

# Surface oxidation of chalcocite (Cu<sub>2</sub>S) under aqueous (pH = 2–11) and ambient atmospheric conditions: Mineralogy from Cu L- and O K-edge X-ray absorption spectroscopy

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## ABSTRACT

We characterized the surface oxidation layer (~50 Å) of chalcocite reacted with air-saturated aqueous solutions at pH = 2–11 and with the ambient atmosphere. Copper L-edge and O K-edge X-ray absorption spectroscopy probes the unoccupied electronic states in the conduction band of the surface alteration phase that, in turn, enables us to identify the mineralogy of the surface layer. At low pH, the surface alteration phase is primarily cuprite (Cu<sub>2</sub>O). At higher pH, tenorite (CuO) is the dominant phase. No evidence for sulfate or carbonate phases are present; however, chalcocite reacted only in air does develop a CuSO<sub>4</sub> surface phase in addition to cuprite and minor tenorite.

## INTRODUCTION

Chalcocite, Cu<sub>2</sub>S, is a common ore mineral of Cu but its surface is unstable to oxidation upon exposure to the atmosphere or to air-saturated aqueous solutions with Eh > 0 (Fig. 1). Oxidation of the chalcocite surface adversely affects the behavior of chalcocite grains during mineral separation by froth flotation methods of ore processing (Tolley et al. 1996; Clark et al. 2000). The formation of an insoluble surface oxidation layer also may passivate chalcocite crystal faces and decrease the rate of chalcocite oxidation during weathering.

Several studies have characterized the surface oxidation layer of chalcocite using electrochemical methods (Velasquez et al. 2001; Fullston et al. 1999; Tolley et al. 1996). Velasquez et al. (2001) observed that during electrochemical oxidation at alkaline pH, Cu (I) is partially oxidized to Cu (II) as CuO, Cu(OH)<sub>2</sub>, or possibly Cu<sub>3</sub>(SO<sub>4</sub>)(OH)<sub>4</sub>. Fullston et al. (1999) studied the oxidation of chalcocite as a function of pH and oxidizing conditions. They interpreted their results as indicating the formation of a Cu hydroxide layer covering a metal-deficient S-rich surface. The hydroxide layer precipitates above pH 6.

The nature of the oxidized chalcocite surface also has been characterized using X-ray photoelectron spectroscopy (XPS) (Velasquez et al. 2001; Fullston et al. 1999). Fullston et al. (1999) corroborated their results from zeta potential data, observing polysulfide or elemental S beneath a Cu oxide/hydroxide covering. Although XPS can characterize the elemental composition and oxidation states of elements on sulfide mineral surfaces, we have found that X-ray absorption spectroscopy (XAS) using synchrotron light-sources, can provide much more information: XAS measures transitions to unoccupied states in the conduction band. These are usually anti-bonding orbitals so that XAS can detect the presence of chemical bonds. From such information, we can often get an unambiguous identification of the surface mineralogy. In two recent studies, we have characterized the surface alteration phases on pyrite (Todd et al. 2003a) and chalcopyrite (Todd et al. 2003b) using this

approach. In the present study, we used XAS to characterize chalcocite surfaces oxidized in aqueous solutions as a function of pH. We also measured the surface mineralogy of chalcocite exposed to the ambient atmosphere (25 °C, P<sub>H<sub>2</sub>O</sub> = 0.02 bar).

## EXPERIMENTAL METHODS

### Sample preparation

A natural chalcocite sample, from Cornwall, England, was used for the oxidation experiments. Chalcocite fragments were coarsely ground in a nitrogen glove box and then immersed in air-saturated 0.1 M sodium nitrate solutions for five days. The pH of the aqueous electrolyte was adjusted initially, and also once during the equilibration period, using 0.1 M nitric acid and 0.1 M sodium hydroxide. The final values ranged between pH 1.75 and 10.07. After conditioning, the samples were dried and stored under nitrogen, before being mounted on stainless steel sample holders using carbon tape. All procedures were carried out under nitrogen to ensure that the only oxidation products were those formed in aqueous solution. A sample ground and stored under nitrogen was retained as a control, and chalcocite oxidized in air also was included for comparison.

