



# Effect of surface oxidation on interfacial water structure at a pyrite (100) surface as studied by molecular dynamics simulation



Jiaqi Jin <sup>a</sup>, Jan D. Miller <sup>a,\*</sup>, Liem X. Dang <sup>b</sup>, Collin D. Wick <sup>c</sup>

<sup>a</sup> Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, 135S 1460E, 412 WBB, Salt Lake City, UT 84112, USA

<sup>b</sup> Physical Sciences Division, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352, USA

<sup>c</sup> Department of Chemistry, College of Engineering and Science, Louisiana Tech University, P.O. Box 10348, Ruston, LA 71270, USA

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## ABSTRACT

In the first part of this paper, a SEM and contact angle study of a pyrite (100) surface is reported describing the relationship between surface oxidation and the hydrophilic surface state. In addition to these experimental results, the following simulated surface states were examined using molecular dynamics simulation (MDS): a fresh unoxidized (100) surface; polysulfide at the (100) surface; and elemental sulfur at the (100) surface. Crystal structures for the polysulfide and elemental sulfur at the (100) surface were simulated using density functional theory (DFT) quantum chemical calculations. The well known oxidation mechanism which involves formation of a metal deficient layer was also described with DFT. Our MDS results of the behavior of interfacial water at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide include simulated contact angles, number density distribution for water, water dipole orientation, water residence time, and hydrogen-bonding considerations. The significance of the formation of ferric hydroxide islands in accounting for the corresponding hydrophilic surface state is revealed not only from experimental contact angle measurements but also from simulated contact angle measurements using MDS. The hydrophilic surface state developed at oxidized pyrite surfaces has been described by MDS, on which basis the surface state is explained, based on interfacial water structure.

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## 1. Introduction

It is well known that most sulfide minerals are naturally hydrophobic under anaerobic conditions. After sufficient oxidation, sulfide mineral surfaces, including pyrite, become hydrophilic and typically are wetted by water. This understanding is consistent with previous contact angle measurements for an oxidized random surface of pyrite (Raichur et al., 2000). It is now well established that pyrite oxidation follows a reaction mechanism in which iron hydroxide products and an underlying metal-deficient or sulfur-rich surface are formed. The reaction products during pyrite oxidation under different conditions have been studied by X-ray photoelectron spectroscopy (Buckley and Woods, 1987). Also, scanning auger microscopy (SAM) and atomic force microscopy (AFM) have been used to image the oxidation products at the pyrite surface (Miller et al., 2002; Smart et al., 2003). However, the study of a specific pyrite surface has not been reported. Thus, in this research, we used scanning electron microscopy (SEM) to image and analyze the products on an oxidized pyrite surface (100). Also, in order to correlate the hydrophilic state of the oxidized pyrite surface (100) with the products on it, we

measured the experimental contact angles for the fresh surface and for oxidized surfaces at different levels of oxidation.

Macroscopic results (laboratory experiments) are related to microscopic behavior (atomic level). In order to explain the hydrophobicity of mineral surfaces, knowledge of the structure of interfacial water molecules at mineral surfaces is of significant importance. Different spectroscopic methods have been applied to understand interfacial water structure at mineral surfaces. For example, the interfacial water structure at soluble salt surfaces has been studied with Fourier transform infrared spectroscopy (FTIR) (Cao et al., 2011; Cheng et al., 2013; Yalamanchili et al., 1991). Also, vibrational sum-frequency generation spectroscopy (SFG) has been used to explore the structure of water molecules at oxide mineral surfaces (Ostroverkhov et al., 2005; Shen, 1994; Shen and Ostroverkhov, 2006; Yeganeh et al., 1999) and fluorite surfaces (Eftekhari-Bafroei and Borguet, 2009; Zhang et al., 2013). However, the spectroscopic signal has been difficult to analyze, and the experimental results require further analysis at the molecular level.

