

Arsenic clustering in arsenian pyrite: A combined photoemission and theoretical modeling study

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ABSTRACT

Arsenian pyrite is known to have a strong association with gold in most auriferous refractory deposits, and thus understanding the chemical speciation of arsenic in localized environments in arsenian pyrite provides an important basis for determining its reactivity and mobility. However, arsenic is fast-oxidizing among elements in the Fe-As-S system and hence it may exist in various chemical states, which renders it difficult to establish arsenic nature under pristine conditions, particularly in arsenian pyrite. Herein, arsenian pyrite samples were analyzed on a synchrotron soft X-ray spectroscopy beamline under ultrahigh vacuum conditions, and As-3d as well as S-2p spectra were collected. A comparison between the spectrum of bulk As-3d in the samples with its bulk counterpart in arsenopyrite revealed a 0.6 eV shift toward lower binding energies. This observation was similar to loellingite (FeAs₂), where the binding energy shift was attributed to high electron density on As of the As-As dimer. Formation of As clusters resulting in comparable binding energy shifts was also proposed from the spectroscopic studies. The experiments were complemented by a series of first-principles calculations simulating four experimentally observed pyrite surfaces where surficial S atoms were randomly substituted by As. As such, six arsenian pyrite crystal surfaces were modeled, two of which constituted surficial As clusters replacing both S and Fe atoms. The surfaces were geometrically optimized, and surface energies were calculated along with the corresponding electronic structure providing a detailed distribution of partial charges for surficial atoms obtained from Löwdin population analysis. The calculated partial charges of atoms located at the surface arsenian pyrite indicated that while the electron density on the As atom of As-S dimers in arsenian pyrite is less negative than the As in bulk arsenopyrite, it is more negative for the As atom of As-As dimers, which were only seen in the surficial As clusters. This validated the description of As presence in arsenian pyrite as local clusters inducing localized lattice strain due to increased bond distances. Our findings offer a good background for future studies into the reactive sites in arsenian pyrite and how that compares with associated minerals, arsenopyrite, and pyrite.

Keywords: X-ray photoelectron spectroscopy, density functional theory, pyrite, arsenian pyrite