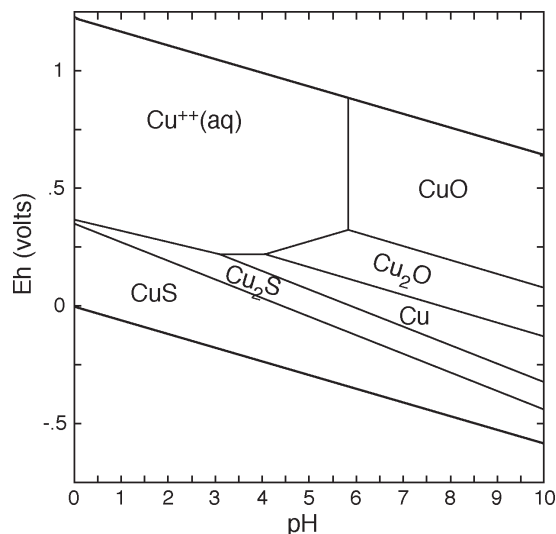


FIGURE 1. Eh-pH diagram for the Cu-O-S system at 25 °C constructed from the data in Wagman et al. (1982) and Helgeson et al. (1978).

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Samples of minerals that are possible oxidation phases were obtained from the Bristol University museum and teaching collection and characterized using powder X-ray diffraction. Tenorite was reagent grade CuO (BDH). Covellite (CuS) was from Sardinia. Cuprite (Cu<sub>2</sub>O) and azurite [Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>] samples were from unknown localities.

### X-ray absorption spectroscopy

Copper *L*- and *O K*-edge X-ray absorption spectra were measured at station 8.01 of the Advanced Light Source, Lawrence Berkeley National Laboratory, California. All XAS spectra were collected using the total electron yield (TEY) method to measure the drain current. The mean probing depth in the TEY mode is 20–50 Å (Abbate et al. 1992), although the analysis depth can vary with energy. Kasrai et al. (1996) states that the maximum probing depth in the TEY mode at the Si *L*-edge (95–120 eV) is ~50 Å, compared to ~700 Å at the Si *K*-edge (1830–1900 eV). For this reason, we might expect to see some bulk contribution at the Cu *L*-edge spectra (932–960 eV) of samples that are only slightly