Because of the remarkable increase in computational capabilities in recent years, density functional theory (DFT) quantum chemical calculations, which can provide electron-level information about interactions between atoms, have been used in the study of sulfide minerals, such as molybdenite (Todorova et al., 2004) and pyrite (Blanchard et al., 2007;

\* Corresponding author.

E-mail address: [jan.miller@utah.edu](mailto:jan.miller@utah.edu) (J.D. Miller).

Hung et al., 2003). However, due to the limitation imposed by the magnitude of the DFT calculation, it would be difficult to study the interfacial water structure using DFT. Using simplified pair potential models, molecular dynamics simulation (MDS) can simulate a system containing a much larger number of atoms and can provide important molecular-level information about the structures and dynamic properties of interfacial water at mineral surfaces. Because of this remarkable ability to simulate large systems, the contact angles of nanodrops at solid surfaces can even be measured by MDS (Werder et al., 2003). Much research based on MDS has been reported on water structures and dynamic properties at mineral surfaces (Du and Miller, 2007; Gallo et al., 2002; Jin et al., 2014; Kalinichev and Kirkpatrick, 2002; Lee and Rossky, 1994; Rustad, 2001; Rustad et al., 2003; Spohr et al., 1999; Wang et al., 2004).

In addition to experimental results, the following simulated surface states without/with the presence of ferric hydroxide were examined for a pyrite (100) surface using molecular dynamics simulation (MDS):

- Fresh unoxidized (100) surface
- Polysulfide at the (100) surface
- Elemental sulfur at the (100) surface.

Lattice parameters for pyrite from a previous XRD study (Rieder et al., 2007) were used to create the fresh unoxidized (100) surface. However, the crystal structure of the oxidized pyrite surface is not well established. In order to describe the famous oxidation mechanism which involves formation of a metal deficient layer, we used DFT calculations to study the accommodation of iron hydroxide at a pyrite (100) surface. Then, the crystal structure of small portions of polysulfide and elemental sulfur at the (100) surface ( $10.8 \text{ \AA} \times 10.8 \text{ \AA}$ ) were simulated by DFT quantum chemical calculations. Next, MDS was used to study the interfacial water molecules at relatively large portions of the polysulfide and elemental sulfur at the (100) surface, which are expanded from the small surfaces generated in DFT quantum chemical calculations. A specific MDS force field for pyrite using the functional forms of the Buckingham potential has been made to study the pyrite crystal structure, but no information about the interaction between a pyrite surface and water molecules was provided (Buckingham, 1938; Sithole et al., 2003). Another MDS study for interfacial water at the pyrite (100) surface using the potential parameters from the universal force field (UFF) and partial charges determined by Mulliken population analysis gave a reasonable prediction of the surface hydrophobicity (Jin et al., 2014; Mulliken, 1955; Rappé et al., 1992). Thus, the same UFF force field parameters for the Fe and S atoms are utilized in our MDS study. The interfacial water structures and dynamic properties at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide are discussed including simulated contact angles, number density distributions, water dipole orientation, water residence time, and hydrogen bonding.

## 2. Methods

### 2.1. Experimental procedures

It is well known that for a cubic pyrite crystal the six surfaces are all pyrite (100) surfaces, which is one of the planes for preferred cleavage. A cubic piece of natural pyrite crystal (about  $3.8 \text{ cm} \times 3.6 \text{ cm} \times 3.5 \text{ cm}$ ) from Canonea city, Sonora, Mexico, was cut parallel to its surface to create a fresh pyrite (100) surface. A tile saw with a 6-inch diamond blade, 0.024 inch in thickness, was used to cut the pyrite crystal. Saw marks were eliminated by polishing with an 8-inch aluminum diamond lap with 150 grit diamond powder for 2 min and fine polishing with a 600 grit metal bonded diamond lap for another 2 min. Polishing procedures involved coarse polishing with a 6 micron diamond suspension on the polishing cloth and fine polishing with a 1 micron diamond

suspension on a “Boehler Trident” polishing cloth. After quick washing with water and drying with kimwipes, the pyrite crystal sample was put into a nitrogen-filled ziplock plastic bag, in order to minimize the surface oxidation. Then the pyrite crystal sample was used for taking SEM images and EDAX analysis of the fresh pyrite (100) surface.

