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HAXPES and XAFS studies of under-surface layers of metal sulfides oxidized in air and aqueous solutions

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Iron and copper sulfides are the most common sulfide minerals, which accompany base and precious metals in their ores, and promising materials for photovoltaic, battery cathode, sensor, thermoelectric and other applications. The electronic and optical properties of metal sulfides and their chemical reactivity strongly depend on the composition and structure of the real surfaces formed during the contact with the environments. XPS and other surface-sensitive techniques have found that metals can be easily released from the lattice of these compounds upon oxidation, leaving non-equilibrium metal-deficient surface layers. However, alterations of the non-stoichiometry with depth and characteristics of under-surface structures remain poorly understood. In order to study near-surface regions of natural polycrystalline pyrite FeS₂, pyrrhotite Fe₉S₁₀, chalcopyrite CuFeS₂ and valleriite (Cu,Fe)S•(Mg,Al)(OH)₂ after oxidation in the atmosphere and aqueous acidic 0.5 M Fe(III) chloride or sulfate solutions, we applied hard X-ray photoelectron spectroscopy (HAXPES) in the excitation photon energy range 2 keV to 6 keV together with S K- and Fe K-edge X-ray absorption spectra measured simultaneously in the total electron (TEY) and partial fluorescence yield (PFY) modes. The experiments were performed at HIKE endstation at BESSY II synchrotron facility (Helmholtz Zentrum Berlin). Both the element concentrations and the chemical state of atoms, e.g., mono-, di-, polysulfide and other S species, as a function of the excitation photon energy and so the probing depth, were determined. The near-surface regions of oxidized metal sulfide lattices are generally composed, in addition to surface oxyhydroxides, of: (i) a thin, no more than 1-4 nm outer layer containing polysulfide species, (ii) a layer with smaller stoichiometry deviations and low, if any, concentrations of polysulfide, which composition and dimensions widely vary for pyrite, pyrrhotite and chalcopyrite, depending on the chemical treatment conditions, and (iii) an almost stoichiometric underlayer extended to at least several dozen of nanometers. The latter shows Fe K-edge spectra altered probably due to a high content of defects for all the metal sulfides, including oxidized in ambient air. We suggest that the lengthy defective regions heavily affect the near-surface conductivity and processes involving surface and interfacial charge transfer. Particularly, the buried layers rather than surface products seem to be responsible for “passivation” of metal sulfides in the oxidative dissolution.