

## DOES PRE-OXIDATION CHANGE THE PRODUCTS OF INTERACTION OF SULFIDE MINERALS WITH THIOL COLLECTORS?

A.N. Buckley<sup>1</sup>, S.W. Goh<sup>1</sup>, R.N. Lamb<sup>1</sup>, R. Woods<sup>2</sup>

<sup>1</sup>School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia -  
a.buckley@unsw.edu.au

<sup>2</sup>School of Science, Griffith University, Nathan, Queensland 4111, Australia

### ABSTRACT

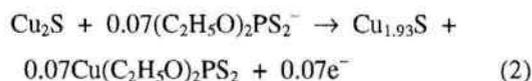
The interaction of chalcocite surfaces, pre-oxidised by exposure to air for 24 h, with diethyl dithiophosphate (DTP) at pH 9.2 has been studied by means of X-ray photoelectron spectroscopy (XPS). The copper oxidation products formed on the mineral surface during the exposure to air were removed by immersion in the aqueous medium alone. Immersion of surfaces in copper-saturated  $10^{-5}$  mol dm<sup>-3</sup> collector solution for 40 s resulted in the formation of chemisorbed DTP rather than adsorbed CuDTP in the monolayer immediately adjacent to the mineral surface. Immersion in a similar collector solution for longer periods gave rise to CuDTP in addition to the chemisorbed collector. The results indicate that the mechanism for the formation of the chemisorbed layer would have been ion exchange with copper-oxygen species followed by reorganisation adjacent to the mineral surface, rather than dissolution of the copper-oxygen species in the aqueous medium followed by chemisorption of the collector at the oxide-free surface.

### INTRODUCTION

Whereas it is generally accepted that chemisorption of thiol collectors induces flotation of unoxidised sulfide mineral particles, there is controversy as to whether this mechanism applies to systems that have undergone a degree of pre-oxidation. It is well established that thiol collectors can chemisorb on freshly formed sulfide mineral surfaces at potentials below the reversible value for formation of the metal thiolate, and hence chemisorption is the thermodynamically favoured process. The collector chemisorbs to metal atoms in the outermost layer of the sulfide lattice *via* an electrochemical mechanism. For example, in the flotation of chalcocite assisted by DTP, the anodic chemisorption reaction:

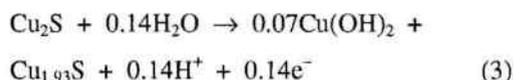


would be coupled with the cathodic reduction of oxygen on the mineral surface. The corresponding anodic reaction occurring at more positive potentials would be the formation of CuDTP from copper atoms removed from the sulfide lattice (Buckley and Woods, 1993), with the concomitant formation of a copper sulfide phase of lower copper content than Cu<sub>2</sub>S, most probably the metastable djurleite phase Cu<sub>1.93</sub>S, previously identified as the first oxidation product of chalcocite (Koch and McIntyre, 1976):

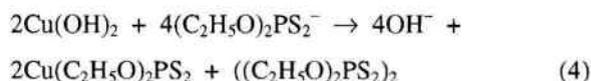


At even higher potentials, formation of the dithiolate could also take place.

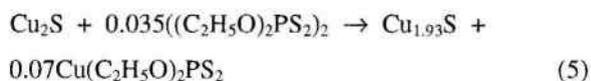
In flotation systems, the mineral can be exposed to aqueous solutions containing oxygen prior to addition of the collector. In this situation, an anodic oxidation of the mineral can be coupled with oxygen reduction. For chalcocite, the anodic oxidation will be represented by reaction 3:



When collector is added, the Cu(OH)<sub>2</sub> is expected to react by an ion exchange process such as that represented by reaction 4 for DTP:

