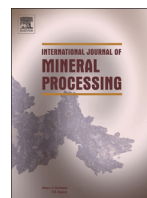




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Interfacial water structure and the wetting of mineral surfaces

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ABSTRACT

Advanced tools, including atomic force microscopy (AFM), sum frequency vibrational spectroscopy (SFVS), and molecular dynamics simulations (MDS), are being used to describe interfacial water structure and to contrast the structure of water at a hydrophilic mineral surface with that at a hydrophobic mineral surface. Specifically, this contrast is revealed from interfacial water features based on the extent of H-bonding, dipole orientation, exclusion zone thickness, and residence time. Progress in our understanding of interfacial water structure and wetting phenomena is reported for different mineral classes including sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, including both semi-soluble and soluble salts.

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1. Introduction

Flotation separation processes are of great significance to the mining industry with millions of tons of mineral resources being processed each day for the separation and recovery of valuable mineral commodities. It is most appropriate to recognize Professor Heinrich Schubert on the occasion of his 90th year since he has made significant contributions to the development of flotation technology, including the flotation chemistry of non-sulfide minerals, particularly the flotation chemistry of potash.

Interfacial water structure and the wetting of mineral surfaces are of fundamental importance in the area of flotation chemistry, as well as having importance in other areas of technology. Now, with advanced tools, the features of interfacial water structure and wetting phenomena at mineral surfaces can be considered in greater detail. These tools include atomic force microscopy (AFM), sum frequency vibrational spectroscopy (SFVS), and molecular dynamics simulations (MDS).

Specifically, atomic force microscopy can be used not only to describe charging of mineral surfaces, but also to describe the wetting characteristics of the surface using selected cantilevers with hydrophobic tips such as a diamond-like-carbon tip (Yin and Miller, 2012; Yin et al., 2012). In this way, a hydrophobic mineral surface can be described by the magnitude of the attractive force at the PZC in the absence of electrostatic forces. Also, with AFM surface force measurements, we have the opportunity to interrogate the surfaces of small particles, such as nanometer clay particles, and from the polarity of such surfaces, describe their wetting characteristics.

In the case of sum frequency vibrational spectroscopy, the surface spectra reveal information regarding the structure and the degree of coordination of water molecules at the mineral surface (Shen and Ostroverkhov, 2006). In this way, the extent to which interfacial water molecules are hydrogen bonded to each other and at the surface can be described based on the frequencies observed for OH vibrations. The SFVS spectra for the hydrophilic surface state, a surface well wetted by water, reveal characteristic absorption peaks for water with complete tetrahedral coordination (ice-like water at $\sim 3200\text{ cm}^{-1}$) and with incomplete tetrahedral coordination (liquid-like water at 3400 cm^{-1}), but no peak for the free OH stretch (vapor-like water at $3600\text{--}3700\text{ cm}^{-1}$). In contrast, the SFVS spectra for the hydrophobic surface state reveal a strong and distinct absorption at $3600\text{--}3700\text{ cm}^{-1}$ corresponding to the free OH stretching vibration which supports the notion of a water exclusion zone ($\sim 3\text{ \AA}$ in thickness) at hydrophobic surfaces.

Finally, molecular dynamics simulations are being used in flotation chemistry (Du et al., 2012) not only to describe interfacial water features (extent of H-bonding, dipole orientation, exclusion zone thickness, residence time), but also to describe wetting phenomena both from sessile drop simulations and from bubble attachment simulations (Jin et al., 2014; Jin and Miller, submitted for publication). In this way, wetting characteristics are examined and hydrophobic surfaces are distinguished from hydrophilic surfaces. Results from MDS contact angle simulations show that hydrophobic surfaces are characterized by the presence of a water exclusion zone, interfacial water dipoles parallel to the surface, a short residence time for interfacial water molecules (usually less than 10 ps), and incomplete wetting.

Progress in our understanding of interfacial water structure and wetting phenomena is reported for different mineral classes including

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Table 1

Simulated and experimental contact angles for selected sulfide mineral surfaces under anaerobic conditions (Jin et al., 2014).

Sulfide mineral surface	Contact angle, degrees	
	Experimental	MDS
Molybdenite face	84	84
Pyrite (100) surface	64	77
Chalcopyrite (012) surface	74 (random surface)	70
Galena (100) surface	82	66
Sphalerite (110) surface	44	49
Molybdenite armchair-edge	36	55
Molybdenite zigzag-edge	36	26

sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, both semi-soluble and soluble salts.

2. Sulfide minerals

The low degree of surface polarity and more hydrophobic character distinguish the sulfide mineral class from other mineral classes. This feature accounts for the fact that the hydrophobic surface state can be created at low concentrations of short chained collector molecules. The sulfide minerals are also distinguished by the fact that generally their surfaces are thermodynamically unstable with respect to oxidation and hydrolysis which increases the surface polarity and hydration. This instability of the sulfide mineral surfaces makes analysis and generalization regarding their wetting characteristics more difficult.

