X-ray photoelectron spectroscopic study of a pristine millerite (NiS) surface and the effect of air and water oxidation

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ABSTRACT

Millerite, NiS, fractured under high vacuum and reacted with air and water has been analyzed by X-ray photoelectron spectroscopy (XPS). The pristine millerite surface gives rise to photoelectron peaks at binding energies of 853.1 eV (Ni 2p3/2) and 161.7 eV (S 2p), thus resolving ambiguities concerning binding energies quoted in the literature. Air-reacted samples show the presence of NiSO4 and Ni(OH)2 species. There is evidence for polysulphide species (S2n-, where 2 ≤ n ≤ 8) on air-oxidized surfaces. These may occur in a sub-surface layer or may be intermixed with the Ni(OH)2 in the oxidized layer. The NiSO4 species at the millerite surface occur as discrete crystallites whereas the Ni(OH)2 forms a thin veneer covering the entire millerite surface. The NiSO4 crystallites form on the surface of millerite but not on surfaces of adjacent minerals. Surface diffusion of Ni2+ and SO42- across the millerite surface is thought to be responsible for the transport and subsequent growth of NiSO4 crystallites developed on millerite surfaces. Although it is clear that Ni and SO42- does not diffuse onto surfaces of adjacent minerals in sufficient quantity to form crystallites, the explanation is uncertain. XPS results for water-reacted surfaces show little difference from the vacuum fractured surfaces with the exception that minor amounts of polysulphide and hydroxy nickel species are present. Similar reaction products to those formed in air [NiSO4 and Ni(OH)2] are believed to be produced, but these are removed from the millerite surface by dissolution, leaving behind a sulfur-enriched surface (polysulphide) and hydroxyl groups chemisorbed to nickel ions at the millerite surface.

INTRODUCTION

Millerite, NiS, is most commonly associated with other Ni-bearing sulphide minerals such as heazlewoodite (Ni,S) and pentlandite (Fe,Ni)9S8. The oxidation of millerite is incompletely documented and there is some discrepancy in core-level binding energy values reported in the literature (Clifford et al. 1975; Shalvoy and Reucroft 1979; Broutin et al. 1984; Buckley and Woods 1991a). The present study attempts to reconcile ambiguities regarding core-level binding energies and to investigate millerite oxidation in air and in air-saturated de-ionized water.

The surface chemistry of millerite is significant because of its relationship with the surface chemistry of economically important Ni-bearing sulphide minerals, and particularly because it can be considered a compositional Ni end-member of pentlandite and nickeliferous pyrrhotite, Fe1−xS (0 < x < 0.2). Its pristine and altered surface properties may consequently provide insight into the properties and reactivities of economically important Ni-bearing sulphides. This study documents the nature of a pristine millerite surface and its surface alteration properties resulting from reaction with the atmosphere and aerated deionized water. Processes affecting the formation of the secondary products are deduced and discussed. The results may provide a guide to the interpretation of surfaces and surface processes affecting other Ni-bearing sulphide minerals.

EXPERIMENTAL methods

Materials and instrumental methods

Millerite samples from Marbridge Mine in LaMotte township, Quebec, Canada, and Strathcona Mine near Sudbury, Ontario, Canada, were obtained from the Department of Earth Sciences mineral collection at the University of Western Ontario. The bulk composition was obtained by electron microprobe analysis (EMPA) of polished sections of millerite using a JEOL JXA-8600 Superprobe. The analyses were carried out with an accelerating voltage of 25 kV and a probe current of 25 nA as measured on a Faraday cup. ZAF matrix corrections were used. Counts were integrated for 20 s on peak and 20 s on background for nickel and sulfur, and for 30 s both on peak and on background for iron, copper, cobalt, and arsenic.

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