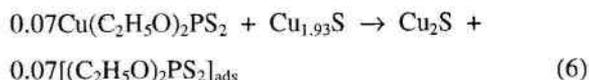


The dithiolate is expected to react with copper in the chalcocite surface to form CuDTP, since the free energy difference for the reaction:



is negative ( $\Delta G = -51.7$  kJ per mole of (DTP)<sub>2</sub>). The question arises as to whether the CuDTP retains its

molecular form on the chalcocite surface, or whether reorganisation occurs resulting in the formation of a monolayer of the thermodynamically more stable species, chemisorbed DTP, even if the potential remains in the region in which CuDTP is stable. This reorganisation could occur by:



In investigations of the potential dependence of flotation of sulfide minerals with thiol collectors in which potential is controlled by redox reagents (e.g. Woods *et al.*, 1993), mineral samples are generally ground in air prior to floatability being determined. The onset of flotation found in these studies lies in the region of chemisorption even when a pre-reduction step is not included. This indicates that pre-reduction, or preparation of the mineral in the absence of oxygen, is not required for chemisorption to occur and induce flotation. The degree of oxidation would, however, not be substantial with the limited exposure times experienced.

Opinions expressed in the literature suggest that it is a widely held view that the products of mineral/collector interaction are different when the surface is pre-oxidised. For example, Laajalehto *et al.* (1993) noted that there was general agreement in the literature that the reaction of galena oxidation products with xanthate should lead to the formation of lead xanthate rather than an adsorbed monolayer. Szymula *et al.* (1996) argued that on the basis of previously published results, the product of the reaction of xanthate ions with an oxidised copper sulfide surface consists mainly of cuprous xanthate, with no evidence for xanthate 'complex' formation.

This view that the products of mineral/collector interaction are different when the surface is pre-oxidised is challenged, and it is argued that chemisorption can just as readily occur on such surfaces as indicated in reactions 5 and 6. A recent study of the interaction of pre-oxidised galena with iso-butyl xanthate revealed that chemisorbed xanthate was formed (Buckley *et al.*, 2000). However, it was found that the oxidation products were removed from the galena surface in an aqueous solution in the absence of collector, and therefore it was possible that the interaction of the collector had been with an unoxidised galena surface. In practice, metal ions would be present in a flotation pulp prior to the addition of collector.

In the work reported here, XPS has been used to determine the surface reaction products when chalcocite is treated with copper-saturated DTP solution as a representative system to investigate the interaction of

thiol collectors with pre-oxidised sulfide minerals under flotation-related conditions. By saturating the solution with copper, practical flotation conditions are more closely simulated, and the situation is avoided in which all the oxidised copper species dissolve and then DTP interacts with a sulfide surface free of oxidation products.

## EXPERIMENTAL DETAILS

The  $\sim 5 \times 5$  mm<sup>2</sup> mineral surfaces investigated were prepared from natural crystals of copper sulfide consisting of 80% chalcocite and 20% djurleite. The only minor element detected at some surfaces by XPS was silver. Oxidised surfaces were prepared by abrasion then exposure to air under ambient conditions (295 K,  $\sim 65\%$  relative humidity) for 24 h.

DTP solutions were prepared by dissolving sodium DTP crystals provided by Cytec, USA, in 0.05 mol dm<sup>-3</sup> sodium tetraborate (pH 9.2), and saturated with copper by adding sufficient 10<sup>-3</sup> mol dm<sup>-3</sup> copper sulfate solution to exceed the solubility of CuDTP. Copper-saturated 10<sup>-5</sup> mol dm<sup>-3</sup> DTP solutions were not noticeably cloudy and were not filtered before use. Treated mineral specimens were washed thoroughly with water before surface analysis.

