (100) valence band (Fig. 2b) can be separated into an outer valence band ranging from 0 to about 2 eV and an inner valence band between 2 and 20 eV binding energy. S–S σ - and σ^* -bands derived from S 3s orbitals are located at 16 and 13 eV binding energies, respectively. S–S σ -orbitals derived from S 3p_z are located at about 7 eV. A S–S π -bond (derived from S 3p_{x,y}) contributes to the valence band spectrum at 5 eV. Fe–S σ -bonds (Fe 3d_{eg}–S 3p_z) are observed at 4 eV binding energy. The peak at 2.5 eV is explained by π -bond formation between Fe 3d_{t2g} orbitals and the π^* -orbitals of the S–S bond. The π^* -contribution of this Fe–S bond is located at the high binding energy side of the outer valence band centered at about 1 eV binding energy. The remaining intensity of the outer valence band is mainly formed by localized non-bonding Fe 3d_{t2g} orbitals.

It has been proposed, however, that during bond scission an occupied Fe 3d_{eg} state is formed which should represent the top of the outer valence band [1,11,12]. Actually, the lower binding energy side of the outer valence band shows some systematic changes depending on excitation energy. However, a conclusive interpretation of this behavior could not be provided because of the superposition of effects caused by the energy dependence of the photo ionization cross section and varying surface sensitivity.

The experimental findings and conclusions based on qualitative molecular orbital considerations have been supported by DFT calculations [13]. The authors provide site specific densities of states of the FeS_2 (100) surface (Fig. 2a). There is clear evidence that the outer valence band contains considerable contributions from the S^{2-} surface species which was shown to be the most reactive sulfur species during air oxidation [14].

Using these findings, in this communication we study a pyrite surface, prepared by fracture in vacuum, after increasing exposure to oxygen gas in order to detect surface states in the pyrite valence band and to explain the initial states of pyrite oxidation. We first discuss spectra obtained from the fractured surface to introduce different surface sites and will then consider the changes caused by the lowest oxygen dose of 10 L to identify the most reactive surface states in the valence band spectra. Additional aspects addressing adsorption and oxidation processes are then discussed and a reaction model is proposed.

2. Experimental

2.1. Instrumentation and spectrum acquisition

Experiments were carried out using a natural pyrite sample from Soria, Spain. The sample was cut from a large specimen with the long axis of the lath parallel to the c-axis of the mineral. It was fractured at a pressure of 5×10^{-6} Pa at room temperature in the ultra-high vacuum preparation chamber connected to the spectrometer analyzer chamber. Transfer from the preparation chamber to the analyzer chamber was completed within 3 min to ensure that the surface was not significantly altered by residual gases.

In order to determine the surface contributions in the valence band spectra and changes in the core level spectra the pristine pyrite surface was exposed consecutively to different amounts of oxygen (10 to 30,000 L, $1 \text{ L} = 10^{-4} \text{ Pa}\cdot\text{s}$) in the preparation chamber.

Valence band, S 2p and Fe 3p core level spectra were obtained at the undulator beam line PGM equipped with a SES200 analyzer (SCIENTA) of the Synchrotron Radiation Center (University of Wisconsin, Madison) at a take-off angle of 78° at room temperature. The pressure in the analyzer chamber during the measurement was less than 5×10^{-8} Pa. Monochromator resolution ($E/\Delta E$) was 17,000 for the valence band spectra, 10,000 for Fe 3p and 5000 for the S 2p signal. Pass energies of 10 eV and 20 eV for the valence band spectra and for the Fe 3p and S 2p signals were chosen, respectively.

2.2. Evaluation of spectra

The spectral intensity of the Fe 3p and S 2p spectra was normalized to the background intensity at the low binding energy side in order to eliminate the influence of varying primary beam intensities.

S 2p spectra were analyzed using Unifit 2008, a sophisticated peak fitting software [15]. A convolution of Gaussian and Lorentzian functions was used to fit the experimental spectra by the least possible number of doublets for the S 2p_{3/2} and S 2p_{1/2} doublet.

Valence band spectra were normalized to the intensity at the high binding energy side of the spectrum and were analyzed after subtracting a Shirley-type background.

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