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Gersdorffite (NiAsS) chemical state properties and reactivity toward air and aerated, distilled water

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ABSTRACT

This first X-ray Photoemission Spectroscopic (XPS) study of gersdorffite (NiAsS) reveals a strong, asymmetric, singlet peak in the Ni 2*p* spectrum. It represents Ni of the bulk phase (fully coordinated), bonded to As-S dimers. The high binding-energy tail on the Ni 2*p* spectrum includes a core-level-shifted Ni surface species and a Doniach-Sunjic high-energy tail characteristic of conductors. A third contribution, likely a hydroxylated Ni species (Ni-OH), is also observed. The XPS characteristics of gersdorffite suggest it is a compound conductor.

Identical secondary surface products form on gersdorffite during reaction with both air and aerated, distilled water. Reaction rates in aerated water are more than tenfold greater than in air with arsenic being the most reactive element toward these oxidizing fluids and sulfur being the least reactive. Arsenate and arsenite are produced either in acidic form or as Ni-salts. The S 2*p* spectrum does not change appreciably with exposure to the oxidized fluids, although minor quantities of surface species of intermediate oxidation state were detected.

The Ni 2*p* signal of gersdorffite becomes weaker relative to the As 3*d* signal, and the O 1*s* signal strength increases, as reaction with air proceeds. Changes to the strengths of these signals probably results from accumulation of H_2O and oxidized As species in the secondary overlayer developed on bulk gersdorffite. The S 2*p* signal strength decreases with respect to the As 3*d* signal during reaction with air, probably because S is “buried” beneath the hydrated, As-enriched secondary overlayer (overlayer deficient in Ni and S). In contrast to air-reacted surfaces, the Ni 2*p* signal of water-reacted surfaces remains strong relative to the intensity of the As 3*d* signal. This may be explained by the high solubility of arsenites and arsenates, relative to $Ni(OH)_2$, present at the oxidized gersdorffite surface.