Electron spectra were determined with a VG ESCA-LAB 220-iXL spectrometer using monochromatised Al K<sub>α</sub> X-rays and an analyser pass energy of 20 eV. The pressure in the analysis chamber was better than 10<sup>-9</sup> mbar. An electron take-off angle of 20° was used to enhance surface sensitivity. Binding energies of 74.95 eV, 932.67 eV, 83.96 eV and 368.26 eV for Cu 3p<sub>3/2</sub>, Cu 2p<sub>3/2</sub>, Au 4f<sub>7/2</sub> and Ag 3d<sub>5/2</sub> from metallic copper, gold and silver, respectively, were used for spectrometer calibration. Mineral specimens were held in place on a copper stub with stainless steel screws. Most specimens were evacuated at ambient temperature, but cooled to  $\sim 180$  K as soon as possible and before application of the X-rays. This procedure was followed because previous XPS studies using both anode- and synchrotron-generated X-rays have indicated that adsorbed thiols are stable in ultra high vacuum, but susceptible to stimulated desorption by intense X-ray beams unless cooled (Johansson *et al.*, 1986). The analysis area was  $\sim 1$  mm<sup>2</sup> and several regions on each surface were examined. The full width at half maximum for the mineral S 2p<sub>3/2</sub> peak was 0.8 eV.

## RESULTS AND DISCUSSION

The unoxidised and pre-oxidised chalcocite surfaces were characterised by XPS before treatment with aqueous alkaline and collector solutions. The S 2p spectrum from fresh fracture surfaces could be fitted with a single doublet at a  $2p_{3/2}$  binding energy of 161.6 eV. The Cu  $2p_{3/2}$  binding energy and Cu( $L_3M_{4,5}M_{4,5}$ ) kinetic energy were 932.5 eV and 917.1 eV, respectively. These values are in close agreement with published data (Buckley and Woods, 1993). The background was featureless in the 130–135 eV P 2p region, and no evidence for the presence of Cu(II) species was observed in the Cu 2p or Cu Auger spectra.

The Cu 2p (Fig. 1a) and Cu Auger (Fig. 2a) spectra from freshly abraded surfaces were similar to those from fracture surfaces. However, the S 2p spectrum (Fig. 3a) could no longer be fitted with a single doublet at 161.6 eV. A minor additional doublet at ~162.5 eV was now required to achieve an adequate fit. This minor doublet is consistent with the surface layer having become slightly sulfur-rich as a result of oxidation and subsequent dissolution of the copper without direct oxidation of the sulfide sulfur.

After an abraded surface of the mineral had been exposed to air for 24 h, Cu(II) species were clearly evident in the Cu 2p spectrum from the primary peak intensity near 933.7 eV and 935 eV and from the associated excited final state satellites (Fig. 1b). A peak at 933.7 eV would be consistent with copper oxide, while that near 935 eV could arise from copper hydroxide (hydrated oxide) or carbonate. The O 1s and C 1s spectra suggested that the Cu(II) species were predominantly hydrated and unhydrated oxide with only a very small amount of carbonate. The copper oxide was also apparent in the Cu( $L_3M_{4,5}M_{4,5}$ ) spectrum. Sulfur-oxygen species were not evident in the S 2p spectrum (Fig. 3b), but the relative intensity of the second minor doublet at 162.5 eV, assigned to a sulfur-rich sulfide lattice, was now slightly higher than for an unoxidised surface.

Spectra determined following immersion of the oxidised surfaces in water or in pH 9 borate or sodium hydroxide solution revealed that the copper oxidation products had been removed from the surface. The S 2p spectrum, however, was essentially unchanged, an observation consistent with the spectrum originating from a sulfur-rich chalcocite surface. If the relative intensities of the Cu 3s and S 2p peaks for a fresh surface are assumed to arise from a stoichiometry of  $Cu_2S$ , then the intensities of those peaks for pre-oxidised surfaces washed free of copper oxide indicated a surface stoichiometry of  $Cu_{1.7}S$ . Note that the analysis

depths for the S 2p and Cu 3s electrons are comparable, with kinetic energies of 1325 eV and 1365 eV respectively, whereas the Cu 2p electrons, with a kinetic energy near 555 eV, are significantly more surface sensitive. Copper LMM Auger electrons (~917 eV) are also more surface sensitive than the S 2p electrons.

