Graphic Abstract

Interfacial water at pyrite (100) surface

Effect of Surface Oxidation on Interfacial Water Structure at a Pyrite (100) Surface as Studied by Molecular Dynamics Simulation

Jiaqi Jin^a, Jan D. Miller^{a*}, Liem X. Dang^b, Collin D. Wick^c

^a Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, 135S 1460E, 412 WBB, Salt Lake City, Utah 84112, U.S.A.

^b Physical Sciences Division, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, Richland, WA 99352, U.S.A.

^c Department of Chemistry, College of Engineering and Science, Louisiana Tech University, P.O. Box 10348, Ruston, LA 71270, U.S.A.

* To whom correspondence should be addressed.

Jan D. Miller

Phone / Fax: 1-801-581-5160 / 1-801-581-4937

E-mail: jan.miller@utah.edu

Effect of Surface Oxidation on Interfacial Water Structure at a Pyrite (100) Surface as Studied by Molecular Dynamics Simulation

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.

Keywords: SEM, contact angle, DFT, MDS, interfacial water

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, 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-Bafrooei 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; 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 angle 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 have been made to study the pyrite crystal structure, but no information about the interaction between a pyrite surface and water molecules were 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 3.8cm × 3.6cm × 3.5cm) from Cananea 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 minutes and fine polishing with a 600 grit metal bonded diamond lap for another 2 minutes. 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 (pH = 4.0) was used to oxidize the pyrite crystal sample. After being soaked in the 30% hydrogen peroxide solution for 90 seconds, 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 Ca^{2+} and 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 for the fresh pyrite (100) surface using the captive bubble technique. The fresh pyrite (100) surface was then oxidized with 30% hydrogen peroxide solution for both 90 seconds and 180 seconds. 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 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 pyrite (100) surface was selected to be the

Fe^{3+} cation, which is the product of pyrite oxidation. Three hydroxide anions (OH^-) were placed about $2\text{\AA}$ away from the Fe^{3+} cation. As shown in Figure 1, the Fe^{3+} cation is orange in color, which is distinguished from other Fe atoms green in color. The simulation periodic box containing a $\text{Fe}(\text{OH})_3$ molecule at the pyrite (100) surface was calculated for geometry optimization. In this simulation, two bottom layers of atoms in the pyrite crystal were fixed, in order to stabilize the bulk pyrite crystal structure.

To simulate the metal deficient layer produced during pyrite oxidation, i.e. polysulfide and elemental sulfur at the (100) surface, different numbers of Fe atoms in the top atomic layer of a fresh unoxidized pyrite (100) surface ($10.832\text{\AA} \times 10.832\text{\AA} \times 10.832\text{\AA}$) were removed from the surface. In the top atomic layer, there is a total of eight Fe atoms and 16 S atoms. In order to simulate the polysulfide at the (100) surface, four Fe atoms were removed (50%), so the chemical formula for the polysulfide at the (100) surface is FeS_4 . To simulate the elemental sulfur at the (100) surface, all eight Fe atoms were removed (100%), so the top layer is only composed of elemental sulfur dimers. These manipulated polysulfide and elemental sulfur dimers at the (100) surface were then calculated for DFT geometry optimization using the same basis set and functional described in the last paragraph. The two bottom layers of the pyrite crystals were also fixed in DFT calculations. It is well known that the atomic structure for one of the most common elemental sulfur allotropes is the 8-member ring (Steudel and Eckert, 2003). In order to stimulate the elemental sulfur 8-member rings at the (100) surface, some of the sulfur dimers in the top layer were twisted by 30° to 90° without moving their centers before the DFT calculations. The same DFT calculations were used for the geometry optimization of this elemental sulfur at the (100) surface with twisted sulfur dimers. Thus, there are two different

elemental sulfur states at the (100) surface studied in this paper: elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface.

2.3. Molecular Dynamics Simulation

Amber, an MDS program, was used for the simulation and analysis of interfacial water at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide. The total energy in MDS is determined by evaluating the appropriate energy terms for every atom-atom interaction of the system. In the Amber program, this total energy is expected to include the Coulombic (electrostatic) interactions, the short-range interactions (van der Waals energy term), and the bonded interactions. The bonded terms include the bond stretch and angle bend energy terms that are represented in the water models as harmonic terms. The Coulombic energy is represented by equation 1 in which the energy of the interaction is inversely proportional to the distance of separation r_{ij} . The terms q_i and q_j are partial charges for atoms i and j. The term e is the charge of an electron, and ϵ_0 is the dielectric permittivity of vacuum (8.85419×10^{-12} F/m).

$$E_{Coulombic} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} \quad (1)$$

The van der Waals energy term, represented by the conventional Lennard-Jones (12-6) function (Jones, 1924), includes the short-range repulsion associated with the increase in energy as two atoms approach each other and the attractive dispersion energy. The term ϵ_{ij} is the depth of the potential well, and $r_{m,ij}$ is the distance at which the potential reaches its minimum.

$$E_{VDW} = \sum_{i \neq j} \epsilon_{ij} \left[\left(\frac{r_{m,ij}}{r_{ij}} \right)^{12} - \left(\frac{r_{m,ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

The interaction parameters between unlike atoms are calculated according to the arithmetic mean rule for the distance parameter, r_m , and the geometric mean rule for the energy parameter, ε :

$$r_{m,ij} = \frac{1}{2(r_{m,i} + r_{m,j})} \quad (3)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (4)$$

In recent decades, various kinds of molecular water models have been developed. The rigid SPC/E water model has the closest average configurational energy to the experimental value (-41.5 KJ mol⁻¹) (Kusalik and Svishchev, 1994; Mahoney and Jorgensen, 2000). Thus, we selected the SPC/E water model for exploring the interfacial water at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide.

The Lennard-Jones parameters r_m , ε and atomic partial charge q for all the atoms in the simulation are listed in Table 1. Lennard-Jones parameters for the Fe and S atoms in the bulk pyrite crystal are from the UFF. Atomic partial charges for the Fe and S atoms in the bulk pyrite crystal are Mulliken charges determined from the periodic DFT quantum chemical calculations of well-defined pyrite unit cells using the Perdew-Wang 1991 (PW91) functional theory and the generalized gradient approximation (Perdew et al., 1996; Perdew et al., 1991). The quantum program DMol3 was used to assign the Mulliken charges (Delley, 2000). For the polysulfide at the (100) surface, all parameters for the Fe and S atoms are the same as for the bulk pyrite atoms, but the atomic partial charge for the S atoms in the polysulfide top layer is half of the value for the bulk pyrite S atoms, in order to make the polysulfide top layer electrically neutral. Similarly, for the elemental sulfur at the (100) surface, the atomic partial charge for the S atoms in the elemental sulfur top layer is set to be 0, but all other parameters are the same as for the bulk

pyrite atoms. For the ferric cations (Fe^{3+}), the Lennard-Jones parameters are also from UFF, but the atomic partial charge is set as +3. The force field parameters for hydroxide anions are from a previous MDS study on chemical reactions of hydroxide groups (Peng and Merz Jr, 1992).

