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Cryogenic XPS study of fast-frozen sulfide minerals: Flotation-related adsorption of *n*-butyl xanthate and beyond

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ABSTRACT

Cryogenic XPS of wet particulate samples separated via centrifugation and fast-frozen allows quasi *in situ* examination of solid surfaces, adsorbates, and reaction products, largely preventing the loss both of volatiles and hydrated species at mineral/water interfaces. Here, the cryo-XPS has been applied to characterize the surfaces and interfacial layers of natural pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and galena (PbS) in solutions of a common flotation collector, potassium *n*-butyl xanthate (KBX), in conjunction with zeta-potential measurement. It was found, in particular, that dibutyl dixanthogen was the major adsorbate at pyrite in 0.1 mM KBX and 10 mM KBX solutions; dixanthogen and cuprous xanthate in the next stage were formed on chalcopyrite, and predominant chemisorbed butyl xanthate was present at galena, including in 10 mM KBX solution. The results may suggest that the production of dixanthogens at the interface has been underestimated while the quantities of surface metal xanthates could be over evaluated in previous studies. Pronounced differential charging effects were observed in the XPS experiment for the samples moderately hydrophobized by the xanthate treatment; we proposed that the effect was due to electrically isolated mineral particles with hydrophobic and ice-repellent surfaces, which retained, however, some frozen water islets.

1. Introduction

Phenomena occurring at hydrophobic solid/aqueous solution interfaces are of considerable fundamental and practical interest for numerous industrial, environmental, and biological systems and processes. Froth flotation takes a central part in the mineral processing of base-metal ores and other raw materials; it is founded on the ability of hydrophobic particles to attach to air bubbles in the flotation pulp. Xanthates and other sulfhydryl collectors are normally applied, along with other reagents, to render hydrophobicity of mineral sulfide surfaces in the flotation practice [1,2]. However, the mechanisms of the interfacial processes are far from being fully understood owing to complex composition of the pulps, numerous factors affecting the solid/liquid/gas interaction and the lack of appropriate techniques for studying the solid/water interfaces. In particular, reflective IR spectroscopy (ATR–FTIR and related methods), which could be applied *in situ* [3–6], is not really surface sensitive and cannot determine total surface compositions. X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and X-ray absorption spectroscopy (XANES) allow determining the elemental composition and/or chemical bonding on the surface but the samples must be evacuated before the measurements [7–13], typically after washing to remove any adhering solution components, so interfacial volatile and soluble species of interest may be lost in the conventional experiments. XPS has been utilized in several studies on metal xanthates and adsorption of xanthates at sulfide minerals dried in air, nitrogen, or low vacuum and then cooled to liquid nitrogen temperature [14–21], and, for instance, dixanthogens evaporating in ultra-high vacuum (UHV) at room temperature have been recognized at pyrite [14,15,19,20]. To date, it has been found using *in situ* and *ex situ* FTIR, *ex situ* XPS, including synchrotron based, and other techniques, that dixanthogen is the main adsorption product at pyrite [1–3,14,15,19,22]. Xanthate radicals, copper (I) xanthate and dixanthogen have been specified at chalcopyrite but data on their proportion and the adsorption mechanism are still contradictory [3,8–10,22–25]; no cryogenic XPS investigation has been reported. Chemisorbed xanthate and lead xanthates have been found at galena [1–7,17,26–34], whereas dixanthogen is believed to arise only at high potentials [4] unusual for technological conditions.

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Understanding the particle attachment to an air bubble via the rupture of interfacial water film, that is a key event in flotation, requires information on the characteristics of the interfacial layer and its changes induced by collector adsorption, in addition to the nature of the adsorbate. Cryogenic XPS of fast-frozen powder samples [35–38] is a technique involving centrifugation of slurries and fast-freezing of the wet pastes, and largely preventing the loss both of volatiles and hydrated species, including physically adsorbed ones, so the solid–solution interface is supposed to remain essentially unaltered. It was reliably proved for numerous systems that contribution from bulk solution species was negligible after centrifugation (see [35–39] for experimental detail, examples of application and more references). Here, the cryo-XPS was used for a comparative quasi *in situ* characterization of interfacial species formed at ground natural pyrite, chalcopyrite, and galena under conditions closely related with flotation. The mineral particles conditioned in xanthate solutions were separated, fast-frozen to liquid nitrogen temperature and then pumped to UHV, without washing, preliminary drying or other sample treatment procedures applied. Along with specifying adsorbed species, a pronounced effect of differential charging induced by the xanthate treatment was observed; the effect was suggested to be due to poor adhesion of ice to the hydrophobic particles.

2. Experimental

2.1. Materials and sample preparation

Natural pyrite (Ozernoye ore deposit, Russia) containing an admixture of quartz (about 2 wt%), chalcopyrite (Primorskoye, Russia) and galena (Zhairem, Kazakhstan) with no visible inclusions of foreign phases were ground in an agate mortar to the size −75 μm just before the experiments. Fresh aqueous 0.1 mM or 10 mM solutions of potassium *n*-butyl xanthate (KBX) were prepared using commercial reagent (about 95%) recrystallized in acetone, and deionized water. Other chemicals were of analytical grade and were used as received. A portion of mineral (0.5 g) was added to 20 mL KBX solution adjusted to pH 8.0 ± 0.2 with fresh saturated solution of calcium hydroxide; the slurry was loaded in a polypropylene test tube and shaken for 20 min, centrifuged at 5000 rpm for 10 min; the supernatant was discarded.