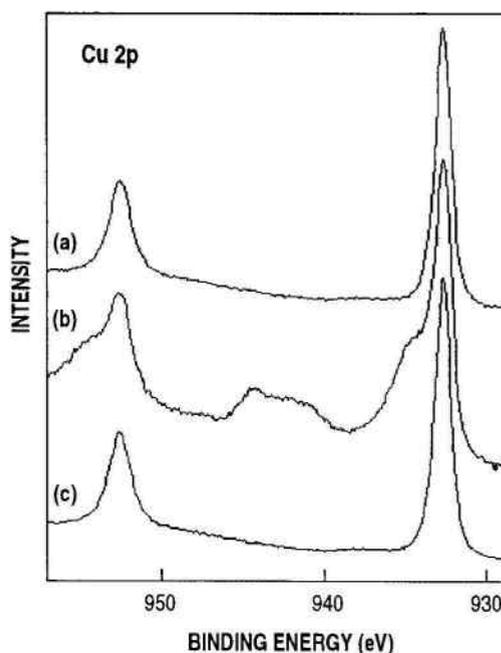


Fig. 1. Cu 2p spectra from chalcocite surfaces: (a) freshly abraded; (b) exposed to air for 24 h; (c) treated with DTP for 40 s after air exposure.

Interaction of the pre-oxidised surfaces with copper-saturated  $2 \times 10^{-5}$  mol  $dm^{-3}$  DTP solution was investigated by immersion of mineral specimens for periods ranging from 40 s to 10 min. The Cu 2p spectrum (Fig. 1c) from specimens treated for 40 s indicated that all Cu(II) oxidation products had been removed from the surface, while the P 2p (Fig. 4) and S 2p (Fig. 3c) spectra revealed the presence of adsorbed DTP, the latter via a component at 162.1 eV (Fig. 5). The P  $2p_{3/2}$  binding energy of 133.0 eV was typical for phosphorus bonded to four oxygen or sulfur atoms. The Cu( $L_3M_{4,5}M_{4,5}$ ) peak (Fig. 2b) was indistinguishable from that for a fresh surface, an observation consistent with not only the removal of Cu(II) species but also the absence of adsorbed molecular CuDTP (Buckley and Woods, 1993). Thus it follows unequivocally that the DTP must have been in the chemisorbed form at the mineral surface. Since the DTP solution was saturated with copper and kept in motion during immersion of the mineral, it also follows that the chemisorbed layer would have been formed by ion exchange with copper-oxygen species (reaction 4) followed by reorganisation adjacent to the mineral surface (reaction 6) rather than

dissolution of the copper oxidation products in the aqueous medium followed by chemisorption of the collector at the oxide-free surface.

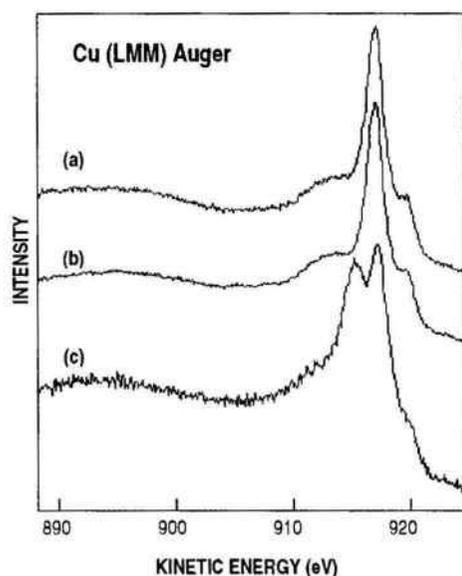


Fig. 2. Cu LMM Auger spectra from chalcocite surfaces: (a) freshly abraded; (b,c) treated with DTP for (b) 40 s or (c) 8 min after air exposure.