To study the interfacial water structure and dynamic properties at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide, we made a simulation periodic box containing a vacuum space at the top, a water phase in the middle, and a pyrite crystal ($43.3\text{\AA} \times 43.3\text{\AA} \times 10.8\text{\AA}$) at the bottom. The purpose for having a vacuum space was to make sure the water phase experienced the same pressure for all simulations. The pyrite crystal for the fresh unoxidized (100) surface was generated based on the lattice parameters from a previous XRD study (Rieder et al., 2007). For the polysulfide and elemental sulfur at the (100) surface, the relatively large portion of the pyrite crystal were expanded from our DFT results. Ferric cations and hydroxide anions were added in the water phase to simulate the accommodation of ferric hydroxide on the fresh and oxidized pyrite (100) surfaces. The number of hydroxide anions is three times the number of ferric cations to keep the system electrically neutral. For the fresh unoxidized (100) surface, the number of ferric cations is half of the number of Fe atoms in the surface. For the polysulfide and elemental sulfur at the (100) surface, the number of ferric cations equals the number of Fe atoms lost in the surface (metal deficient layer). After a simulation time of 2 ns for equilibration, we performed another 2 ns simulation for interfacial water analysis. Each simulation was for a constant number, constant volume and constant temperature assembly (the NVT ensemble) with the temperature fixed at 298K.

To measure the simulated contact angle of water drops at the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide by MDS, a water drop containing 1270

water molecules was put on the surface at the bottom of a simulation periodic box. According to the previous MDS study (Jin et al., 2014), in the size range from 850 to 1700 water molecules, drop size doesn't have much effect on the simulated contact angle measured by MDS. In order to remove the periodic images of the droplets in measuring the simulated contact angle, the surface needed to have sufficient area. In our study, the horizontal extent of the fresh and oxidized pyrite (100) surfaces without/with the presence of ferric hydroxide used for simulated contact angle measurement is $173.3\text{\AA} \times 173.3\text{\AA}$. These large surfaces are expanded from the relatively smaller surfaces ($43.3\text{\AA} \times 43.3\text{\AA}$), which are the simulation results of the interfacial water study described in the last paragraph. Also, the vertical extent of the periodic simulation boxes was set at $100\text{\AA}$ to avoid the influence of periodic conditions on the water drops. One water molecule in this periodic volume about $3.0 \times 10^6 \text{\AA}^3$ would provide a saturated atmosphere, so the water drop is stable under these conditions. Because of the large number of atoms (over 40,000) in this simulation, we used a total simulation time of 1 ns (1×10^6 steps each of 1 fs), including a 500 ps equilibration period and another 500 ps analysis period. The contact angles were measured on an average for the second 500 ps. It is well known that the solubility of pyrite is very low. In order to improve the calculation efficiency, crystal atoms were fixed as their respective initial positions during the simulation.

3. Results and Discussion

3.1. Experiments with the (100) pyrite surface

The polished fresh pyrite (100) surface is flat and smooth as established by the SEM image shown in Figure 1 (a). In contrast, as shown in Figure 1 (b), after oxidation in the 30% hydrogen peroxide solution for 90 seconds, the pyrite (100) surface has a large number of very obvious

light colored islands about 1 to 2 microns in diameter. Also, scratches on the oxidized pyrite (100) surface become more distinct. These bright spots are expected to be iron oxide/hydroxide. Since iron oxides (Fe_2O_3) are nearly insulators (Palacky, 1988), electrons would gather on the islands and make them brighter than the background pyrite crystal. Figure 1 (c) shows the SEM image of the oxidized pyrite (100) surface washed with EDTA. As expected, after being washed with the saturated EDTA solution, the oxidized pyrite (100) surface became clean and smooth again when examined by SEM. The light iron oxide/hydroxide islands were dissolved and washed away by the saturated EDTA solution. EDAX analysis found oxygen present at the pyrite (100) surface after 90 seconds oxidation in 30% hydrogen peroxide solution, which helps to confirm that the islands in the SEM image for the oxidized pyrite (100) surface are iron oxide/hydroxide. Unfortunately, the EDAX analysis is not able to show the composition change of the metal deficient layer at the oxidized pyrite (100) surface. The thickness of the metal deficient layer formed during the 90 seconds oxidation of pyrite in 30% hydrogen peroxide solution appears to be much smaller than the minimum depth SEM could distinguish. More depth sensitive techniques, such as XPS, Scanning Tunneling Microscopy (STM) or Transmission Electron Microscopy (TEM), will be involved in future studies of pyrite oxidation. However, the results of both the SEM imaging and EDAX analysis are consistent with previous AFM studies on the oxidation of the pyrite surface (du Plessis et al., 2004).

Experimental contact angles for the fresh and oxidized pyrite (100) surfaces measured by the captive bubble approach are listed in Table 2. The large contact angle for the polished fresh pyrite (100) surface, which is consistent with that reported in the literature (Raichur et al., 2000), reveals the natural hydrophobic character and floatability for pyrite. However, after oxidation in 30% hydrogen peroxide solution for 90 seconds, the contact angle for the oxidized pyrite (100)

surface decreased to 23 degrees, indicating that the surface has become more hydrophilic. This is again consistent with previous contact angle measurements on a random pyrite surface (Raichur et al., 2000). As is discussed, after oxidation in 30% hydrogen peroxide solution for 90 seconds, part of the pyrite (100) surface is covered by an iron oxide/hydroxide surface deposit which is responsible for the hydrophilic character and wettability of the oxidized pyrite (100) surface. How these iron hydroxide islands change the hydrophobic character of the pyrite (100) surface is discussed at the molecular level based on MDS. As the oxidation time increased to 180 seconds, the contact angle for the oxidized pyrite (100) surface decreased further. The coverage of iron oxide/hydroxide islands on the oxidized pyrite (100) surface is expected to increase as the oxidation time increases, making the oxidized pyrite (100) surface more hydrophilic. The contact angle for the oxidized pyrite (100) surface washed with saturated EDTA solution is as large as the contact angle for the polished fresh pyrite (100) surface. As expected, when washed with the saturated EDTA solution, the oxidized pyrite (100) surface became hydrophobic again. After washing with EDTA solution, the iron oxide/hydroxide islands at the oxidized pyrite (100) surface were removed, so the surface becomes hydrophobic and is not well wetted by water. As a result, the collectorless flotation of oxidized pyrite can be obtained easily after complexing the iron with EDTA in solution (Smart et al., 2003).

3.2. Accommodation of iron hydroxide at the pyrite (100) surface described by DFT

The initial and final positions of the ferric cation and three hydroxide anions at the pyrite (100) surface, based on DFT quantum chemical calculations are shown in Figure 2. During the whole geometry optimization process, the total energy of the system decreased from -2920937.5 Kcal/mol to -2921125.7 Kcal/mol. Both the Z coordinates for the Fe atoms in the pyrite (100)

surface before and after the simulation are about 9.30Å. However, the Z coordinate for the ferric cation increased from 9.30Å to 11.27Å during the simulation, which means that the ferric cation was stabilized at a distance of almost 2Å from the pyrite crystal surface. This is consistent with the pyrite oxidation mechanism revealed in a previous XPS study (Buckley and Woods, 1987), in which iron hydroxide products and an underlying metal-deficient surface are formed. The number of S atoms adjacent to the ferric cation before and after the simulation is also evidence for the well known pyrite oxidation mechanism. The distance between an Fe atom and an adjacent S atom in pyrite is around 2.26Å. Before the simulation, there were five S atoms adjacent to the ferric cation (about 2.3Å). However, only two S atoms are adjacent to this ferric cation (2.49Å and 2.57Å) after the geometry optimization. These results suggest that there is not much interaction between the ferric cation and the pyrite (100) surface. The average distance between the ferric cation and the oxygen atoms in hydroxide anions decreased from 1.966Å to 1.855Å during the simulation. The formation of Fe(OH)₃ in this way requires that the iron atom leave the pyrite (100) surface. Pyrite oxidation is a complex process because of the structure of the oxidized pyrite surface and the environmental conditions, such as pH value of the aqueous phase. This DFT simulation is just a simple case to illustrate that the Fe atoms on the pyrite (100) surface will leave the surface once oxidized to ferric cations and form iron hydroxide with hydroxide anions, which is consistent with previous experimental studies. The surface state is important to create the crystal structure of the oxidized pyrite (100) surface, such as stabilization of polysulfide and/or elemental sulfur at the (100) surface, for our MDS study of interfacial water molecules.