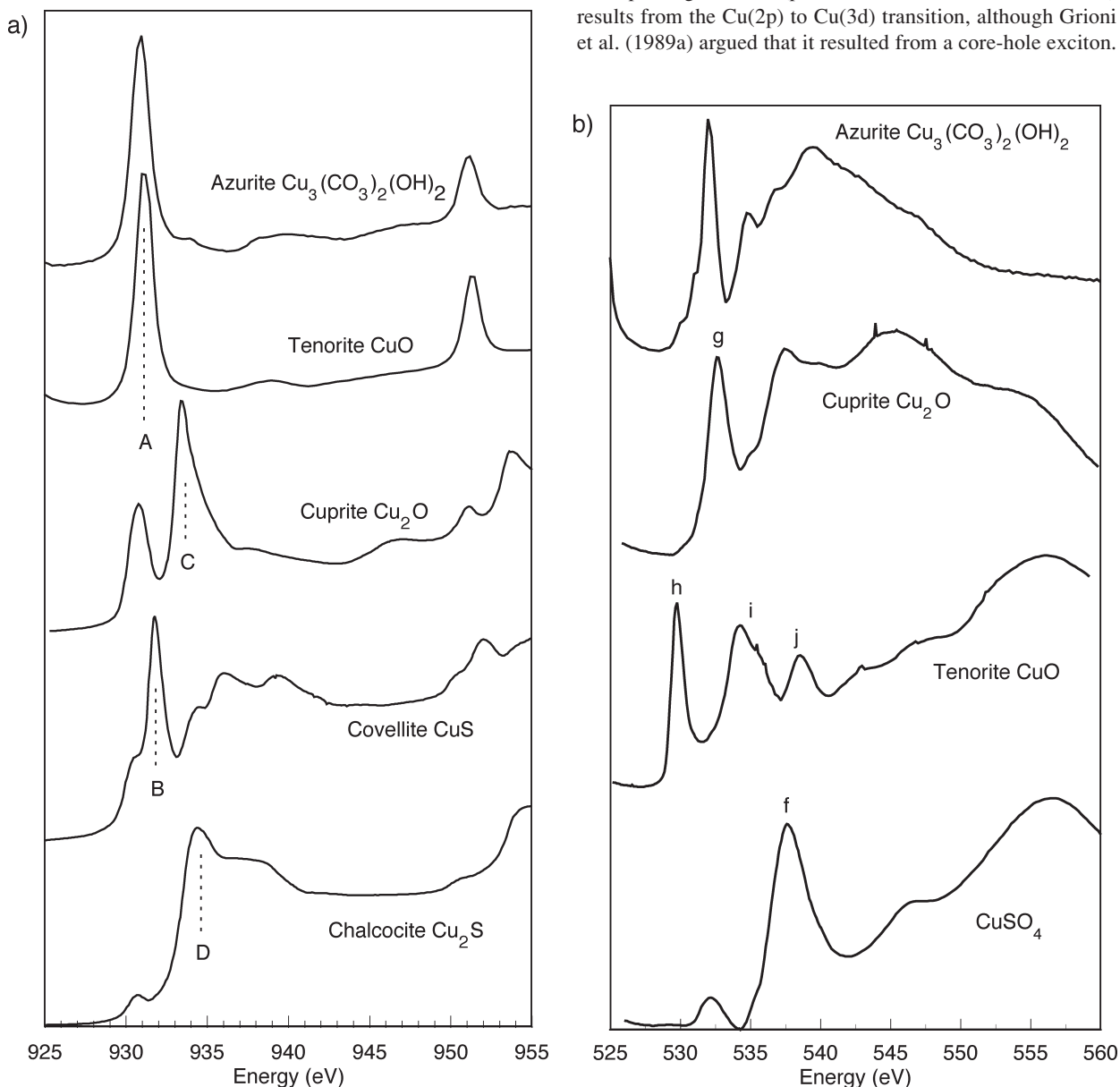
oxidized. The *O K*-edge can sample only the oxidation products, as there is no O present in the bulk sulfide.

To correct for synchrotron-intensity loss during measurement, the XAS spectra were normalized by dividing the signal, *I*, by the reference *I*<sub>0</sub>, where *I*<sub>0</sub> is the intensity of the photon flux and *I* is the total electron yield. Copper *L*-edge energies were calibrated by comparison with those published by Grioni et al. (1989b).

### RESULTS AND DISCUSSION

#### Copper *L*-edge spectra of nominally pristine chalcocite and possible oxidation phases

The Cu *L*-edge XAS spectra of nominally unoxidized chalcocite and other Cu phases are shown in Figure 2a. In the spectra of Cu (II) phases with Cu in a d<sup>9</sup> configuration, the main pre-edge feature (peaks “A” in CuO and “B” in CuS) results from the Cu(2p) to Cu(3d) transition, although Grioni et al. (1989a) argued that it resulted from a core-hole exciton.



**FIGURE 2.** (a) Copper *L*-edge spectra of nominally pristine Cu<sub>2</sub>S surface and potential surface oxidation phases. (b) Oxygen *K*-edge spectra of potential surface oxidation phases.

Covellite, CuS, contains both Cu(I) and Cu(II) (Kurmaev et al. 1998), so that peak "B" of CuS is analogous to peak "A" but for the sulfide.

In chalcocite, Cu occurs in two kinds of triangular coordination (Evans 1971): one third of the metal atoms are in distorted triangular coordination within the hexagonal close-packed S layers, and the remainder are in triangular sites between the layers. All S is present as single  $S^{2-}$  monomers. Because chalcocite contains only  $Cu^+$ , which has fully occupied d-orbitals (a  $d^{10}$  configuration), we would not expect to see any peaks in the pre-edge region of the Cu *L*-edge spectrum. However, this simple picture of electronic structure breaks down because of hybridization between the Cu(3d) and Cu(4s) orbitals. The main peak ("D") in the spectrum of chalcocite (at 934.7 eV) is created by 3d-character in the 4s-band (Grioni et al. 1989a). The small peak near 931 eV in the pre-edge spectra of  $Cu_2S$  suggests a small Cu (II) contamination; the energy of this peak is 0.3 eV different from the analogous peak ("A") in CuO.

