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 (AlKα) 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 (S2–) whereas the second contribution probably is a surface dimeric species (S22–, binding energy = 162.3 eV). Surface dimers, if present, indicate surface reconstruction of millerite surfaces upon cleavage. Monoclinic (Fe2S8) and hexagonal (Fe10S11) 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 (AlKα source) indicates the presence of a monomeric surface species (S2–). 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 (S22–) or both.

INTRODUCTION

Semiconductors with zincblende and wurtzite structures, such as GaAs, ZnS, and ZnO, undergo surface relaxation and reconstruction resulting in distinctive surface species and surface electronic states (Eastman et al. 1980; Tossell and Vaughan 1992; Gibson and LaFemina 1996). Surface properties of semiconductors with other structures, although important to the minerals industry, have received less attention. Millerite is associated with Ni-bearing sulfide ores and study of its surface properties may provide insight into the near-surface properties of the ore-forming mineral pentlandite. Such properties are critically important to flotation behaviour. Pyrrhotite is a common gangue mineral of some massive sulfide deposits, and where present contributes to acid mine drainage. Study of its surface properties may allow better understanding of its reactivity in these wastes.

Due to abrasion and comminution in sedimentary and mining environments, fracture surfaces are frequently exposed to the atmosphere or to solutions and, as emphasized by Berner (1978), reactions between fluids and minerals occur primarily at these surfaces. Evaluation of mineral reactivity consequently begins by documenting the properties of fracture surfaces, and interpreting these properties within a chemical kinetics framework. Millerite and pyrrhotite near-surface properties are here documented and interpreted in light of structural and XPS studies. The study is a first attempt to document sulfur surface states of millerite (NiS) and pyrrhotite (Fe10S11) using synchrotron radiation X-ray photoelectron spectroscopy (SXPS).

A synchrotron photon source is critical to surface studies because it can be tuned to about 50 eV above the photoemission line to be studied, thus allowing for maximum surface sensitivity (Tanuma et al. 1990; Seah 1990, p. 207). Previous SXPS studies have demonstrated that 40 to 50% of S 2p photoemissions are derived from the first atomic layer of the surface (Bronold et al. 1994; Leiro et al. 1998; Schaufuss et al. 1998), whereas only 5 to 15% of the S signal is derived from the surface layer in conventional XPS spectra. Comparison of SXPS and conventional XPS spectra permits identification of surface and bulk species, determination of their oxidation states and bonding characteristics (chemical states). The conventional XPS provides, in essence, the properties of the bulk states whereas the difference between it and the SXPS spectrum reveals surface core-level shifts; hence the presence of distinct surface species (surface chemical states). Both types of spectra are presented here to elucidate the bulk and surface contributions of millerite and pyrrhotite.

SAMPLE PREPARATION AND ANALYTICAL CONSIDERATIONS

Preparation and instrumental aspects

Samples. A cleaved surface of millerite and fractured surfaces of hexagonal and monoclinic pyrrhotite were produced in the vacuum of the introduction chambers of the conventional instrument (10–6 Pa) and SXPS instrument (10–7 Pa). Samples

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