3.3. Crystal structure of polysulfide and elemental sulfur stabilized at the pyrite (100) surface

The crystal structure of the polysulfide at the pyrite (100) surface generated from DFT quantum chemical calculations are shown in Figure 3 (a, b). The top view of the polysulfide (100) surface shows very good symmetry. There are four sulfur dimers around each Fe atom, and every two Fe atoms share one sulfur dimer. As a result, the electrical charge distribution on the polysulfide (100) surface is homogeneous. Two elemental sulfur states at the (100) surface have been studied in this paper: the elemental sulfur dimers at the (100) surface, as shown in Figure 3 (c, d), and the elemental sulfur 8-member rings at the (100) surface, which are shown in Figure 3 (e, f). The total energies of these two surfaces are almost the same (-2270090.3 Kcal/mol vs. -2270089.7 Kcal/mol). However, the simulated densities for elemental sulfur at these two surfaces are very different (2.59g/cm^3 vs. 1.9g/cm^3). The simulated density for the elemental sulfur 8-member rings (100) surface is much closer to the literature values for elemental sulfur density at room temperature, which are all about 2 g/cm^3 (Steudel and Eckert, 2003). The wrong estimation of elemental sulfur density for the elemental sulfur dimers at the (100) surface could be a result from the local energy minimum during the DFT quantum chemical calculations. In our study, both of these two elemental sulfur (100) surfaces have been studied using MDS for simulated contact angle measurements and interfacial water analysis.

3.4. Simulated contact angle measurements

Simulated contact angle measurements without and with ferric hydroxide were made for each case. To determine the contact angle, we post-processed the water number densities using the grid size of $0.5\text{ \AA}$ in two center planes: the x-z plane and y-z plane. A two-dimensional droplet with a contour line corresponding to the average of the liquid and vapor densities defines the boundary of the water droplet (Peng et al., 2012; Shi and Dhir, 2009a). The results for the fresh

unoxidized pyrite (100) surface without/with the presence of ferric hydroxide for the y-z plane are expressed as a best fit contour line shown, by way of example, in Figure 4. As is shown in Figure 4 (a), the water drop at the fresh unoxidized (100) surface without the presence of ferric hydroxide doesn't wet the surface and forms a hemispherical drop, which indicates a hydrophobic surface. However, for the fresh unoxidized (100) surface with the presence of ferric hydroxide shown in Figure 4 (b), the water drop spreads significantly on the surface, which reveals the relative hydrophilic character of the surface. The spaces on the bottom of the water drop are the ferric hydroxide islands on the fresh unoxidized (100) surface, see Figure 5 (c, d). As is shown in Figure 5 (g, h, k, and m) and as will be discussed in the next section, interfacial water molecules for the polysulfide and elemental sulfur 8-member rings at the (100) surfaces with the presence of ferric hydroxide are influenced by the ferric hydroxide islands. Thus, the simulated contact angles should be measured at a distance from the fresh and oxidized pyrite (100) surfaces, in order to stabilize determination of the contact angle for each condition. In this study, we define the position of the fresh and oxidized pyrite (100) surfaces by the top most atoms of the surface. The contact angle was measured by drawing a tangent line from the point at the foot of the contour line at a height of 10 Å away from the fresh and oxidized pyrite (100) surfaces to avoid the influence from density fluctuations at the water/mineral interface (Werder et al., 2003) and the atomic roughness at the surface. For each contact angle measurement, the contact angles were measured in the x-z and y-z planes and then averaged (Shi and Dhir, 2009b). In the same way, similar measurements were made for each case, and the results are presented in Table 3.

As expected, the large simulated contact angle for the fresh unoxidized (100) surface without ferric hydroxide reveals the natural hydrophobicity and floatability of pyrite, which is consistent

with our experimental contact angle measurement. However, once these ferric hydroxide islands are present on the fresh unoxidized (100) surface, the simulated contact angle decreased significantly becoming more hydrophilic. The ferric hydroxide islands formed on the fresh unoxidized (100) surface make the surface wettable by water. This is important MDS evidence for the significance of the formation of ferric hydroxide islands and the corresponding hydrophilic surface state. Also, these results are consistent with the fact that after grinding the pyrite surface becomes substantially covered by the hydrophilic iron hydroxide species and no significant flotation is observed without addition of collector (Smart et al., 2003).

The simulated contact angles for the polysulfide at the (100) surface without/with the presence of ferric hydroxide show very similar results to the fresh unoxidized (100) surface. The hydrophobic character of the polysulfide at the (100) surface without ferric hydroxide revealed by the relatively large simulated contact angle confirms the experimental contact angle measurements for the EDTA washed oxidized pyrite (100) surface. As expected, the simulated contact angle for the polysulfide at the (100) surface with the presence of ferric hydroxide is comparably small and indicates a more hydrophilic surface.

For the elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface without/with the presence of ferric hydroxide, the simulated contact angle measurements gave similar results. The elemental sulfur at the (100) surface without ferric hydroxide is hydrophobic and floatable, while the elemental sulfur at the (100) surface with the presence of ferric hydroxide becomes relatively hydrophilic and wettable by water. Compared to the polysulfide at the fresh unoxidized (100) surface with ferric hydroxide, the elemental sulfur at the (100) surface with ferric hydroxide has a relatively smaller simulated contact angle. The comparably larger

number of ferric hydroxide islands for the elemental sulfur (100) surface should be responsible for this relatively more hydrophilic surface state. More details about the formation of ferric hydroxide islands and the corresponding hydrophilic surface state will be discussed with respect to the interaction between interfacial water, ferric hydroxide and the pyrite (100) surface in the following section.

3.5. Interfacial water structures and dynamic properties

MDS snapshots in the x-z plane (left column) and in the y-z plane (right column) for interfacial water at the fresh unoxidized pyrite (100) surface and the polysulfide and elemental sulfur 8-member rings at the (100) surface without/with the presence of ferric hydroxide are presented in Figure 5. For the fresh unoxidized (100) surface and the polysulfide at the (100) surface without ferric hydroxide shown in Figure 5 (a, b, e and f), the gap presented between the water phase and the surface, reflecting the "water-excluded volume" (Abraham, 1978; Yu et al., 1999) or "water exclusion zone," indicates that the interaction between the water molecules and the surface is relatively weak, which is the origin of their macroscopic hydrophobic character. For the elemental sulfur dimers at the (100) surface without ferric hydroxide, which is not presented, the "water exclusion zone" reflecting the relatively weak interaction between water and the surface is also very distinct. However, for the fresh unoxidized (100) surface and the polysulfide at the (100) surface with ferric hydroxide shown in Figure 5 (c, d, g and f) as well as the elemental sulfur dimers at the (100) surface with ferric hydroxide, the "water exclusion zone" is still obvious. This means that the interaction between water molecules and the surfaces remains weak, even when ferric hydroxide is present at the surface making the surfaces hydrophilic. Thus, the interaction between water molecules and the surfaces is not the origin for the hydrophilic

character for the surfaces with the presence of ferric hydroxide. Note that this "water exclusion zone" is not obvious for the elemental sulfur 8-member rings at the (100) surface without/with ferric hydroxide shown in Figure 5 (i, j, k and m), because of the atomic roughness at the surface caused by the elemental sulfur 8-member rings. Although the "water exclusion zone" remains between the ferric hydroxide islands and the (100) surface with/without polysulfide/elemental sulfur, it is more important to note the water structure surrounding the ferric hydroxide.