A 30% hydrogen peroxide solution ( $\text{pH} = 4.0$ ) was used to oxidize the pyrite crystal sample. After being soaked in the 30% hydrogen peroxide solution for 90 s, the pyrite crystal sample was quickly washed with water and dried in a vacuum chamber. Then the oxidized pyrite crystal sample was used for taking SEM images and EDAX analysis of the oxidized pyrite (100) surface.

EDTA is able to “sequester” metal ions such as  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  because of its role as a hexadentate (“six-toothed”) ligand and chelating agent. Saturated EDTA solution was used to wash the oxidized pyrite crystal sample, in order to get rid of the iron oxide/hydroxide at the oxidized pyrite (100) surface. After quickly being washed with water and dried in a vacuum chamber, the oxidized pyrite crystal sample was used for taking SEM images and EDAX analysis for the oxidized pyrite (100) surface without iron oxide/hydroxide.

The same procedures were used to prepare the pyrite crystal sample for measuring the experimental contact angle, using the captive bubble technique. The fresh pyrite (100) surface was then oxidized with 30% hydrogen peroxide solution for both 90 s and 180 s. Contact angles for these oxidized surfaces with different extents of oxidation were also measured by the captive bubble technique. The oxidized pyrite crystal was washed with saturated EDTA solution to remove the iron oxide/hydroxide at the surface. Contact angles were then measured at this EDTA washed oxidized pyrite (100) surface.

Contact angles were measured with a Rame-Hart goniometer using the captive bubble method. A bubble was released from the needle tip after formation with a syringe. The bubble was then captured and attached at the pyrite (100) surface. Since the contact angle was measured for cases when attachment occurred, contact angles reported in this study are intermediate contact angles, which are between advancing and receding contact angles. For each specific measurement, at least ten bubbles were generated and measured. The reported contact angle values are the average of these measurements. The maximum experimental variation in contact angle values was found to be  $\pm 1^\circ$ .

### 2.2. Density functional theory (DFT) calculations

Quickstep package of the CP2K program can perform accurate and efficient DFT calculations on large, complex systems including e.g. liquids, crystals, proteins and interfaces (Mundy et al., 2000; VandeVondele et al., 2005). Quickstep is based on the Gaussian and plane waves method (GPW) and its augmented extension (GAPW). In our study, Quickstep was used to describe the organization of iron hydroxide and simulate the crystal structure of the polysulfide and elemental sulfur at the pyrite (100) surface.

To study the accommodation of an iron hydroxide  $\text{Fe}(\text{OH})_3$  molecule at the pyrite (100) surface, a simulation periodic box with a piece of pyrite crystal in the bottom was created. The surface was the pyrite (100) surface. The pyrite crystal lattice parameters are from a previous X-ray diffraction (XRD) study on pyrite (Rieder et al., 2007). The size of the simulation periodic box was  $10.832 \text{ \AA} \times 10.832 \text{ \AA} \times 20.000 \text{ \AA}$ , and size of the cubic pyrite crystal was  $10.832 \text{ \AA} \times 10.832 \text{ \AA} \times 10.832 \text{ \AA}$ . There are 32 Fe atoms and 64 S atoms in the pyrite crystal. The DZVP-MOLOPT-SR-GTH shorter range basis set (VandeVondele and Hutter, 2007) and PBE correlation functional (Perdew et al., 1996) were used in our DFT quantum chemical calculations. Depending on location, the pyrite (100) surface can have three different surface endings (Fe–S–S, S–Fe–S and S–S–Fe). In this study, only the S–Fe–S surface ending was studied, because the bond between sulfur dimers is comparably easier to be broken than S–S or Fe–S bonds. Different surface endings might have an effect on interfacial water molecules, and this should be studied in future research. One of the Fe atoms on the top atomic layer of the

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