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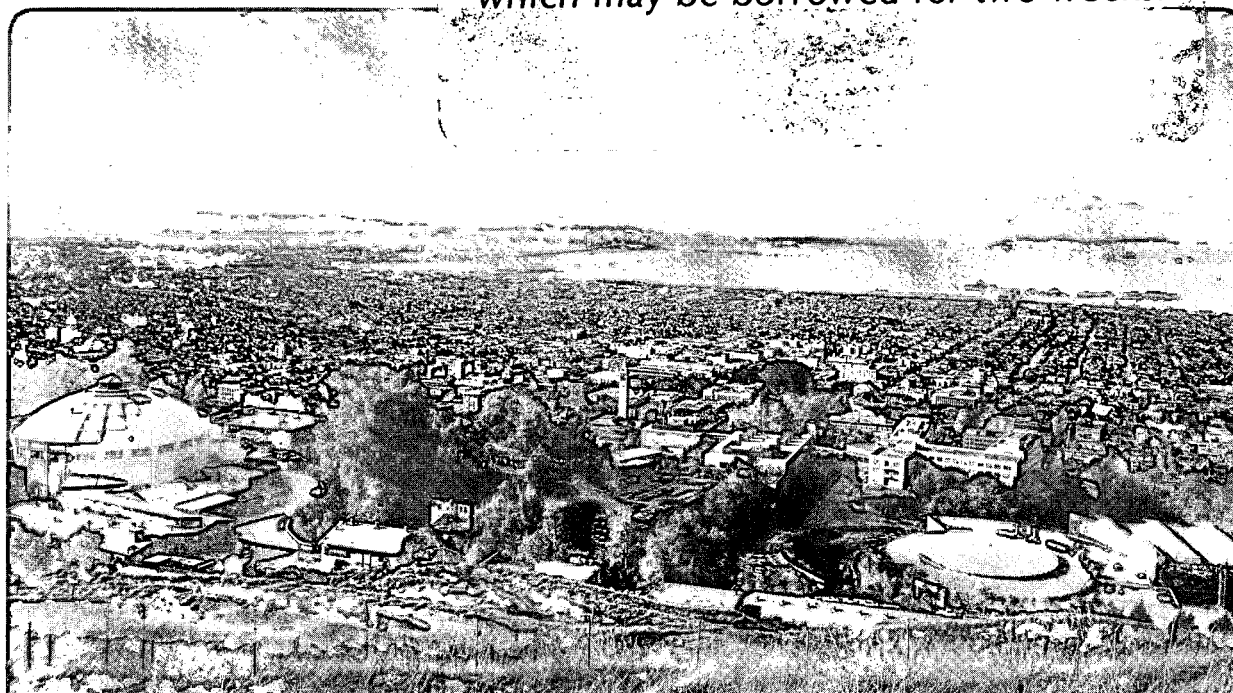# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

SURFACE STUDIES OF THE INTERACTION OF COPPER
IONS WITH METAL SULFIDE MINERALS

D.L. Perry, L. Tsao, and J.A. Taylor

May 1984

DISCLAIMER

SURFACE STUDIES OF THE INTERACTION OF
COPPER IONS WITH METAL SULFIDE MINERALS

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Abstract

The interaction of copper ions in aqueous
solution with the surface of galena (PbS) and
sphalerite (ZnS) has been studied using x-ray
photoelectron spectroscopy (XPS), scanning Auger
microscopy (SAM), and scanning electron microscopy
(SEM). These studies were conducted with several
of the experimental parameters of the chemical
reaction systems being varied, the parameters
including copper ion concentration, variation of
the anion associated with the initial copper salt,
temperature, reaction time, and pH. Scanning Auger
microscopy was used for studying elemental segrega-
tion and mapping of the reacted mineral surfaces.
A rigorous use of model compounds was made in the
study of each mineral surface reaction system.

INTRODUCTION

Copper ions play an extemely important role in the froth
flotation processing of many metal sulfide minerals. Chang and
co-workers (1) have reported experimental results from an inves-
tigation of the flotation characteristics of pyrrhotite in the
presence of copper(II) sulfate. Similar effects have been studied
with pyrite (2) when copper(II) was included in the flotation
process. Gaudin and his co-workers (3) have conducted a rather
extensive study of the interaction of copper(II) with sphalerite,
while other researchers (4) have looked at the kinetics of this
reaction. Shimoiizaka et al. (5) have studied the activation of
galena by copper(II) sulfate.