Patrick et al. (1993) found that the intensity of the Cu (II) edge in minerals is approximately 25 times that of the Cu (I)

edge; therefore, compounds containing both Cu (I) and Cu (II) will be dominated by the Cu (II) contributions. The chalcocite Cu *L*-edge spectrum obtained in this study differs greatly from that of Patrick et al. (1997) where a strong peak at 932 eV was found; we suspect that those authors may have been observing a sample contaminated with CuS as peak "B" in CuS is at 932 eV. This circumstance led to a miss-assignment of the valence state of Cu in CuS and  $CuFeS_2$  in their paper; a revised picture of the electronic structures of Cu-S phases will be presented elsewhere.

Our spectra of  $Cu_2S$ , CuS, and CuO are identical to those obtained by Grioni et al. (1989a) where fresh crystal surfaces were obtained by scraping the sample surfaces in vacuum. Our spectrum of  $Cu_2O$ , however, shows a peak at 931 eV that could not be removed by Ar sputtering. This peak may be caused by the same Cu (II) phase contaminating the Cu *L*-edge spectrum of  $Cu_2S$ . This peak shows up weakly in the spectrum of  $Cu_2O$  published by Grioni et al. (1989a).

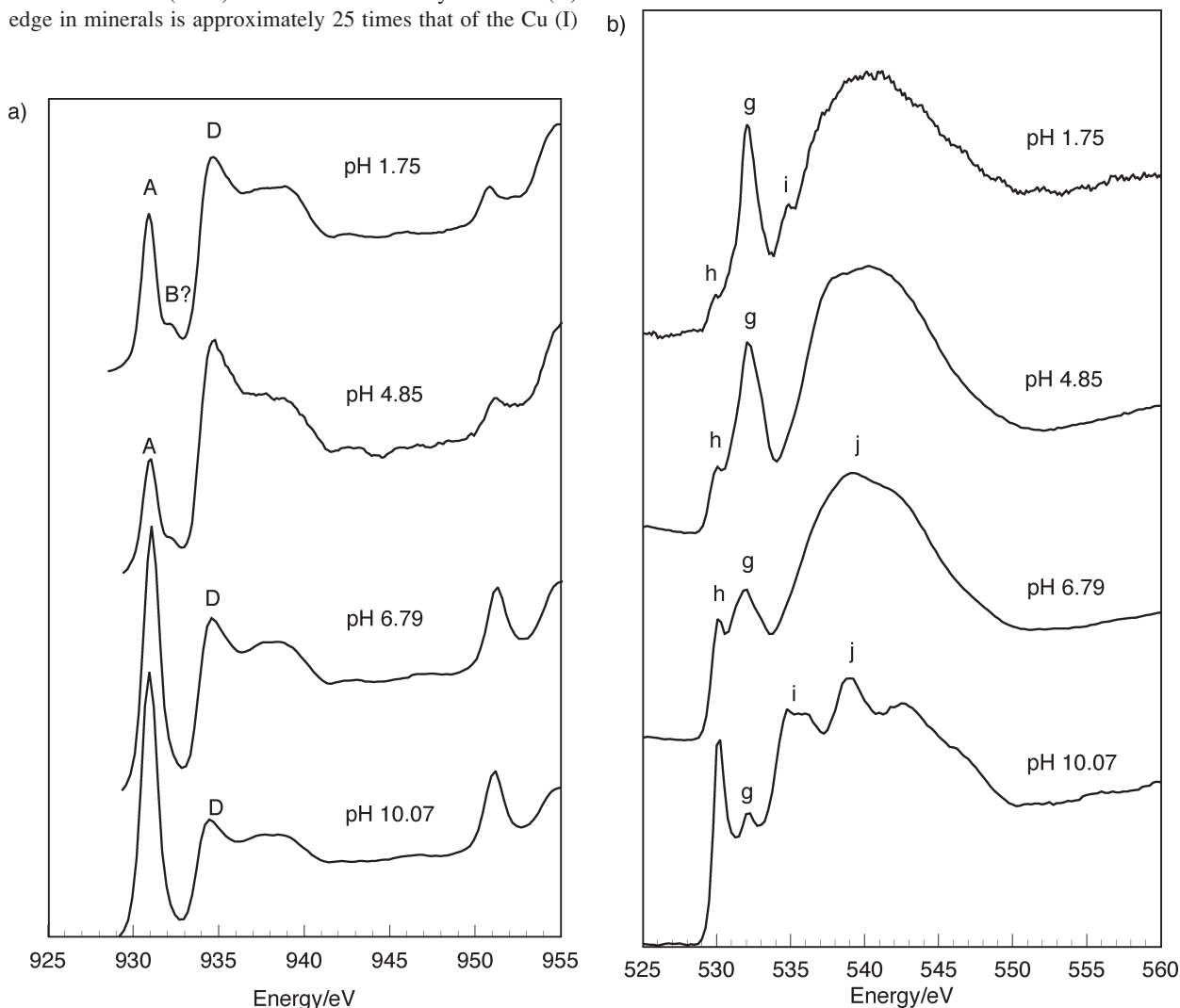


FIGURE 3. (a) Copper *L*-edge spectra of  $Cu_2S$  surfaces reacted with air-saturated  $H_2O$  as a function of pH. (b) Oxygen *K*-edge spectra of  $Cu_2S$  surfaces reacted with air-saturated  $H_2O$ .

