

## **Reactivity of surface sites on fractured arsenopyrite (FeAsS) toward oxygen**

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### **ABSTRACT**

The reactivity of arsenopyrite (FeAsS) fractured surfaces toward oxygen was studied using synchrotron radiation excited photoelectron spectroscopy (SXPS). The spectra of the pristine surface provide evidence of different As and S surface sites. Signals for As3d with 0.33 eV lower and 0.37 eV higher binding energy than the bulk signal are attributed to arsenic surface sites with filled and unfilled dangling bonds, respectively, caused by the rupture of Fe-As and As-S bonds. Sulfur surface sites with filled dangling bonds, bonded to three iron as well as to two iron and one arsenic atom, give rise to a composite signal in the S2p spectra shifted by 0.79 eV to lower binding energy. Reaction of oxygen with FeAsS surfaces in ultra-high vacuum reveals fast oxidation of As surface sites with filled dangling bonds to As species of increasing oxidation state. The detection of oxidation states As<sup>0</sup>, As<sup>2+</sup>, As<sup>3+</sup>, and As<sup>5+</sup> indicate a consecutive reaction scheme for arsenic oxidation involving elementary one-electron transfer steps. The Fe3p spectra have a corresponding intensity increase of a component with a binding energy 1.1 eV higher than the Fe3p signal emitted from the pristine surface. This signal is assigned to Fe bonded to oxidized arsenic. The very small changes in the S2p spectra together with their decreased intensity indicate the formation of an arsenic and iron containing overlayer of oxidation products on top of the FeAsS mineral surface where the S2p signal arises from. In air oxidation of arsenic continues with As<sup>5+</sup> being the final oxidation product. An additional Fe3p signal at 56.1 eV binding energy is attributed to Fe bonded to O atoms formed during Fe oxidation. Sulfur oxidation leads to numerous intermediate oxidation products with sulfate being the final product. During air oxidation of up to 30 min, the sulfur signal at the low binding energy side of the S2p spectrum is broadened which is probably caused by S<sup>2-</sup> formed in layers underneath As and Fe oxidation products. These oxidation products reach the surface by diffusion from the bulk (reaction induced segregation). A model of homogeneous oxidized layers on arsenopyrite indicates that reaction with air has produced a layer containing iron bonded to oxygen on top of the increasingly oxidized arsenic and iron containing layer. The Fe-O overlayer is about 1.8 monolayers thick and is probably formed through interaction of water with iron surface sites.