The wet precipitate after centrifugation was placed on the molybdenum sample holder and frozen in the spectrometer airlock under dry N_2 (g) for 45 s prior to pumping to a vacuum of 10^{-7} Torr. The sample was transferred to the pre-cooled manipulator in the analytical chamber; the vacuum and the sample temperature were maintained at 10^{-9} Torr and −155 °C, respectively, over the measurement. In some experiments, the samples were warmed in the vacuum to room temperature overnight and reexamined. The photoelectron spectra were also acquired from the samples, which were dried in vacuum after centrifugation at room temperature. No washing was applied at any stage of the sample preparation.

2.2. X-ray photoelectron spectroscopy

The photoelectron spectra were recorded with Kratos Axis Ultra electron spectrometer equipped with a delay line detector at electron take-off angle 90°, and a hybrid lens system with a magnetic lens providing an analysis area of $0.3 \times 0.7\,\mathrm{mm}^2$. A monochromated Al Kα source (1486.7 eV) operated at 150 W was used. A co-axial neutralization system operated at filament current and bias of 1.9 A and 1.2 V, respectively, and charge balance (electron energy) of 3.2 V was used in the experiments; the sample holder was earthed. The binding energy (BE) scale was referenced to the C 1s peak of aliphatic carbon at 285.0 eV of a predominant band, and weaker ones emerged due to differential charging were arbitrary referred as "charge shifted", regardless of their real charging under the experimental conditions. The "normal" charge corrections were about 1 eV for pyrite, 0.5 eV for chalcopyrite, and ~1.8 eV for galena, and those were of 3.2–3.5 eV for strongly charged "isolated" fractions of all these minerals. The spectra were acquired from 2 to 3 samples prepared under the same or slightly changed conditions as described above. The experiments at ambient temperature were also performed using a SPECS instrument equipped with a hemispherical analyzer PHOIBOS 150 MCD 9 using the monochromatic Al Kα irradiation. The lines were fitted with Gaussian–Lorentzian peak profiles (50% for S 2p and O 1s and 70% Lorentzian for Cu 2p and Pb 4f) after Shirley background subtraction with CasaXPS software. Spin-orbit energy splitting and an intensity ratio for S $2p_{3/2,1/2}$ doublet were assumed of 1.19 eV, and 2:1, respectively, with the components of the doublet having equal linewidth.

2.3. Zeta-potential measurement

For zeta-potential measurement, minerals were ground to −44 μm; a portion of the precipitate obtained via centrifugation as described above was re-suspended in 1–2 mL water, the pH value was adjusted to pH 8.0 with $Ca(OH)_2$ solution, and the suspension was loaded into a folded polystyrene cell with Pd electrodes. Zeta-potential distributions were measured with a Zetasizer Nano ZS device (Malvern Instruments) using a combination of the electrophoresis and laser Doppler velocimetry (Laser Doppler Electrophoresis) at 20 °C.

3. Results

3.1. Pyrite

Fig. 1 shows cryogenic photoelectron Fe 2p, O 1s, C 1s and S 2p spectra collected from dry pyrite and the samples conditioned in water and KBX solutions. The detailed results of band fitting, survey spectra, and surface concentrations of the elements can be seen in Supplementary materials, along with the spectra acquired from the samples dried by pumping in the lock chamber at room temperature. The Fe 2p spectra are composed of a narrow low-spin Fe(II) peak at about 707.2 eV (above 50% of total iron), a band centered at 708.7 eV from surface Fe atoms bonded to sulfur, and a wide band at about 710.8 eV from Fe(III) oxyhydroxides (multiplet structure peaks were not used in the fit for simplicity), that is common for pyrite surfaces [40–47]. The contribution of Fe—O species somewhat increased for the mineral conditioned in water and reduced to approximately the same magnitude for pyrite treated in butyl xanthate solutions. In addition, some intensity (up to 15% of total iron) was observed at nominally lower binding energies. Similar features of the same magnitude take place also in the spectra of sulfur, carbon, and oxygen, indicating that the ones are due to charging effects, particularly, pyrite particles charged more strongly (about −3.5 eV before correction using C 1s line) due to poor electrical contact with the underlying material than the majority (less than −1 eV before the correction). Such particles remain minor in water, but the intensity of the shifted lines of carbon and oxygen notably increase, suggesting that a share of carbonaceous contaminant is not in electronic equilibrium with the pyrite substrate. The binding energies of the main lines increase by ~0.2 eV in aqueous media as compared with dry material, probably, owing to negative surface charging (zeta-potential of pyrite in water at pH 8 was below 0 mV) and the potential drop in arising electric double layer [37]. The wide O 1s spectrum of dry pyrite is composed of several lines attributable to