

Properties of As and S at NiAs, NiS, and Fe_{1-x}S surfaces, and reactivity of niccolite in air and water

H. WAYNE NESBITT* AND M. REINKE

Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada N6A 5B7

ABSTRACT

Niccolite (NiAs), NiS (high temperature form), and pyrrhotite (Fe_{1-x}S) are structurally related, with sulfur and arsenic sixfold coordinated. Their fracture or cleavage necessarily produces surface As and S species of lower coordination. Some sp³ hybridized As and S ions likely form at these surfaces, as observed for As at GaAs and S at pyrite surfaces. Upon relaxation, lone pairs of electrons occupy As and S dangling bonds, with the lone pair directed away from the surface and poised to react with adsorbates. According to the valence shell electron pair repulsion (VSEPR) model, the lone pair should repel the three hybrid orbitals forming metal-As or metal-S bonds, causing tetrahedral angles to contract and As and S ions to “protrude” from the surface.

X-ray photoelectron spectroscopic (XPS) study of niccolite (NiAs) surfaces fractured under high vacuum (10⁻⁹ torr) indicate that arsenic is more reactive than Ni toward residual gases of the XPS analytical chamber, as evident from development of small As¹⁺ and As³⁺ photopeaks in the As(3d) XPS spectrum. Hydroxide observed in the O(1s) XPS spectrum suggests formation of As(OH)₃. The O(1s) spectrum also revealed adsorbed H₂O and atomic oxygen radical (produced by dissociation of O₂) at the NiAs surface. Initiation of arsenic oxidation probably involved reduction of adsorbed atomic oxygen radicals, followed by hydration to produce hydroxyl, and finally to produce the observed As(OH)₃ surface species. There was no evidence for Ni reaction with residual gases.

Reaction of NiAs with air over 30 h yields a thin (~10 Å) oxidized overlayer containing Ni(OH)₂, arsenite, and arsenate. Similarly thin oxidized layers, composed of oxyhydroxides and sulfates, are produced on millerite and pyrrhotite surfaces. All three surfaces are largely passivated toward air after only a few hours reaction.

A thicker oxidized overlayer (~120 Å thick) containing the same secondary products as the air-oxidized surface is produced on NiAs after 7 days reaction with aerated, distilled water. The accumulation of arsenite and arsenate salts at the niccolite surface distinguishes it from millerite and pyrrhotite surfaces reacted with aerated solutions. Ni- and Fe-sulfate salts produced from these latter two minerals are highly soluble, hence do not accumulate at the mineral surfaces whereas Ni-arsenate (and apparently Ni-arsenite) salts are less soluble and accumulate on oxidized niccolite surfaces along with Ni(OH)₂.