Several investigations have demonstrated that many sulfide minerals exhibit native floatability and can be floated without a collector. Flotation of various sulfides in the virtual absence of oxygen (i.e., in water containing less than 5 ppb oxygen) has shown the natural

floatability of these minerals under such conditions (Fuerstenau and Sabacky, 1981). Under anaerobic conditions, the sulfide minerals are not well wetted by water and exhibit a hydrophobic surface state, as revealed in Table 1.

MDS sessile drop contact angles for selected sulfide mineral surfaces are consistent with experimental results. See Table 1. An MDS snapshot of a water drop at a fresh pyrite (100) surface is shown in Fig. 1a. According to MDS interfacial water analysis, a “water exclusion zone” of 3 Å accounts for the hydrophobic surface state of sulfide mineral surfaces under anaerobic conditions (Jin et al., 2014). These results are supported by the SFVS results for hydrophobic surfaces and X-ray reflectivity measurements. In addition, water residence times of less than 10 ps and reduced H-bonding of interfacial water molecules are further characteristics of the hydrophobic sulfide mineral surfaces. Thus, the MDS interfacial water features reveal the relatively weak interaction between interfacial water and the selected sulfide mineral surfaces, which accounts for the origin of the natural hydrophobic character of the sulfide minerals under anaerobic conditions.

However, due to the instability of these sulfide mineral surfaces with respect to oxidation, the surfaces become hydrophilic on exposure to air and water. For example, after oxidation of the pyrite surface with a 30% hydrogen peroxide solution for 90 s, the experimental sessile drop contact angle for a pyrite (100) surface dropped from 63° to 23° (Jin et al., 2015). The hydrophilic character of the oxidized pyrite surface with ferric hydroxide islands (Miller et al., 2002) is also revealed by the MDS snapshot of a water drop wetting the pyrite surface and creating a 22° contact angle as shown in Fig. 1b. In the case of the oxidized pyrite surface, the interfacial water molecules form hydrogen bonds with ferric hydroxide clusters and exhibit a residence time of about 16 ps, according to the MDS interfacial water analysis. The electrostatic interaction and hydrogen bonding between the ferric hydroxide and interfacial

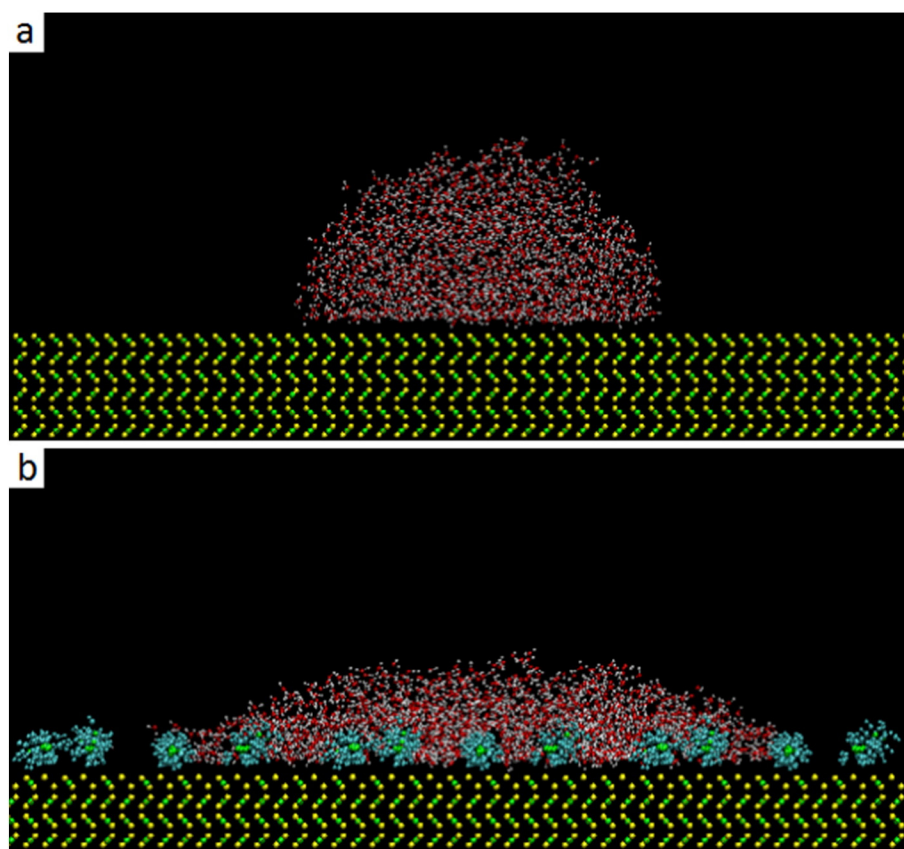


Fig. 1. Snapshot of a water drop containing 1270 water molecules spreading at (a) fresh pyrite (100) surface and (b) oxidized pyrite surface with ferric hydroxide islands. The simulation time is 1 ns. The color code for the atoms is as follows: blue, OH⁻; green, Fe; yellow, S; red, O; white, H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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