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Oxidation/alteration of pentlandite and pyrrhotite surfaces at pH 9.3: Part 1. Assignment of XPS spectra and chemical trends

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ABSTRACT

Using X-ray photoelectron spectroscopy, the oxidation/alteration of massive coexisting pentlandite [$(Fe,Ni)_9S$] and pyrrhotite ($Fe_{1-x}S$) from Voiseys Bay has been studied in aqueous solution at pH 9.3. The Fe 2*p*, Ni 2*p*, S 2*p,* and O1*s* spectra were obtained for each mineral from polished surfaces, and from surfaces reacted with the solutions for up to 180 minutes. Both minerals oxidize rapidly to give mostly a relatively thin layer (tens of angstroms) of Fe(III) oxyhydroxide (probably FeOOH). In addition, violarite ($FeNi_2S_4$), $Ni(OH)_2$, and $NiSO_4$ are found in the pentlandite oxidized overlayer, and Fe(III)-S and polysulfide species are found in the overlayers of both minerals. A protocol was developed to fit quantitatively all spectra in a consistent fashion. Fe $2p_{3/2}$ spectra were fitted with two Fe(II)-S peaks depending upon Fe coordination (four and six) in pentlandite, pyrrhotite, and violarite. An Fe(III)-S multiplet, an Fe(III) oxyhydroxide multiplet, as well as Ni Auger peaks, were also required to fit the Fe 2*p* spectra. The Ni $2p_{3/2}$ spectra for pentlandite were fit with two Ni(II)-S peaks from the original pentlandite or violarite (four and six coordination), as well as $Ni(OH)_2$ and $NiSO_4$ peaks. The S 2*p* spectra for both minerals were fit with four and five coordinate S peaks from the original minerals and violarite, as well as polysulfides and sulfate. Finally, the O 1*s* spectra of both minerals were fit with peaks from oxide, hydroxide, and adsorbed water.

The pyrrhotite surface oxidizes more rapidly than the pentlandite surface. For example, after five minutes of reaction the extent of oxidation of pyrrhotite to give an FeOOH overlayer is similar to that of pentlandite after thirty minutes of reaction. In both minerals, iron diffuses from the bulk to the surface and is oxidized. Pentlandite shows small amounts of $Ni(OH)_2$ and $NiSO_4$ in the Fe(III) oxyhydroxide-dominated overlayer even after 180 minutes of reaction. These observations of the oxidation and alteration of the pentlandite surface are entirely consistent with thermodynamic calculations of the relative stabilities of pentlandite, violarite, $Ni(OH)_2$, $NiSO_4$, and FeOOH. The first stage of reaction is characterized by formation of violarite and FeOOH on pentlandite. With continued oxidation, this assemblage yields $NiSO_4$ plus FeOOH plus violarite, which is eventually converted to $Ni(OH)_2$ plus violarite plus FeOOH. Finally, after the violarite is consumed, the $NiSO_4$ plus FeOOH combination occurs as the thermodynamically stable assemblage.