

Nature of Sulphide Mineral Surfaces Under Atmospheric Conditions: Results from NEXAFS

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Previous studies suggest that sulphide surfaces oxidise quickly in air and that sulphate species (Laajalehto et al., 1997) or iron oxide/hydroxides (Mielczarski et al., 1996) are the main oxidation products. In order to investigate the nature of sulphide surfaces at ambient conditions, Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectra of a series of transition-metal sulphides and their corresponding oxide/oxyhydroxides were measured at station 5U.1 of the Daresbury Synchrotron Radiation Source, England. Spectra were collected using a total electron yield (TEY) detector to measure the drain current. The mean probing depth in the TEY mode is 20-50Å (Abbate et al., 1992), allowing probing of the surface layers only. For oxide minerals, recordings were of the oxygen K-edge and metal L-edge spectra. For sulphide minerals, recordings were of the sulphur L-edge and metal L-edge. The oxygen K-edge was also sampled to examine the nature of the oxidised surface layers. Sulphide samples were subsequently cleaned by sputtering with an argon gun to remove surface oxygen and rescanned.

Study of the NEXAFS spectra of pyrrhotite (FeS), pyrite (FeS₂), chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), chalcocite (Cu₂S) and alabandite (MnS), reveals that although the metal L-edge spectra of the oxidised surfaces are well-defined, the sulphur L-edge spectra for many sulphides show only a minor signal. The oxygen K-edge surface spectra however, are strong for all the sulphides studied. Comparison of the sulphide oxygen spectra with the corresponding spectra for transition metal oxides reveals some similarity in the electronic structure of the surface oxygen species. From these observations it is proposed that the main oxidation product of pyrrhotite is the iron oxyhydroxide, goethite. This supports the results of an electrokinetic study of pyrite oxidation (Fornasiero et al., 1991), which suggest that with exposure to oxygen, gradual oxidation of metal sulphide surfaces leads to charge development very similar to that found for the corresponding metal oxyhydroxides. The isoelectric point shifts from pH 1.2 up to pH 7 on oxidation - similar to the values reported for FeOOH colloids, suggesting that iron sulphide surfaces acquire an oxyhydroxide coating, which governs the properties. In this study however, there is no evidence of surface hydroxide species on pyrite. The oxygen does not appear to be bonded with iron, and in light of the strong

sulphur L-edge, it is proposed that the main oxidation species is sulphate, supporting the results of Laajalehto et al. (1997).

Examination of the oxygen and copper spectra for chalcocite (Cu₂S) and bornite (Cu₅FeS₄) reveal that these minerals oxidise to the same compound. Neither contains iron species, and it is tentatively proposed that the oxidised surface comprises tenorite (CuO). The absence of surface iron is confirmed in the Fe L-edge spectra for bornite. Prior to sputtering the iron absorption intensity is insignificant, whereas the 'clean' surface displays a strong iron spectrum. The copper spectra for chalcocite show a progressive decrease in the relative intensity of the Cu(II) L-edge peak with increasing sputtering of the surface, indicating a transition to dominantly Cu(I) surface groups bonded to sulphur. Chalcopyrite also contains Cu(I) in the bulk structure, but the oxygen spectra suggest that this mineral forms a different oxidation species. Mielczarski et al. (1996) propose that the surface consists of various ferric and ferrous oxides and hydroxides, and that there is an insignificant amount of copper oxidation species at the interface on the basis of Cu 2p and Cu Auger spectra. The Cu L-edge for chalcopyrite is, however, well-defined and it is proposed that the surface contains oxidised copper species as well as iron. Alabandite (MnS) shows a strong oxygen spectrum and very weak sulphur spectrum prior to sputtering. This suggests that the surface consists of manganese oxide (MnO) or hydroxide (Mn(OH)₂), with no significant sulphur species present in the oxidised layer.

NEXAFS spectra obtained after successive sputtering of the samples with argon display an enhanced sulphur signature, as demonstrated by alabandite, suggesting that sputtering is at least partially effective in removing oxidised surface species. This technique may be effective in allowing observation of the bulk sulphide electronic structure.

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