In an attempt to understand better the role of copper salts in froth flotation processes, surface studies have been conducted on the metal sulfide minerals galena and sphalerite that have undergone reaction with aqueous solutions of copper(II) ions. These studies were made with several of the parameters of the chemical reaction systems being varied so as to study the effects on the surface characteristics of the different minerals, parameters including the initial copper ion concentration, variation of the anion in the copper salt being used, temperature, time of reaction, and pH.

X-ray photoelectron spectroscopy (6) was used to determine the surface chemical species of the copper, sulfur, zinc, and lead. This was done by performing high resolution studies on core photoelectron lines. In addition to the satellite, or "shake-up", structure of the copper lines, extensive use was made of binding energies, line widths, and multiplet splitting. Auger spectroscopy(7) was used to study the heterogeneity of the surfaces, while elemental segregation and mapping of the surfaces was effected using scanning Auger microscopy. All of these studies have been made in conjunction with pure chemical models of chemical species that might possibly result from the galena/sphalerite copper(II) interaction.

EXPERIMENTAL

High quality galena was obtained from Ward's Natural History Establishment, while sphalerite was obtained from the Museum of Mineralogy, University of California, Berkeley. For purposes of the experiments involving the interaction of the copper(II) ions with galena, two types of galena were used: oxidized and unoxidized. Oxidized galena was prepared by roasting "as received" samples at 300 °C for $\sim$0.5-1 hr, followed by monitoring the sulfur 2p photoelectron line in order to assure a coating of lead sulfate being present on the surface. Unoxidized galena was prepared by immersing freshly cleaved samples of galena in boiling, distilled (using quartz apparatus) water for several seconds as previously reported (8); again, the surface was shown to be free of oxidation products (such as sulfate and sulfur) by monitoring the sulfur 2p line. Sphalerite, unlike galena, did not perceptibly oxidize to form a sulfate coating, even at 300 °C for periods greater than 1 hr. Instead, a thin film of oxide formed on the surface that did not increase with extended periods of heating. Consequently, it was used "as received" in all experiments.

All copper(II) salts ($CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $CuCl_2 \cdot 2H_2O$) were the purest grade reagents available. All copper(I) salt samples, also of the highest purity available,

were found to contain some contaminant copper(II) as evidenced by the copper 2p photoelectron spectra. As a result, all experiments aimed at chemisorbing copper(I) onto galena and sphalerite surfaces were abandoned, since the possibility of the chemisorbed copper coming from the initial copper(II) contaminants could not be precluded.

A Physical Electronics Model 595 scanning Auger microprobe was used for taking Auger data, while a Physical Electronics Model 555 x-ray photoelectron spectrometer equipped with a Mg Kα (1253.6 eV) anode source was used for obtaining all x-ray photoelectron spectra. The adventitious carbon 1s = 285.0 eV line was used for charge referencing. All samples were studied as either fine powders moounted on polymer film based adhesive tape with a metallic backing or as freshly cleaved chips mounted on the same type tape. All scanning electron microscopy data were taken with an ISI Model DS 130.

Samples of galena (oxidized and unoxidized) and sphalerite were exposed to distilled water solutions of copper(II) ions that were typically 100 ppm in copper; this concentration was varied for purposes of concentration dependency studies. Exposure times were 15 min except for time dependency studies. After exposure to the copper solutions, each sample was flushed with a stream of cold, distilled water in order to remove non-bonded copper and then air-dried at room temperature for several minutes before introduction into the x-ray photoelectron and Auger spectrometers.

RESULTS AND DISCUSSION

As expected in light of previous studies involving the aqueous copper(II) ion interaction with galena and sphalerite, the surface chemistry of the two systems proved to be quite complex. Changing reaction parameters such as temperature, pH, and reaction time invariably changed the reaction chemical characteristics of each mineral. In general, the surface chemical complexity was found to be greater for the galena/copper(II) interaction than that resulting from the sphalerite/copper(II) interaction. Scanning Auger microscopy, used to elementally map the reacted surfaces, showed a strong degree of segregation of copper sulfide islands. The nature of this copper sulfide species is discussed below. Some of the general results and observations were as follows:

Oxidized vs. Unoxidized Galena - The only unequivocal effect result-ing from reacting air oxidized galena (as apposed to clean, freshly cleaved galena) with copper(II) salts was a much more pronounced number of nucleated oxidation product particles that were enriched in copper sulfide. This is discussed in greater detail below.

