Reactive Surfaces Prepared under Controlled Environments

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The surface composition of a material in a particular chemical environment can be of crucial importance in the utilisation or processing of that material. Accordingly, it is essential that the surface of such a material be characterised either while still in that chemical environment, or after having been moved to UHV in such a way as to leave it chemically unchanged from when it was in that particular environment. Even when *bulk* electronic environment information is being sought by means of XPS or NEXAFS spectroscopy for materials that are reactive towards air, it is also necessary to prepare a surface under an oxygen-free environment, as ion beam etching can cause intolerable damage to the underlying lattice.

In these cases, a soft X-ray end-station is required that allows the transfer of specimens to UHV from controlled atmosphere transfer vessels, or the preparation of surfaces under controlled environments, including fracture under vacuum. When reaction products that can sublime under UHV at ambient temperature are formed at chemically treated surfaces, it is also necessary to cool the specimen before it is subjected to UHV in order to retain such reaction products. These features will be available on the ASRP soft X-ray spectroscopy end-station when it is fully commissioned at the NSRRC in early 2006. To date, only preliminary experiments for this project have been possible in the ASRP end-station and in another end-station without all the necessary features. The preliminary experiments reported here are those on the electronic environment in cubanite, and on the effect of short chain alkyl alcohols on metal sulfide surfaces. Nearly all metal sulfide surfaces react rapidly with air, but the Cu-Fe sulfides react more rapidly than the Cu sulfides covellite (CuS) or chalcocite (Cu_2S).

Cubanite ($CuFe_2S_3$) is of particular interest because of its close relationship to chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4), and because of the expected intermediate formal oxidation state for the Fe, *viz* ($Cu^{I}Fe^{II}Fe^{III}S_3$), in the equivalent Fe sites in the crystal structure, assuming Cu(I) rather than $Cu^{II}Fe^{II}{}_2S_3$. The Cu $L_{2,3}$-edge spectrum supports the assignment from the Cu 2p photoelectron spectrum of Cu(I), the leading absorption peak being at an energy 0.1 eV greater than that for $CuFeS_2$. The Fe $L_{2,3}$-edge spectrum was similar to that for chalcopyrite, which is generally accepted to be Fe(III). Surface-optimised S 2p spectra revealed the formation of some sulfate during limited exposure to air. It was concluded that there are only very subtle differences in electronic environment in cubanite and chalcopyrite. Surprisingly, no clear evidence was obtained to indicate that the Fe in cubanite behaves as if it is more 'Fe(II)-like' than the Fe in chalcopyrite. The experimental observations and *ab initio* calculations carried out using FEFF8 and WIEN2k suggest significant S 3p → Fe 3d charge transfer for both cubanite and chalcopyrite, and even greater transfer in the case of bornite.

When there is a need to use freshly abraded surfaces of sulfide minerals instead of fracture surfaces, and there is no glove box attached to the end-station, in order to remove swarf specimens are typically washed with, or even immersed in, ethanol or propan-2-ol prior to insertion into the end-station. Cu $L_{2,3}$-edge NEXAFS spectra have revealed that immersion of abraded surfaces of CuS and Cu_2S in ethanol or propan-2-ol leads to more extensive alteration of the surface than unrestricted exposure to air for a similar period. This effect had not been evident from conventional (~1487 eV photon energy) XPS data, most probably because the sensitivity for detection of Cu(II) is much greater in Cu $L_{2,3}$-edge NEXAFS spectra than in Cu 2p photoelectron spectra. A similar effect of AR grade ethanol and electronics grade propan-2-ol on Cu-Fe sulfides has established that the Fe rather than the Cu is oxidised, and confirmed that an impurity other than moisture in the hygroscopic alcohols is not the culprit. It was concluded that ethanol and propan-2-ol should be avoided for washing or protecting metal sulfide specimens for surface studies, at least when the alcohols are stored in equilibrium with ambient air. To date, no similar problem has been identified in the use of acetone for specimen washing.

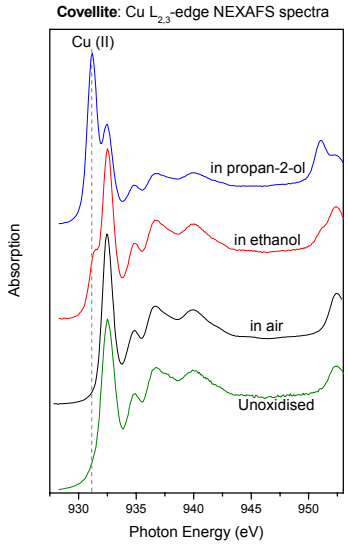

Figure 1. Cu $L_{2,3}$-edge spectra for abraded CuS surfaces exposed only briefly to air (unoxidised) or exposed to air, ethanol or propan-2-ol for 15 min.