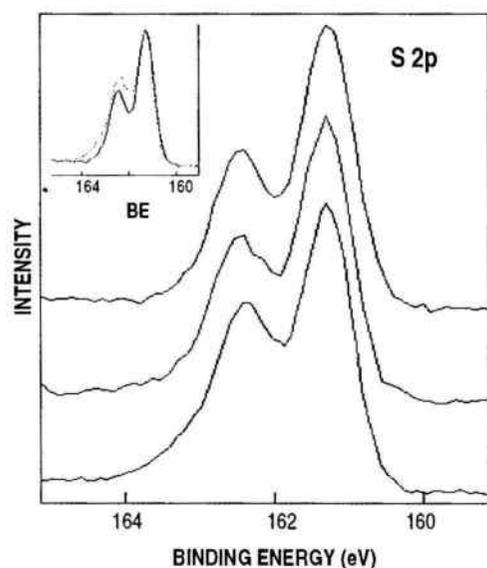


Fig. 3. S 2p spectra from chalcocite surfaces: (a) freshly abraded; (b) exposed to air for 24 h; (c) treated with DTP for 40 s after air exposure. Insert: spectrum (c) superimposed on (a).

The relative intensities of the 162.1 eV S 2p component and the P 2p and Cu 3s peaks were consistent with the adsorption of DTP. In particular, the adsorbate S:P ratio was marginally less than 2:1, reflecting a more

vertical than horizontal orientation, and the substrate appeared slightly more sulfur rich relative to a surface treated with an alkaline medium only, reflecting sub-monolayer chemisorption of the DTP to copper atoms in the mineral surface.

When pre-oxidised surfaces were treated with DTP solution for periods longer than 40 s, the relative intensity of the P 2p peak increased progressively, and a peak at ~914.9 eV in the Cu Auger spectrum indicated the presence of molecular CuDTP adsorbed at the surface (Fig. 2c). The corresponding Cu 2p spectrum revealed the presence of the molecular CuDTP only through a high binding energy side peak broadening.

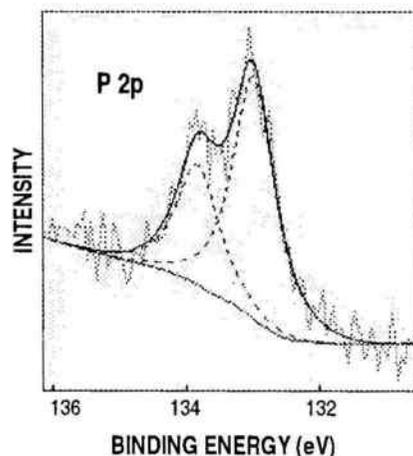


Fig. 4. P 2p<sub>1/2,3/2</sub> doublet from a pre-oxidised chalcocite surface treated with DTP for 40 s.

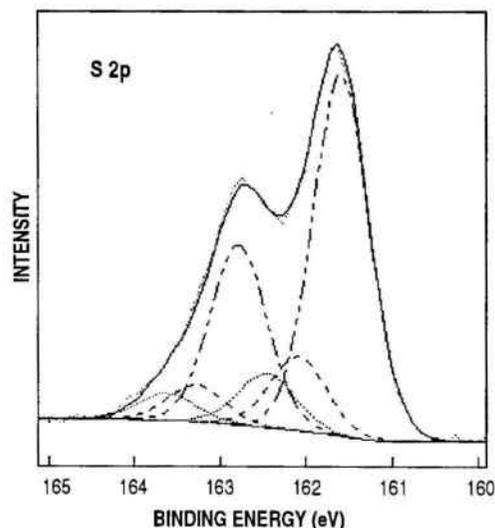


Fig. 5. S 2p spectrum from a pre-oxidised chalcocite surface treated with DTP for 40 s fitted with three 2p<sub>1/2,3/2</sub> doublets.

