



Characterizing mineral wettabilities on a microscale by colloidal probe atomic force microscopy



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ABSTRACT

For finely intergrown ores the characterization of reagent-mineral interactions in flotation systems holds difficult challenges for the applicability of standard techniques like Hallimond tube tests or contact angle experiments or renders them impossible, while other techniques might not work in an aqueous environment. We present the utilization of an atomic force microscope with a hydrophobic colloidal probe to characterize the wettabilities of individual mineral grains on a microscale. A sulfidic ore sample containing chalcopyrite, pyrite and quartz is investigated in an aqueous environment. The mineralogy of the sample is characterized by SEM + EDX and its wettability by contact angle measurements. Force mappings on the respective minerals are performed and allow for a distinction between quartz, chalcopyrite and pyrite with the resulting force distributions. An additional focus of this paper lies on the heterogeneities within one mineral surface domain and the applicability for grain mappings.

1. Introduction

As the process result in flotation is to a great extent governed by the wettabilities of the involved particle systems it is crucial to gain an understanding of particle – reagent interactions. For finely intergrown ores the characterization of these interactions holds difficult challenges for the applicability of standard techniques like Hallimond tube tests or contact angle experiments due to the availability of suitable sample material in quantity and quality. This also applies to techniques like the capillary pressure method reported by Stevens et al. (2009). For more sophisticated techniques like XPS, AES, vibrational spectroscopy and (ToF-)SIMS limitations are given by the measurement conditions. ToF-SIMS was successfully applied as an indicator for the wettability of a model system (Priest, 2008) and chalcopyrite particles, allowing to calculate individual contact angles with the disadvantage of a high cost system, more time consumption and a necessary calibration (Brito e Abreu et al., 2010). Being limited to metal sulfides, electrochemical measurements allow a rapid assessment of the mineral surface state (Grano et al., 1990). Hence, there is a need to develop a relatively simple technique able to characterize mineral wettabilities in an aqueous environment with a high spatial resolution that allows investigations on complex mineral systems. One versatile tool to measure surface forces is the atomic force microscope (AFM) (Butt et al., 2006). In 2014 Rudolph and Peuker (2014a,b) described the application of an AFM utilizing a polystyrene probe to measure force interactions on polished

mineral samples with different measuring modes. A similar concept was also applied by Xie et al. who functionalized a conventional cantilever to probe the nanoscale hydrophobicity on a sphalerite surface (Xie et al., 2017) and Wada et al. who used the colloidal probe AFM (CP-AFM) technique to probe the local hydrophobicity of a sapphire surface (Wada, 2017).

This paper aims to critically display the advantages and limitations of the CP-AFM technique to characterize the wettabilities of mineral surfaces. The term hydrophobic will be used in the context of froth flotation, i.e. when a particle is able to attach to a gas bubble and not by its classical definition, i.e. the water contact angle is larger than 90°, although it is handled differently in the literature cited. The technique presented in this paper utilizes the concept of hydrophobic interactions, which has been extensively studied over the past decades by various research groups and was first reported by Blake and Kitchener (1972). Described as a long-range attractive interaction the adhesive forces associated are about an order of magnitude higher than maximum possible van der Waals dispersion forces. Israelachvili and Pashley suggested that the interaction might be related to the local water structure at solid-liquid interfaces (Israelachvili and Pashley, 1982). Parker et al. concluded that the long-range attraction between hydrophobic surfaces most likely originates from submicroscopic bridging bubbles or cavities (Parker et al., 1994), while this mechanism was questioned due to the lifetime of nanoscopic bubbles in water ranging from 1 μs to 100 μs for bubble radii of 10 nm to 100 nm due to their

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Laplace pressure (Ljunggren and Eriksson, 1997). A variety of sources for the interactions were discussed in a review by Attard (2003).

Today nanobubbles are widely accepted as the cause for the long-range attractive interaction (5–275 nm) (Yakubov et al., 2000), as they were imaged by AFM based techniques and additional methods (Switkes and Ruberti, 2004; Zhang et al., 2008; Yang, 2003). Detecting heights and shapes, the authors described these gas domains either as isolated (Yang, 2003), networks (Switkes and Ruberti, 2004) or as micropancakes (Seddon and Lohse, 2011), which gives an indication for the extreme variability in the range of the measured forces due to variability in the coverage and size of such nanobubbles (Attard, 2003).