As is shown in Figure 5 (c, d, g and h), cylindrical ferric hydroxide islands are formed on the fresh unoxidized (100) surface and the polysulfide at the (100) surface. In the cylindrical ferric hydroxide islands, positively charged ferric cations are in the middle and surrounded by negatively charged hydroxide anions, which have their oxygen atoms oriented toward the ferric cations. This structure is the result of electrostatic interaction between the ferric cations and hydroxide anions. Because the cylindrical ferric hydroxide islands are surrounded by water molecules, the ferric cations and hydroxide anions will also have interaction with the surrounding water molecules, which is revealed by the fact that no "water exclusion zone" is present between the water molecules and the ferric hydroxide islands. As is shown in Figure 5 (k and m), for the elemental sulfur 8-member rings at the (100) surface with ferric hydroxide, the ferric hydroxide islands are not cylindrical mainly because of the large number of ferric cations and hydroxide anions, but they still stay close to the elemental sulfur 8-member rings. Again, there is no "water exclusion zone" between the water molecules and the ferric hydroxide islands. The same thing happened in the case for elemental sulfur dimers at the (100) surface with the presence of ferric hydroxide. The interaction between ferric hydroxide and interfacial water molecules should be the origin of the macroscopic relatively hydrophilic character developed during pyrite grinding and the oxidation of the pyrite (100) surface. In this way, the surface has

been modified. Air bubbles do not penetrate the water film at the surface. As a result, after oxidation, pyrite particles will be difficult to float at typical collector concentrations.

3.5.1. Number density distribution of ferric cations, hydroxide anions and interfacial water molecules

In the analysis of the number density distribution of ferric cations, hydroxide anions and interfacial water molecules, the simulation periodic box is divided into $0.5\text{\AA}$ bins parallel to the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface. The number of molecules or ions in each bin is counted. In this study, the position of a water molecule is defined as the position of the center of mass for the water molecule. These numbers of molecules or ions in all the bins are plotted versus the bin's distance from the surface, making the number density profile. The number density profiles for the fresh unoxidized (100) surface without/with the presence of ferric hydroxide, are shown, by way of example, in Figure 6. For the fresh unoxidized (100) surface without ferric hydroxide, the first water density peak is about $3\text{\AA}$ away from the surface, which is consistent with a previous study (Jin et al., 2014). It means water molecules are excluded from the unoxidized fresh (100) surface. This distance is greater than the distance between hydrogen-bonded water/water molecules, which is approximately $2.8\text{\AA}$ (Dang and Pettitt, 1990; Lee and Rasaiah, 1996; Lynden-Bell and Rasaiah, 1997; Rasaiah and Zhu, 1990; Smith and Dang, 1994). This result demonstrates the relatively weak interaction between the water molecules and the fresh unoxidized (100) surface. Note that the number density of water becomes a constant when the distance is further than $10\text{\AA}$ from the surface, which represents the region for bulk water. The number density profiles for the polysulfide, elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface without ferric

hydroxide are similar to the fresh unoxidized (100) surface without ferric hydroxide. The distances between the polysulfide, elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface without ferric hydroxide and their first water density peak are also about 3 Å, which indicates the relatively weak interaction between interfacial water molecules and such surfaces.

For the fresh unoxidized (100) surface with the presence of ferric hydroxide, the first water density peak is also about 3 Å away from the surface. The number density profile for the polysulfide, elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface with the presence of ferric hydroxide (not presented) gave the same results. This is consistent with the "water exclusion zone" shown in the snapshots. The fresh unoxidized, polysulfide and elemental sulfur at the (100) surface don't have strong interactions with interfacial water molecules, even when ferric hydroxide is present.

As shown in Figure 6 (b), according to the position of the ferric cation and hydroxide anion peaks in the number density profile as well as the decrease of the first water density peak, the ferric hydroxide stays on the surface and occupies a large portion of space. The ferric cation peak is in the middle of two hydroxide anions peaks, which confirms the structure of cylindrical ferric hydroxide islands observed in Figure 5 (c, d). The major point is that the number density profile for the fresh unoxidized (100) surface with ferric hydroxide confirms the elimination of the "water exclusion zone" between water molecules and the ferric hydroxide islands. The information about ferric hydroxide from the number density profile for the polysulfide, elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface with ferric hydroxide are identical to the fresh unoxidized (100) surface with ferric hydroxide, except that the ferric cation

and hydroxide anion peaks for the two elemental sulfur (100) surfaces are comparably higher and wider because of more ferric hydroxide added on the surface. The fact that the ferric hydroxide stays on the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface during the whole simulation period of about 4 ns confirms the well known low solubility of ferric hydroxide. The ferric hydroxide islands present on the surface would attract the surrounding water molecules by electrostatic interactions and hydrogen bonding. This condition accounts for the elimination of the "water exclusion zone" at the surface of the ferric hydroxide islands and the hydrophilic surface character induced by the ferric hydroxide. Other MDS analysis in our study, especially the water residence time and hydrogen bonding sections, give better evidence of this.

3.5.2. Relative density distribution for water dipoles and hydrogen positions

A schematic illustration describing the orientation of a water dipole moment and the hydrogen position relative to the surface normal is shown in Figure 7. Angle α is the angle between the water dipole moment (oriented from negative to positive) and the surface normal. Angle β is the acute angle between the surface normal and a line connecting the two hydrogen atoms.

The water dipole and hydrogen position relative density distributions for the fresh unoxidized pyrite (100) surface without/with the presence of ferric hydroxide are shown as an example in Figure 8, because the results for the polysulfide and elemental sulfur at the (100) surface are all similar to the case for the fresh unoxidized (100) surface. For all the cases without the presence of ferric hydroxide, the majority of water molecules in the primary water density layer, which are about 3 Å from the surface, have almost the same water dipole orientation and hydrogen position. Both the water dipole moment and the line connecting the two hydrogen atoms are perpendicular

(90°) to the surface normal, indicating that the interfacial water molecules are in the plane parallel to the surface. Thus, the interfacial water molecules for the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface without the presence of ferric hydroxide have relatively weak interaction with the S or Fe atoms of the surface. The water dipole moment and hydrogen position relative density distributions for the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface without ferric hydroxide confirm their macroscopic hydrophobic character. This is also consistent with our number density distribution analysis.

Figure 8 (b) shows the water dipole and hydrogen position relative density distributions for the fresh unoxidized (100) surface with the presence of ferric hydroxide. As discussed, the ferric hydroxide islands occupy a large portion of space close to the surfaces. As a result, in the water dipole and hydrogen position relative density distributions for the fresh unoxidized (100) surface with the presence of ferric hydroxide, the volume of the peaks close to the surfaces are comparably smaller than for the fresh unoxidized (100) surface without ferric hydroxide. This is similar for the polysulfide at the (100) surface with ferric hydroxide and even more obvious for the elemental sulfur at the (100) surface with ferric hydroxide, because there is more ferric hydroxide added on the elemental sulfur at the (100) surface.