### Oxygen *K*-edge spectroscopy of possible oxidation phases

The O *K*-edge spectra reveal a great deal about electronic structure and bonding in oxides and sulfates (e.g., Grioni et al. 1989b; de Groot et al. 1989; Chen 1997), and are extremely sensitive to surface oxidation products of sulfides (Todd et al. 2003a, 2003b). Spectra of several phases expected to form on the chalcocite surface are shown in Figure 2b. The peaks below 545 eV result from transitions from the O(1s) core orbitals to the empty Cu(3d) and Cu(4s) orbitals (e.g., peaks “h”, “i”, and “j” in CuO, and peak “g” in Cu<sub>2</sub>O). The intensity of the peaks reflect the O(2p) character of the unoccupied states. The Cu(3d) and Cu(4s) states are really Cu-O anti-bonding orbitals with significant O(2p) character if the bonding is covalent. The broad features at higher energies are better interpreted as multiple scattering features rather than O(1s)-Cu(4p) transitions. In CuSO<sub>4</sub>, the peak “f” results from transitions from O(1s) to the S-O anti-bonding orbitals. The weak peak at 532 eV is the O(1s)-Cu(3d) transition. The low intensity of this peak reflects the low covalency of the bonding between the Cu(3d) and sulfate O(2p) orbitals. The peak “g” in Cu<sub>2</sub>O results from hybridization between the Cu(3d) and Cu(4s) orbitals so that the d<sup>10</sup> configuration is not a correct description of electronic structure. The complex O *K*-edge spectrum in azurite results from the O(1s)[CO<sub>3</sub>]-Cu(3d) and O(1s)[OH]-Cu(3d) transitions, together with transitions to the C-O anti-bonding orbitals in (CO<sub>3</sub>)<sup>2-</sup>.

### Effect of pH on aqueous oxidation of Cu<sub>2</sub>S

Copper L- and O *K*-edges were collected for each of five chalcocite samples reacted in air-saturated 0.1 M NaNO<sub>3</sub> solutions at a range of pH.