For 10 min treatment, the Cu 2p<sub>3/2</sub> peak could be fitted with a component at 932.9 eV in addition to the chalcocite peak at 932.5 eV, and the P 2p<sub>3/2</sub> peak could be fitted with components at 133.4 eV and 133.0 eV. However, the Cu 2p binding energy is usually insensitive to minor changes in chemical environment, and the P 2p binding energy would not be expected to differ significantly in the chemisorbed and molecular species. Therefore it is most probable that the 0.4 eV shift is the result of differential charging of the multilayer species. A shift of 0.3 eV was observed for 8 min treatment. The modified Auger parameter is unaffected by charging, and the low value of this parameter (1847.8 eV) for the thiolate is indicative of a Cu(I) species. The absence of excited final state satellites in the Cu 2p spectrum also showed that a Cu(II) species was not present. These two observations confirm that the molecular species is CuDTP rather than Cu(DTP)<sub>2</sub>.

As also found by Buckley and Woods (1993), an additional 2p<sub>3/2</sub> component at ~162.9 eV was required to fit the S 2p spectrum in the multilayer regime. In that earlier study, the 162.9 eV component did not appear to have arisen from multilayer CuDTP, however the present results from higher spectral resolution suggest molecular CuDTP is the most probable explanation, especially when ~0.4 eV of the observed S 2p shift can be attributed to charging. The relative intensities of the P 2p peak, and the S 2p components at 162.1 eV and 162.9 eV, support this assignment. Fortuitously then, charging of the multilayer reveals the presence of the adsorbed monolayer under the molecular CuDTP.

## CONCLUSION

The interaction of pre-oxidised chalcocite surfaces with copper-saturated pH 9.2 DTP solution results in the formation of chemisorbed DTP at the mineral surface, rather than an adsorbed CuDTP species in the monolayer immediately adjacent to the mineral surface. Chemisorption occurs by ion exchange followed by reorganisation of the CuDTP in the surface layer rather than by a dissolution/adsorption mechanism.

In light of these findings for chalcocite, and similar previous results for the interaction of pre-oxidised galena with xanthate, it can be concluded that pre-oxidation does not change the products of interaction of sulfide minerals with thiol collectors. It is expected that under industrial flotation conditions, chemisorbed collector would be the hydrophobic species responsible for sulfide mineral floatability.

## REFERENCES

- Buckley, A.N. and Woods, R. Underpotential Deposition of Dithiophosphate on Chalcocite. *J. Electroanal. Chem.*, 357:387, 1993.
- Buckley, A.N., Gong, B., Lamb, R.N. and Woods, R. Interaction of Collectors with Pre-oxidised Sulfide Mineral Surfaces; Adsorption of Iso-butyl Xanthate on Galena. In: R. Woods and F.M. Doyle (Editors), *Proc. Fifth Int. Symp. Electrochemistry in Mineral and Metal Processing*, Electrochem. Soc., Pennington, NJ, PV 2000-14, pp.72-83, 2000.
- Johansson, L.-S., Juhanoja, J. Laajalehto, K., Suoninen, E. and Mielczarski, J. XPS Studies of Xanthate Adsorption on Metals and Sulphides. *Surf. Interface Anal.*, 9:501, 1986.
- Koch, D.F.A. and McIntyre, R. The Application of Reflectance Spectroscopy to a Study of the Anodic Oxidation of Cuprous Sulphide. *J. Electroanal. Chem.*, 71:285, 1976.
- Laajalehto, K., Nowak, P. and Suoninen, E. On the XPS and IR Identification of the Products of Xanthate Sorption at the Surface of Galena. *Int. J. Miner. Process.*, 37:123, 1993.
- Szymula, M., Koziol, A.E. and Szczypa, J. Effect of Xanthate Chain Length on Decrease of Xanthate Concentration in Solutions in Contact with Copper Sulphides. *Int. J. Miner. Process.*, 46:123, 1996.
- Woods, R., Kim, D.S. and Yoon, R.-H. The Potential Dependence of Flotation of Chalcocite with Diethyl Dithiophosphate. *Int. J. Miner. Process.*, 39:101, 1993.