Instead of a 90° large peak for angle α about 3Å from the surface, for the fresh unoxidized (100) surface with ferric hydroxide, a 105° peak about 3Å from the surface and two other peaks about 5Å from the surface with 75° and 180° α angles are presented. Also, on the fresh unoxidized (100) surface with the presence of ferric hydroxide there is a relatively large 90° peak for angle β about 3Å from the surface and a small 30° peak for angle β about 5Å away from the surface. Note that

water molecules in the primary water density layer 3Å from the surface are still parallel to the surface, indicating relatively weak interaction between interfacial water molecules and the surface, even with the presence of ferric hydroxide. This is also consistent with our water number density results. The relatively less ordered water dipole orientation and hydrogen position of water molecules about 5Å from the surface is the result of electrostatic interaction and hydrogen bonding induced by the ferric hydroxide. The water dipole and hydrogen position analysis results for the polysulfide and elemental sulfur (100) surfaces gave the same conclusion.

3.5.3. Water residence time

Besides the structural analysis of interfacial water, the dynamic properties of interfacial water molecules, such as water residence time, can also be studied using MDS. The water residence time, τ , is described as the time a water molecule spends in each water layer along the surface. It has been calculated using the residence-time correlation function defined by Eq. (5). The term $\langle R(t) \rangle$ is derived from time correlation functions (Berendsen et al., 1987; Chowdhuri and Chandra, 2001; Koneshan et al., 1998) and is defined by Eq. (6).

$$\tau = \int_0^{\infty} \langle R(t) \rangle dt \quad (5)$$

$$R(t) = \frac{1}{N_h} \sum_{i=1}^{N_h} [\theta_i(0) \theta_i(t)] \quad (6)$$

Note that the term $\theta_i(t)$ is the Heaviside unit step function, which has the value 1 if a water molecule, i , is in the hydration shell of the reference water molecule at time t , and is zero otherwise. Water molecules in the hydration shell for more than 2 ps are considered to constitute the hydration shell. The term N_h is the apparent dynamic hydration number.

The water residence times at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur 8-member rings at the (100) surface without/with the presence of ferric hydroxide are listed in Table 4. The water residence time results for the elemental sulfur dimers at the (100) surface is the same as for the elemental sulfur 8-member rings at the (100) surface. The magnitude of water residence time at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur 8-member rings at the (100) surface without ferric hydroxide is very similar to other hydrophobic selected sulfide mineral surfaces, such as galena (100), chalcopyrite (012) and molybdenite (001) surfaces (Jin et al., 2014). These values are much smaller than the over 20 ps water residence times reported for the hydrophilic kaolinite alumina or silica surfaces (Du and Miller, 2007). The Fe and S atoms at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surfaces without ferric hydroxide do not provide many hydrogen-bonding donors and accepters for the interfacial water molecules. Thus, they have relatively weak interaction with the interfacial water molecules, compared to the hydroxyl groups in the kaolinite alumina or silica surfaces. These results confirm the hydrophobic character for the fresh unoxidized (100) surface and for the polysulfide and elemental sulfur at the (100) surface without the presence of ferric hydroxide, as revealed by the experimental and simulated contact angle measurements.

On the other hand, the magnitude of water residence time at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur 8-member rings at the (100) surface with ferric hydroxide is comparably much larger than it is for the cases without ferric hydroxide. These values are close to the water residence time for the hydrophilic sylvite (100) and muscovite (001) surfaces reported by previous MDS studies (Wang et al., 2013; Yin, 2012), which are around 20 ps. This is significant evidence for the strong interaction between the ferric hydroxide and

interfacial water molecules at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface with the presence of ferric hydroxide. As proven in our simulation, the ferric hydroxide has low solubility and stays on the fresh unoxidized (100) surface and on the polysulfide and elemental sulfur at the (100) surface. Because there are electrostatic interactions and hydrogen bonding between the ferric hydroxide and interfacial water molecules, the interfacial water molecules will be "slowed down" or "stabilized" by the ferric hydroxide islands present on the surface. Thus, the surfaces with the presence of ferric hydroxide have a comparably larger water residence time than the surfaces without ferric hydroxide. The strong interaction between the ferric hydroxide and interfacial water molecules is the origin of the corresponding macroscopic hydrophilic surface character.

3.5.4. Hydrogen bonding

MDS results also provide information about the hydrogen bonding between water molecules as well as the hydrogen bonding between hydroxide groups and water molecules. For the SPC/E water model, two water molecules are defined as hydrogen bonded if the distance between the two oxygen atoms is less than 3.5 Å and the O...O-H angle is simultaneously less than 30° (Luzar and Chandler, 1996). The hydrogen bonding between a hydroxide group and a water molecule is defined in the same way as the hydrogen bonding between two water molecules.

Distribution of the average number of hydrogen bonds per water molecule along the surface normal for the fresh unoxidized (100) surface is shown, by way of example, in Figure 9. For the fresh unoxidized (100) surface without/with ferric hydroxide, from the surface to the bulk water, the total number of hydrogen bonds per water molecule increases until it reaches a plateau value close to 3.35 about 4 Å from the surface, which is very close to the value of 3.5 reported in the

literature (Nieto-Draghi et al., 2003). Note that the number of hydrogen bonds from other water molecules per water molecule equals the total number of hydrogen bonds per water for the fresh unoxidized (100) surface without ferric hydroxide. According to previous MDS research about quartz, the distribution of the number of hydrogen bonds per water molecule at the hydrophilic quartz surface has a large and distinct peak about 4 less than 1 Å from the surface (Wang et al., 2012). This reveals that most of the interfacial water molecules are tetrahedrally bonded at the hydrophilic quartz surface. However, because of the exclusion of water molecules at the fresh unoxidized (100) surface without/with ferric hydroxide, there are very few hydrogen bonds in the interfacial region over a distance of 2 Å from the surface. The distinct difference between the distribution of the number of hydrogen bonds per water molecule for the hydrophilic quartz surface and the fresh unoxidized (100) surface without/with ferric indicates that the hydrophilic character for the fresh unoxidized (100) surface with iron hydroxide does not come from the interaction between the surface atoms and interfacial water molecules. Distribution of the average number of hydrogen bonds per water molecule for polysulfide and elemental sulfur at the (100) surface without/with ferric hydroxide showed exactly the same results. This is consistent with our experimental and other simulation discussions.

For the fresh unoxidized (100) surface with the presence of ferric hydroxide, as is shown in Figure 9 (b), the red shadowed part between the total number of hydrogen bonds per water molecule and the number of hydrogen bonds from other water molecules per water molecule indicates the hydrogen bonds per water molecule contributed by hydroxide anions. The hydrogen bonding analysis for the polysulfide and elemental sulfur (100) surfaces gave very similar results. The hydroxide anion (OH⁻) is a very good acceptor of hydrogen bonds, with the first water molecule binding strongly to form H₃O₂⁻ (where the proton is off-center, giving rise to a low-

barrier hydrogen bond) bihydroxide anions (Abu-Dari et al., 1979). This hydroxide ion H_3O_2^- is much more stable than the hydrogen bonding between two water molecules. Furthermore, these bihydroxide anions will also form weak hydrogen bonding between them and adjacent water molecules. As a result, the hydroxide ions facilitate the interactions among water molecules and make a significant contribution to the hydrophilic character of the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface with the presence of ferric hydroxide.