Mechanisms of nanobubble formation are the supersaturation of the solvent (Yang, 2003) e.g. by addition of ethanol in water or temperature change (Parker et al., 1994), submersion of a hydrophobic and or rough surface and formation of nanobubbles in the contact region of hydrophobic surfaces (Parker et al., 1994; Wallqvist, 2009). Therefore, the range of the attraction is governed by the aeration state of the solvent, leading to shorter attraction distances in degassed water (Attard, 2003). Mezger et al. investigated the water-octadecyltrichlorosilane (OTS) interface on a molecular smooth surface by X-ray reflectivity experiments in degassed and gas saturated water deriving an electron depleted layer due to the rearrangement of H₂O molecules. The authors stated an upper limit of 6 Å for the hydrophobic gap with no effect of dissolved gas on the gap size (Mezger, 2006). These findings contradict results of neutron reflectivity measurements by Doshi et al., which indicated a difference for reduced water density regions at the water-OTS interface for naturally aerated and degassed water, also stating a slightly increased size of the water density depletion region (Doshi, 2005). Both Authors stated no indication for nanobubbles on the investigated smooth surfaces. Yang et al. investigated surfaces with a different degree of surface hydrophobicity and nanoscale roughness, concluding that the bubbles formed on rough surfaces were larger and less densely distributed than those on a smooth surface of similar hydrophobicity (Yang, 2003). This should lead to broader distributed values in force spectroscopic measurements in terms of long range attraction and maximum adhesion. Contradicting results were published by Wallqvist (2009). For more detailed information on nanobubbles refer to the reviews compiled by Attard (2003); Hampton and Nguyen (2010).

In the last years, in contrast to the beginning of the research on nanobubbles, the focus shifted from investigating the hydrophobic effect itself to utilizing it to characterize solid-liquid interfaces on AFM based techniques (Rudolph and Peuker, 2014a,b; Xie et al., 2017; Wada, 2017; Ditscherlein et al., 2016; Fritzsche and Peuker, 2014, 2015; Wallqvist, 2006). Force spectroscopic imaging has so far been published by multiple authors in a biological context (Willemsen, 1998; Sullan et al., 2009), with functionalized silica surfaces of varying roughness (Wallqvist, 2009) and by probing a sphalerite surface (Xie et al., 2017). To the best knowledge of the author it was not yet reported on a natural ore section with varying wettabilities.

2. Materials and methods

2.1. Chemicals

HCl, NaOH, KCl and ethanol (ROTISOLV® HPLC Gradient Grade), which were used to prepare the background solution, for pH adjustment and sample cleaning, were supplied by Carl Roth GmbH and used as received. Potassium octylxanthate was used to hydrophobize the sulfidic minerals and DYNASYLAN® F8261 for the colloidal probes and the reference sample. For the preparation of the colloidal probes epoxy glue (Uhu Plus Endfest 300) was utilized and the polishing of the substrate was performed with DiaPro ¼ µm diamond suspension by Struers.

Table 1
Cantilever properties, * indicates a cantilever reequipped with a new SiO₂ particle.

Cantilever	Probe	Force constant in N/m	Application
1	CP1	2.16	Force distributions
2	CP2	2.07	Force distributions
3	CP3	2.01	Force distributions
4	CP4	2.18	Force distributions
5	CP5	2.01	Force distributions
6	CP6	2.22	Force distributions
1*	CP7	2.07	Grain mapping
2*	CP8	2.01	Grain mapping
7	CP9	5.79	Reference sample

2.2. Colloidal probe preparation

Colloidal probe cantilevers were prepared by gluing 19.59 µm (standard deviation (SD) 0.69 µm) spherical and smooth SiO₂ particles (microparticles GmbH) onto All-In-One B and C type cantilevers (nano and more GmbH) after determining their resonance frequency for force constant calibration as described in (Butt et al., 2005). After setting of the glue the probes were plasma cleaned to remove organic contamination and to provide a high surface density of OH groups. Subsequently the probes and a similarly cleaned glass slide were functionalized by a procedure adapted from Hozumi et al. (1999). The parameters were set to 2 h at 115 °C with 50 µl DYNASYLAN® F8261. The result of the silanization was checked by contact angle measurements. An overview of the used cantilevers and probes is provided in Table 1. CP9 is a C type cantilever with a different dimensioning resulting in a higher force constant. All other cantilevers are B type cantilevers.

2.3. Sample characterization and regions of interest

The sample consists of a sulfidic ore section embedded in epoxy resin, which was gradually machine polished and finished by the procedure described in 2.4. The mineralogical composition of the sample was characterized by automated mineralogy, i.e. SEM + EDX and the main minerals are chalcopyrite, pyrite and quartz. The size of the mineral domains is sufficient to allow a macroscopic wettability characterization by sessile drop contact angle measurements. For the microscopic investigations three regions of interest (ROI) were defined as displayed in Fig. 1.

2.4. Sample preparation

As sulfides tend to oxidize altering their surface properties, prior to the contact angle and AFM measurements the sample was polished with a diamond suspension on a DP-Nap polishing cloth, also supplied by Struers. Following this step, the sample was cleaned in a beaker with KCl solution in an ultrasonic bath, rinsed with ethanol and swiped with a lint free cloth. Finally the sample was sonicated for 5 min in DI water to ensure the removal of residual ethanol. The author is aware that this procedure might already be changing the surface properties of the minerals. Therefore, the results obtained in this study might not reflect their known process behavior. To account for a possible alteration, the adsorption behavior of potassium octylxanthate was verified. The sample was submerged in 50 ml KCl solution set to pH 7 for 5 min. After 2.5 min the potassium octylxanthate stock solution was added setting the concentration to 10⁻⁶ M. During conditioning the solution was stirred with a magnetic stirrer and the pH adjusted if necessary. In addition to the measurements on the natural ore sample contact angles and adhesion forces were measured on a hydrophobized glass slide.

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