The Cu *L*-edge spectra of the chalcocite surfaces (Fig. 3a) change as the oxidation pH rises from 1.75 to 10.07. Each spectrum exhibits the characteristic peak “D” (at 934.7 eV), corresponding to the Cu (2p) to Cu (3d, 4s) transition in Cu (I)-S. The small feature (peak “B”) at 932 eV may represent small amounts of Cu (II)-S on the surface, as might be observed in covellite. The dominant feature in the pre-edge is peak “A” (at 931 eV), which increases in relative intensity with increasing oxidation pH. By comparing the Cu *L*-edges of oxidized chalcocite with those of reference phases (Fig. 2a), we assign peak “A” to the transition from Cu(2p) to the Cu(3d,4s)-O(2p) anti-bonding states of tenorite CuO or Cu(OH)<sub>2</sub>. At low pH, the surface appears to be only slightly oxidized and only small amounts of CuO are present. As the pH rises, the surface becomes progressively more oxidized and Cu (II) oxide becomes the dominant phase. The presence of cuprite, Cu<sub>2</sub>O, is not indicated by the Cu *L*-edge spectra; however, peak “C” in cuprite may be masked by peak “D” in chalcocite.

The O *K*-edges (Fig. 3b) provide the most useful information about surface oxidation due to the fact that there can be no bulk contribution to the spectra. The O *K*-edges of chalcocite conditioned in aqueous solution show a marked change between pH 4.85 and 6.80. A similar phenomenon has been observed for pyrite and chalcopyrite prepared under the same conditions (Todd et al. 2003a, 2003b). Under acidic conditions, the O *K*-edge is dominated by a very strong feature (peak “g”) at 532 eV. There is also a small shoulder (peak “h”) at 530 eV. The

main change in the O *K*-edge spectra on going from pH 4.85 to 6.80 is that the intensity of peak “g” decreases relative to that of peak “h.” At pH 10.07, the pre-edge is dominated by peak “h”, and peak “g” has reduced dramatically. These changes in the O *K*-edge resemble the pattern seen in the Cu *L*-edge. By comparing these results with the reference spectra of the Cu oxides cuprite, Cu<sub>2</sub>O, and tenorite, CuO (Fig. 1b), we assigned peak “g” to the O(1s) to Cu(3d, 4s)-O(2p) anti-bonding state in Cu<sub>2</sub>O. Peak “h” was assigned to the Cu(3d)-O(2p) anti-bonding state in CuO. The changes in the pre-edge reflect the increasing oxidation of the chalcocite surface as the pH rises. Under acidic conditions, the surface is only slightly oxidized, and Cu<sub>2</sub>O (peak “g”) is the dominant surface phase. There is minor CuO, producing peak “h.” Under neutral conditions, both Cu (I) and Cu (II) oxides are important phases on the chalcocite surface. At alkaline pH, the surface is strongly oxidized, and CuO is the major oxidation product. There is no evidence for sulfate or carbonate phases forming on the Cu<sub>2</sub>S surface.

### Air oxidation

Copper *L*- and O *K*-edges (Fig. 4) were collected for a chalcocite sample oxidized in the ambient atmosphere for seven days. The Cu *L*-edge has two main features (peaks “A” and “D”), similar to those seen for the aqueous oxidized samples. Peak “D” is typical of bulk chalcocite (Fig. 2), and corresponds to the Cu (2p) to Cu (3d-4s) electronic transition. Peak A reveals the presence of Cu (II) bonded to O on the mineral surface. The same feature can be observed in the Cu *L*-edge of tenorite, CuO. The spectra suggest that surface Cu has been oxidized to Cu (II) in CuO. The fact that there is still a bulk

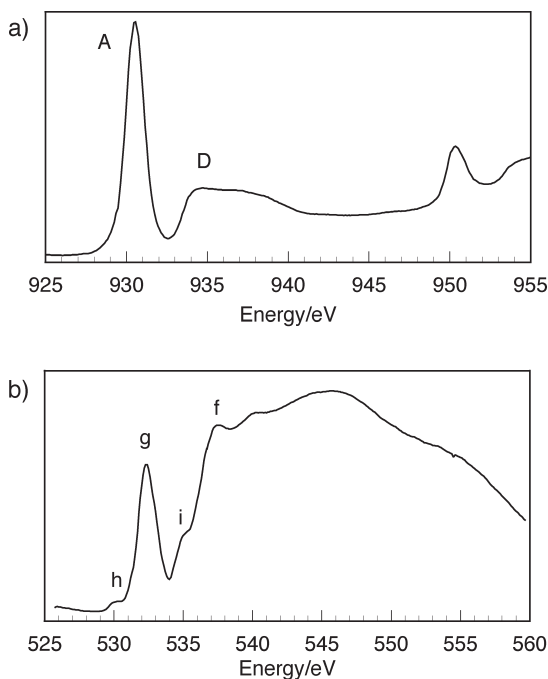


FIGURE 4. (a) Copper *L*-edge spectra and (b) oxygen *K*-edge spectra of Cu<sub>2</sub>S surface reacted with ambient air for 7 days.

