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# Sulfide oxidation and distribution of metals near abandoned copper mines in coastal environments, Prince William Sound, Alaska, USA

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### Abstract

The oxidation of sulfide-rich rocks, mostly leftover debris from Cu mining in the early 20th century, is contributing to metal contamination of local coastal environments in Prince William Sound, Alaska. Analyses of sulfide, water, sediment, precipitate and biological samples from the Beatson, Ellamar, and Threeman mine sites show that acidic surface waters generated from sulfide weathering are pathways for redistribution of environmentally important elements into and beyond the intertidal zone at each site. Volcanogenic massive sulfide deposits composed of pyrrhotite and (or) pyrite + chalcopyrite + sphalerite with subordinate galena, arsenopyrite, and

cobaltite represent potent sources of Cu, Zn, Pb, As, Co, Cd, and Hg. The resistance to oxidation among the major sulfides increases in the order pyrrhotite < sphalerite < chalcopyrite < pyrite; thus, pyrrhotite-rich rocks are typically more oxidized than those dominated by pyrite. The pervasive alteration of pyrrhotite begins with rim replacement by marcasite followed by replacement of the core by sulfur, Fe sulfate, and Fe-Al sulfate. The oxidation of chalcopyrite and pyrite involves an encroachment by colloform Fe oxyhydroxides at grain margins and along crosscutting cracks that gradually consumes the entire grain. The complete oxidation of sulfide-rich samples results in a porous aggregate of goethite, lepidocrocite and amorphous Fe-oxyhydroxide enclosing hydrothermal and sedimentary silicates. An inverse correlation between pH and metal concentrations is evident in water data from all three sites. Among all waters sampled, pore waters from Ellamar beach gravels have the lowest pH (6.4) and highest concentrations of base metals (to 25,000 µg/L), which result from oxidation of abundant sulfide-rich debris in the sediment. High levels of dissolved Hg (to 4100 ng/L) in the pore waters probably result from oxidation of sphalerite-rich rocks. The low-pH and high concentrations of dissolved Fe, Al, and SO<sub>4</sub> are conducive to precipitation of interstitial jarosite in the intertidal gravels. Although pore waters from the intertidal zone at the Threeman mine site have circumneutral pH values, small amounts of dissolved Fe<sup>2+</sup> in the pore waters are oxidized during mixing with seawater, resulting in precipitation of Fe-oxyhydroxide flocs along the beach-seawater interface. At the Beatson site, surface waters funneled through the underground mine workings and discharged across the waste dumps have near-neutral pH (6.7-7.3) and a relatively small base-metal load; however, these streams probably play a role in the physical transport of metalliferous particulates into intertidal and offshore areas during storm events. Somewhat more acidic fluids, to pH 5.3, occur in stagnant seeps and small streams emerging from the Beatson waste dumps. Amorphous Fe precipitates in stagnant waters at Beatson have high Cu (5.2 wt%) and Zn (2.3 wt%) concentrations that probably reflect adsorption onto the extremely high surface area of colloidal particles. Conversely, crystalline precipitates composed of ferrihydrite and schwertmannite that formed in the active flow of small streams have lower metal contents, which are attributed to their smaller surface area and, therefore, fewer reactive sorption sites. Seeps containing precipitates with high metal contents may contribute contaminants to the marine environment during storm-induced periods of high runoff. Preliminary chemical data for mussels (*Mytilus edulis*) collected from Beatson, Ellamar, and Threeman indicate that bioaccumulation of base metals is occurring in the marine environment at all three sites.



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