According to our number density analysis, the ferric hydroxide islands stay in the region less than $7\text{\AA}$ from the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface. Thus, Table 5 lists the percentage of hydrogen bonds between water and hydroxide anion in the total number of hydrogen bonds in the region less than $7\text{\AA}$ from the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface with ferric hydroxide.

For the fresh unoxidized (100) surface and the polysulfide at the (100) surface with ferric hydroxide, about 18% of the hydrogen bonds per water are hydrogen bonds between water molecules and hydroxide anions. This reveals that the hydrogen bonds of interfacial water at the fresh unoxidized (100) surface and the polysulfide at the (100) surface with ferric hydroxide are relatively stronger than at the fresh unoxidized (100) surface and the polysulfide at the (100) surface without ferric hydroxide. The hydrogen bonding between the hydroxide anions and the interfacial water molecules makes a significant contribution to the macroscopic hydrophilic character for the fresh unoxidized (100) surface and the polysulfide at the (100) surface with the presence of ferric hydroxide. For the elemental sulfur 8-member rings at the (100) surface with

the presence of ferric hydroxide, the percentage of hydrogen bonds between water and hydroxide anions is comparably higher, which means the hydrogen bonding interaction of the interfacial water molecules at this surface is relatively stronger. The elemental sulfur dimers at the (100) surface gave the same results. This is consistent with the comparably more hydrophilic character for the elemental sulfur at the (100) surface with the presence of ferric hydroxide revealed in the simulated contact angle measurement and water residence time analysis.

4. Conclusions

Results of SEM and experimental contact angle measurements for the fresh pyrite, oxidized pyrite and EDTA washed oxidized pyrite (100) surfaces indicate that the formation of iron hydroxide at the oxidized pyrite (100) surface is the origin of the hydrophilic surface state developed during pyrite oxidation.

The famous pyrite oxidation mechanism involving the formation of a metal deficient layer was described using the DFT quantum chemical calculations about the accommodation of ferric hydroxide on the pyrite (100) surface. Based on this pyrite oxidation mechanism, the polysulfide, elemental sulfur dimers and elemental sulfur 8-member rings at the (100) surface were generated by our DFT quantum chemical calculations. We used the force field including the UFF Lennard-Jones parameters and Mulliken charges in our MDS study to predict the interfacial water characteristics at the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface without/with the presence of ferric hydroxide. The simulated contact angle measurements confirmed the relationship between the formation of ferric hydroxide and the corresponding hydrophilic character for the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface with ferric hydroxide.

Our MDS results about the interfacial water structures and dynamic properties reveal the hydrophobic character for the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface without the presence of ferric hydroxide, which is consistent with our experimental results. The relatively weak interactions between the surface atoms and the interfacial water molecules are the primary reason for this. On the other hand, for the fresh unoxidized (100) surface and the polysulfide and elemental sulfur at the (100) surface with the presence of ferric hydroxide, the electrostatic interaction and hydrogen bonding between the ferric hydroxide and interfacial water molecules are the origin of their macroscopic hydrophilic character and wettability, according to our MDS analysis about the interfacial water structures and dynamics properties.

Acknowledgements

Part of the financial support for this study was provided by the U.S. Department of Energy (DOE) under Basic Science Grant No. DE-FG-03-93ER14315. The Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences (BES), of the DOE funded work performed by Liem X. Dang. Battelle operates the Pacific Northwest National Laboratory for DOE. The calculations were carried out using computer resources provided by BES. The authors are grateful to Professor Tsun-Mei Chang for valuable discussions.

References:

- Abraham, F.F., 1978. The interfacial density profile of a Lennard-Jones fluid in contact with a (100) Lennard-Jones wall and its relationship to idealized fluid/wall systems: A Monte Carlo simulation. *The Journal of Chemical Physics* 68, 3713.
- Abu-Dari, K., Raymond, K.N., Freyberg, D.P., 1979. The bihydroxide (H_3O_2^-) anion. A very short, symmetric hydrogen bond. *Journal of the American Chemical Society* 101, 3688-3689.
- Berendsen, H., Grigera, J., Straatsma, T., 1987. The missing term in effective pair potentials. *Journal of Physical Chemistry* 91, 6269-6271.
- Blanchard, M., Alfredsson, M., Brodholt, J., Wright, K., Catlow, C.R.A., 2007. Arsenic incorporation into FeS_2 pyrite and its influence on dissolution: a DFT study. *Geochimica Cosmochimica Acta* 71, 624–630.
- Buckingham, R., 1938. The classical equation of state of gaseous helium, neon and argon. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 168, 264-283.
- Buckley, A., Woods, R., 1987. The surface oxidation of pyrite. *Applied Surface Science* 27, 437-452.
- Cao, Q., Wang, X., Miller, J.D., Cheng, F., Jiao, Y., 2011. Bubble attachment time and FTIR analysis of water structure in the flotation of sylvite, bischofite and carnallite. *Minerals Engineering* 24, 108–114.
- Cheng, F., Cao, Q., Guan, Y., Cheng, H., Wang, X., Miller, J.D., 2013. FTIR analysis of water structure and its influence on the flotation of arcanite (K_2SO_4) and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). *International Journal of Mineral Processing* 122, 36–42.

Chowdhuri, S., Chandra, A., 2001. Molecular dynamics simulations of aqueous NaCl and KCl solutions: Effects of ion concentration on the single-particle, pair, and collective dynamical properties of ions and water molecules. *The Journal of Chemical Physics* 115, 3732.

Dang, L.X., Pettitt, B.M., 1990. A theoretical study of like ion pairs in solution. *Journal of Physical Chemistry* 94, 4303-4308.

Delley, B., 2000. DMol3 DFT studies: from molecules and molecular environments to surfaces and solids. *Computational Materials Science* 17, 122-126.

Du, H., Miller, J.D., 2007. A molecular dynamics simulation study of water structure and adsorption states at talc surfaces. *International Journal of Mineral Processing* 84, 172-184.

Du Plessis, R., 2004. Thiocarbonate Flotation Chemistry of Auriferous Pyrite, Ph.D. Thesis, Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah.

Eftekhari-Bafrooei, A., Borguet, E., 2009. Effect of surface charge on the vibrational dynamics of interfacial water. *Journal American Chemical Society* 131, 12034–12035.

Gallo, P., Rapinesi, M., Rovere, M., 2002. Confined water in the low hydration regime. *The Journal of Chemical Physics* 117, 369.

Hung, A., Yarovsky, I., Russo, S.P., 2003. Density-functional theory studies of xanthate adsorption on the pyrite FeS (110) and (111) surfaces. *The Journal of Chemical Physics* 118, 6022–6029.

Jin, J., Miller, J.D., Dang, L.X., 2014. Molecular dynamics simulation and analysis of interfacial water at selected sulfide mineral surfaces under anaerobic conditions. *International Journal of Mineral Processing* 128, 55-67.

Jones, J.E., 1924. On the determination of molecular fields. I. From the variation of the viscosity of a gas with temperature. *Proceedings of the Royal Society of London. Series A, containing papers of a mathematical and physical character* 106, 441-462.

Kalinichev, A.G., Kirkpatrick, R.J., 2002. Molecular dynamics modeling of chloride binding to the surfaces of calcium hydroxide, hydrated calcium aluminate, and calcium silicate phases. *Chemistry of Materials* 14, 3539-3549.

