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XPS measurement of fivefold and sixfold coordinated sulfur in pyrrhotites and evidence for millerite and pyrrhotite surface species

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ABSTRACT

Collection of S 2p XPS spectra of millerite (NiS), using a conventional (Al*K*α) and a synchrotron photon source, demonstrates the presence of one surface species on millerite (NiS) and spectral deconvolution indicates a second surface contribution. The observed surface core-level shift (binding energy = 161.1 eV) is attributed to a surface monomeric species (S^{2-}) whereas the second contribution probably is a surface dimeric species (S_2^{2-}, binding energy = 162.3 eV). Surface dimers, if present, indicate surface reconstruction of millerite surfaces upon cleavage. Monoclinic (Fe_7S_8) and hexagonal ($Fe_{10}S_{11}$) pyrrhotite are non-stoichiometric due to vacancies on metal sites. The conventional S 2p XPS spectra of these phases, which sample primarily bulk sulfur states, reveal contributions from fivefold and sixfold coordinated S atoms, the proportion of which is consistent with structural refinement studies. The more intense signal is derived from S in fivefold coordination (80–85%) and the remainder represents the sixfold contribution. Comparison of a highly surface sensitive S 2p XPS spectrum of pyrrhotite (photon energy tuned to 210 eV) with a conventional S 2p XPS signal (Al*K*α source) indicates the presence of a monomeric surface species (S^{2-}). Spectral deconvolution of the surface sensitive spectrum indicates another contribution near 162 eV, the origin of which is uncertain. It may represent S atoms in sixfold coordination, surface dimers (S_2^{2-}) or both.