contribution to the spectrum suggests that the oxidation layer thickness is less than the penetration depth of the TEY method at the Cu *L*-edge energy range (~500 Å). The Cu *L*-edge samples both the oxidized surface, and bulk Cu (I) sulfide.

The O *K*-edge (Fig. 4b) is the most sensitive probe of surface oxidation products. There is a small contribution from CuO (peaks "h" and "i") at 530.2 and 534.7 eV, but the spectrum is dominated by peak "g" of Cu<sub>2</sub>O at 532 eV. The spectrum is similar to that of chalcocite conditioned in acidic aqueous solution, suggesting that the surface is only mildly oxidized. The disparity between the Cu *L*-edge (showing mainly CuO) and O *K*-edge (showing mainly Cu<sub>2</sub>O) reflects the low intensity of the Cu(2p) to Cu(3d,4s) transition in Cu<sub>2</sub>O relative to that in CuO (Patrick et al. 1993). Also, the Cu *L*-edge samples deeper into the mineral surface and, therefore, has a strong bulk Cu<sub>2</sub>S contribution. The most interesting difference between the air-oxidized and aqueous samples is that the former shows a peak ("f") at 537.5 eV. The same feature shows up in the spectrum of Cu (II) sulfate, and we assign it to a transition to the S(3p,4s)-O(2p) anti-bonding orbitals.

### CONCLUDING REMARKS

The surface of chalcocite is readily oxidized both in air and in aqueous solution. The nature of the surface oxidation products varies with pH and oxidising conditions. In aqueous solution at low pH the dominant oxidation phase is cuprite, Cu<sub>2</sub>O. As the pH rises, the surface becomes more extensively oxidized. At pH 6, both Cu<sub>2</sub>O and CuO are present. Under alkaline conditions, the dominant surface oxidation phase appears to be tenorite, CuO. Tenorite is the most stable oxide phase under all pH conditions at atmospheric conditions (Fig. 1); the occurrence of cuprite may simply reflect a metastable intermediate resulting from slow reaction kinetics under acidic conditions. There is no evidence of sulfoxy species on the mineral surface for samples oxidized in aqueous solutions. The surface of chalcocite oxidized in air consists of cuprite (Cu<sub>2</sub>O) and a sulfate-bearing phase. There is also evidence for minor CuO.

The formation of a surface oxidation layer on chalcocite means that the apparent surface properties of chalcocite in aqueous environments will be determined by the surface properties of tenorite and cuprite. The oxide surfaces are hydrophilic and, consequently, their formation hinders chalcocite recovery by froth flotation. Prevention of surface oxide formation using an inert atmosphere, or reduction of the surface oxidation layer by sulfidization, enhances recovery (Clark et al. 2000).

The formation of surface oxidation layers must affect the release of metals from sulfides during weathering. In particular, the initial aqueous concentration of Cu released into solution by anodic dissolution of chalcocite will be determined by the aqueous solubilities of tenorite and cuprite. Under the low pH conditions of acid-mine drainage, the initial aqueous concentration of Cu will be determined by the solubility of cuprite if chalcocite is the only Cu sulfide present. By comparison, the oxidation of chalcopyrite (CuFeS<sub>2</sub>) yields a Cu-deficient surface layer with only FeOOH and, possibly, a ferric hydroxy sulfate phase (Todd et al. 2003b). In the latter study, we were unable to find any CuO or Cu<sub>2</sub>O layer on CuFeS<sub>2</sub> suggesting

that Cu<sup>2+</sup> was completely released into solution during the oxidation of chalcopyrite.

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