Koneshan, S., Rasaiah, J.C., Lynden-Bell, R., Lee, S., 1998. Solvent structure, dynamics, and ion mobility in aqueous solutions at 25 C. *The Journal of Physical Chemistry B* 102, 4193-4204.

Kusalik, P.G., Svishchev, I.M., 1994. The spatial structure in liquid water. *Science* 265, 1219-1221.

Lee, S.H., Rasaiah, J.C., 1996. Molecular dynamics simulation of ion mobility. 2. Alkali metal and halide ions using the SPC/E model for water at 25 C. *The Journal of Physical Chemistry* 100, 1420-1425.

Lee, S.H., Rossky, P.J., 1994. A comparison of the structure and dynamics of liquid water at hydrophobic and hydrophilic surfaces—a molecular dynamics simulation study. *The Journal of Chemical Physics* 100, 3334.

Luzar, A., Chandler, D., 1996. Effect of environment on hydrogen bond dynamics in liquid water. *Physical Review Letters* 76, 928-931.

Lynden-Bell, R., Rasaiah, J., 1997. From hydrophobic to hydrophilic behaviour: A simulation study of solvation entropy and free energy of simple solutes. *The Journal of Chemical Physics* 107, 1981.

Mahoney, M.W., Jorgensen, W.L., 2000. A five-site model for liquid water and the reproduction of the density anomaly by rigid, nonpolarizable potential functions. *The Journal of Chemical Physics* 112, 8910.

Miller, J.D., Du Plessis, R., Kotylar, D., Zhu, X., Simmons, G., 2002. The low-potential hydrophobic state of pyrite in amyl xanthate flotation with nitrogen. *International Journal of Mineral Processing* 67, 1-15.

Mulliken, R., 1955. Report on notation for the spectra of polyatomic molecules. *The Journal of Chemical Physics* 23, 2338.

Mundy, C., Mohamed, F., Schiffman, F., Tabacchi, G., Forbert, H., Kuo, W., Hutter, J., Krack, M., Iannuzzi, M., McGrath, M., 2000. CP2K software package.

Nieto-Draghi, C., Ávalos, J.B., Rousseau, B., 2003. Transport properties of dimethyl sulfoxide aqueous solutions. *The Journal of Chemical Physics* 119, 4782.

Ostroverkhov, V., Waychunas, G.A., Shen, Y., 2005. New information on water interfacial structure revealed by phase-sensitive surface spectroscopy. *Physical Review Letters* 94 046102-1-046102-4.

Palacky, G., 1988. Resistivity characteristics of geologic targets. *Electromagnetic Methods in Applied Geophysics* 1, 53-130.

Peng, Z., Merz Jr, K.M., 1992. The gas-phase and solution-phase free energy surfaces for carbon dioxide reaction with hydroxide ($\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$). *Journal of the American Chemical Society* 114, 2733-2734.

Peng, H., Nguyen, A.V., Birkett, G.R., 2012. Determination of contact angle by molecular simulation using number and atomic density contours. *Molecular Simulation* 38, 945-952.

- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865.
- Perdew, J.P., Ziesche, P., Eschrig, H., 1991. *Electronic Structure of Solids' 91*. Akademie-Verlag, Berlin, pp. 11-20.
- Raichur, A., Wang, X., Parekh, B., 2000. Quantifying pyrite surface oxidation kinetics by contact angle measurements. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 167, 245-251.
- Rappé, A.K., Casewit, C.J., Colwell, K., Goddard III, W., Skiff, W., 1992. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *Journal of the American Chemical Society* 114, 10024-10035.
- Rasaiah, J.C., Zhu, J., 1990. Cavity functions and association in models for weak electrolytes and sticky hard spheres. *The Journal of Chemical Physics* 92, 7554.
- Rieder, M., Crelling, J.C., Šustai, O., Drábek, M., Weiss, Z., Klementová, M., 2007. Arsenic in iron disulfides in a brown coal from the North Bohemian Basin, Czech Republic. *International Journal of Coal Geology* 71, 115-121.
- Rustad, J.R., 2001. Molecular models of surface relaxation, hydroxylation, and surface charging at oxide-water interfaces. *Reviews in Mineralogy and Geochemistry* 42, 169-198.
- Rustad, J.R., Felmy, A.R., Bylaska, E.J., 2003. Molecular simulation of the magnetite-water interface. *Geochimica et Cosmochimica Acta* 67, 1001-1016.
- Shen, Y.R., 1994. Surfaces probed by nonlinear optics. *Surface Science* 299, 551-562.
- Shen, Y.R., Ostroverkhov, V., 2006. Sum-frequency vibrational spectroscopy on water

interfaces: polar orientation of water molecules at interfaces. *Chemical Reviews* 106, 1140–1154.

Shi, B., Dhir, V.K., 2009. Molecular dynamics simulation of the contact angle of liquids on solid surfaces. *The Journal of Chemical Physics* 130, 034705.

Sithole, H., Ngoepe, P., Wright, K., 2003. Atomistic simulation of the structure and elastic properties of pyrite (FeS_2) as a function of pressure. *Physics and Chemistry of Minerals* 30, 615–619.

Smart, R.S., Amarantidis, J., Skinner, W.M., Prestidge, C.A., La Vanier, L., Grano, S.R., 2003. Surface analytical studies of oxidation and collector adsorption in sulfide mineral flotation. K. Wandelt, S. Thurgate (Eds.), *Solid-Liquid Interfaces: Topics in Applied Physics*, Springer-Verlag: Berlin Heidelberg 85, pp. 3-62.

Smith, D.E., Dang, L.X., 1994. Computer simulations of NaCl association in polarizable water. *The Journal of Chemical Physics* 100, 3757.

Spohr, E., Hartnig, C., Gallo, P., Rovere, M., 1999. Water in porous glasses. A computer simulation study. *Journal of Molecular Liquids* 80, 165-178.

Steudel, R., Eckert, B., 2003. Solid sulfur allotropes. *Elemental Sulfur and Sulfur-rich Compounds I*, Topics in Current Chemistry, Springer-Verlag: Berlin Heidelberg 230, pp. 1-79.

Todorova, T., Alexiev, V., Prins, R., Weber, T., 2004. Ab initio study of 2H-MoS₂ using Hay and Wadt effective core pseudo-potentials for modelling the (100) surface structure. *Physical Chemistry Chemical Physics* 6, 3023–3030.

VandeVondele, J., Hutter, J., 2007. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *The Journal of Chemical Physics* 127, 114105.

VandeVondele, J., Krack, M., Mohamed, F., Parrinello, M., Chassaing, T., Hutter, J., 2005. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* 167, 103-128.

Wang, J., Kalinichev, A.G., Kirkpatrick, R.J., 2004. Molecular modeling of water structure in nano-pores between brucite (001) surfaces. *Geochimica et Cosmochimica Acta* 68, 3351-3365.

Wang, X., Pan, B., Cheng, H., Miller, J.D., 2013. Separation of carnallite from halite by reverse flotation with dodecyl morpholine for the production of potash. Presentation, 2013 SME Annual Meeting, Denver, Colorado.

Wang, X., Yin, X., Nalaskowski, J., Du, H., Miller, J.D., 2012. Molecular features of water films created with bubbles at hydrophilic and hydrophobic surfaces. In: *Proceedings XXVI IMPC 2012* New Delhi, India, pp. 05819-05828

Werder, T., Walther, J.H., Jaffe, R., Halicioglu, T., Koumoutsakos, P., 2003. On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes. *The Journal of Physical Chemistry B* 107, 1345–1352.

Yalamanchili, M.R., Kellar, J.J., Miller, J.D., 1991. In-situ internal reflection spectroscopy of collector adsorption phenomena in soluble-salt flotation systems. Preprints XVII International Mineral Processing Congress, Dresden, Germany, pp. 131–142.

Yeganeh, M., Dougal, S., Pink, H., 1999. Vibrational spectroscopy of water at liquid/solid interfaces: crossing the isoelectric point of a solid surface. *Physical Review Letters* 83, 1179.

Yin, X., 2012. Anisotropic Surface Features of Selected Phyllosilicates. Ph.D. Thesis, Metallurgical Engineering. University of Utah.

Yu, C.-J., Richter, A., Datta, A., Durbin, M., Dutta, P., 1999. Observation of molecular layering in thin liquid films using X-ray reflectivity. *Physical Review Letters* 82, 2326.

Zhang, X., Du, H., Wang, X., Miller, J.D., 2013. Surface chemistry considerations in the flotation of rare-earth and other semisoluble salt minerals. *Minerals and Metallurgical Processing* 30, 24–37.

Table 1 Potential Parameters for the Atoms in Pyrite, Polysulfide, Elemental Sulfur, and Ferric Hydroxide.

Atom	r_m (Å)	ϵ (Kcal/mol)	q (Coulomb)
Fe in Bulk Pyrite	2.912	0.013	0.1476
S in Bulk Pyrite	4.035	0.274	-0.0738
Fe in Polysulfide	2.912	0.013	0.1476
S in Polysulfide	4.035	0.274	-0.0369
S in Elemental Sulfur	4.035	0.274	0.0000
Fe ³⁺ Cation	2.912	0.013	3.0000
O in Hydroxide Group	1.640	0.152	-1.3167
H in Hydroxide Group	1.000	0.000	0.3167

Table 2 Experimental Contact Angles.

Pyrite (100) Surface	Contact Angle, Degree
After Polishing	62.5
Oxidized in 30% Hydrogen Peroxide Solution for 90 Seconds	23.0
Oxidized in 30% Hydrogen Peroxide Solution for 180 Seconds	12.0
Washed with EDTA Solution	64.5

Table 3 Simulated Contact Angles for the Pyrite (100) Surface.

Mineral Surface	Ferric Hydroxide	Contact Angle , Degree
Fresh Unoxidized (100) Surface	No	70.0
	Yes	24.0
Polysulfide at the (100) Surface	No	72.5
	Yes	22.0
Elemental Sulfur 8-Member Rings at the (100) Surface	No	71.0
	Yes	14.0
Elemental Sulfur Dimers at the (100) Surface	No	72.5
	Yes	14.0

Table 4 Water Residence Time for the Pyrite (100) Surface.

Mineral Surface	Ferric Hydroxide	Water Residence time , ps
Fresh Unoxidized (100) Surface	No	7.5
	Yes	17.2
Polysulfide (100) Surface	No	7.0
	Yes	14.0
Elemental Sulfur 8-Member Rings (100) Surface	No	6.0
	Yes	18.6

Table 5 Proportions of Hydrogen Bonds between Water and Hydroxide in the Total Number of Hydrogen Bonds in the Region less than 7Å from the Pyrite (100) Surface.

Mineral Surface	Ferric Hydroxide	Nh _{water-hydroxide} /Nh _{total} , %
Fresh Unoxidized (100) Surface	No	0
	Yes	18.3
Polysulfide at the (100) Surface	No	0
	Yes	17.0
Elemental Sulfur 8-Member Rings at the (100) Surface	No	0
	Yes	22.8

Figure Captions:

Figure 1 SEM images for: (a) the fresh pyrite (100) surface; (b) the pyrite (100) surface oxidized in 30% hydrogen peroxide solution for 90 seconds; (c) the oxidized pyrite (100) surface washed with EDTA.

Figure 2. Snapshots for the initial state and final state of the DFT calculations for ferric hydroxide organized at the pyrite (100) surface. The atoms' color codes are as follow: yellow, S; green, Fe in pyrite crystal; orange, ferric cation; red, O; white, H (see web version for figures in color).

Figure 3. Top and side views of the polysulfide and two elemental sulfur states at the pyrite (100) surface. The atoms' color codes are as follow: yellow, S in pyrite crystal; green, Fe in pyrite crystal; dark green, Fe atoms in polysulfide; light green, S atoms in polysulfide; light yellow, elemental sulfur (see web version for figures in color).

Figure 4. Water drop at a fresh unoxidized pyrite (100) surface: (a) without ferric hydroxide; (b) with ferric hydroxide.

Figure 5. Snapshots for interfacial water at the pyrite (100) surface. The atoms' color codes are as follow: red, O in water; white, H in water; blue, O in hydroxide; light blue, H in hydroxide; orange, ferric cation; yellow, S in pyrite; green, Fe in pyrite or polysulfide; light green, S atoms in polysulfide; light yellow, elemental sulfur (see web version for figures in color).

Figure 6. Number density distribution plots for the fresh unoxidized pyrite (100) surface without/with the presence of ferric hydroxide.

Figure 7. Schematic illustration describing the orientation of a water dipole moment (α) and hydrogen position relative to the surface normal (β).

Figure 8. Water dipole moment (angle α) and hydrogen position (angle β) relative density distribution along the surface normal for the fresh unoxidized pyrite (100) surface without/with ferric hydroxide.

Figure 9. Distribution of hydrogen-bonding number per water molecule along the fresh unoxidized pyrite (100) surface without/with ferric hydroxide.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure Captions:

Figure 1 SEM images for: (a) the fresh pyrite (100) surface; (b) the pyrite (100) surface oxidized in 30% hydrogen peroxide solution for 90 seconds; (c) the oxidized pyrite (100) surface washed with EDTA.

Figure 2. Snapshots for the initial state and final state of the DFT calculations for ferric hydroxide organized at the pyrite (100) surface. The atoms' color codes are as follow: yellow, S; green, Fe in pyrite crystal; orange, ferric cation; red, O; white, H (see web version for figures in color).

Figure 3. Top and side views of the polysulfide and two elemental sulfur states at the pyrite (100) surface. The atoms' color codes are as follow: yellow, S in pyrite crystal; green, Fe in pyrite crystal; dark green, Fe atoms in polysulfide; light green, S atoms in polysulfide; light yellow, elemental sulfur (see web version for figures in color).

Figure 4. Water drop at a fresh unoxidized pyrite (100) surface: (a) without ferric hydroxide; (b) with ferric hydroxide.

Figure 5. Snapshots for interfacial water at the pyrite (100) surface. The atoms' color codes are as follow: red, O in water; white, H in water; blue, O in hydroxide; light blue, H in hydroxide; orange, ferric cation; yellow, S in pyrite; green, Fe in pyrite or polysulfide; light green, S atoms in polysulfide; light yellow, elemental sulfur (see web version for figures in color).

Figure 6. Number density distribution plots for the fresh unoxidized pyrite (100) surface without/with the presence of ferric hydroxide.

Figure 7. Schematic illustration describing the orientation of a water dipole moment (α) and hydrogen position relative to the surface normal (β).

Figure 8. Water dipole moment (angle α) and hydrogen position (angle β) relative density distribution along the surface normal for the fresh unoxidized pyrite (100) surface without/with ferric hydroxide.

Figure 9. Distribution of hydrogen-bonding number per water molecule along the fresh unoxidized pyrite (100) surface without/with ferric hydroxide.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.