Reaction Time – When the reaction time of the exposure of the minerals was lengthened beyond the normal 15 min. period, more copper was adsorbed as a function of time. The nucleation of the copper sulfide surface particles, presumably occurring at surface defect sites, became more complex as a function of both time and temperature. When the reaction was under a minute at 25 °C using unoxidized galena, a thin film of probably a couple of monolayers of copper sulfide formed, along with a few dispersed islands. As the reaction time was extended, more particles formed on the surface. For oxidized galena, these same trends were observed, but the formation of the copper sulfide-rich particles occurred more rapidly and extensively.

Temperature – Temperature-dependent studies were conducted at 25 °C and 100 °C. While x-ray photoelectron and Auger spectra for both the reacted galena and sphalerite remained invariant as a function of reaction temperature, the morphology of the reacted surfaces (and the species observed on the surfaces) did not. Fig. 1, for example, shows sphalerite that had been reacted with copper(II) at 25 and 100 °C. In Fig. 1a, one can see the features that were generally observed for all the 25 °C reactions. The copper complex existed as a thin film, and no morphologically distinct phases attributable to a copper sulfide complex could be detected on the surface; the particles seen in Fig. 1a were shown to be sphalerite. Figs. 1b and c, however, show the sphalerite/copper-reacted surface resulting from the reaction at 100 °C. New surface features, observed only for the reaction that had been conducted at 100 °C, were observed.

Varying the temperature of the reaction also dramatically changed the amount of copper observed on the reacted surface. The maximum Cu: Pb ratio, for example, was found to be $\sim$1.5 (using x-ray photoelectron spectroscopy) for the copper(II)/galena reaction run at 25 °C, whereas the ratio increased to a maximum of $\sim$9.0 when the reaction was effected at 100 °C.

Counterion Effects – Experiments were conducted using the nitrate, sulfate, and chloride salts of copper(II). No unequivocal major differences in the surface chemistries of either the copper-reacted galena or sphalerite could be attributed to this effect using the sulfate and nitrate, although differences were observed when $CuCl_2$ was used. In this case, significant amounts of sulfur were seen on the reacted galena, with the amount of sulfur many times being equal to the amount of sulfide being observed in the spectrum. This may have reflected differences in nucleation processes on the surface and in the bulk that are observed for other metal reaction systems involving the chloride (9,10) ion. These

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findings are preliminary, however, and more work will be needed to determine the role of the chloride ion in these reactions.

Concentration of Copper Ion - While the original concentration of the copper(II) ion did effect the amount of copper complexed to the galena and sphalerite surfaces, it did not affect the chemistry. There was no change in spectral features (other than quantitative ones) as a function of concentration, an observation that was in agreement with data reported by other workers (8,11,) involving x-ray photoelectron studies of the interaction of aqueous dichromate with galena.

Variation of pH - In general, less copper was retained on the galena and sphalerite reacted at higher pH values (10-12) than at lower pH (less than pH = 4) values, all other reaction parameters being held constant. The Cu: Zn ratio on the surface of the reacted sphalerite (25 °C), for example, was found to be a maximum of 1.5-2.0 at low pH and $\sim$0.3 at high pH on the basis of x-ray photoelectron data. This is not surprising, since the copper(II) ion exists as a non-hydrolyzed ion at low pH and thus a rather simple ionic system. At high pH values, however, the copper(II) exists as polymeric hydroxide complexes (12,13); any interaction of these copper(II) polymers with galena and sphalerite, therefore, would involve a decidedly different reactant than an interaction with a simple copper ion found at low pH. Also, these polymerization reactions result in precipitation of much of the copper(II), effectively changing the solution concentration of copper available to react with the minerals. If the reactions were conducted at high pH values at 100 °C, however, considerably more copper was found on the surface than was found for 25 °C reactions. Two possible explanations for this observation were the probably increased solubility of the copper(II) polymers and more probably the increased kinetics of the copper(II)-mineral reactions at the elevated temperatures.

X-Ray Photoelectron and Auger Data

X-ray photoelectron and x-ray-induced Auger spectral data were obtained for high purity reagent grade standards of possible oxidation products of galena and sphalerite (such as $PbSO_4$, $ZnSO_4$, $S°$, etc.), the unreacted galena and sphalerite, and the minerals that had been reacted with the aqueous solutions of the Cu(II) ion. These data are presented in Tables I and II in an abbreviated form (in order to conserve space, only the pertinent model compounds have been presented). Both the unreacted galena and sphalerite showed sulfur 2p lines of 161 eV, values that may unequivocally be assigned as the

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lattice sulfide (14,15). On standing in air, however, both the lead 4f and sulfur 2p photoelectron lines indicated the formation of oxidation products on the galena surface. A close examination of the oxygen 1s line revealed a doublet (Table I), consistent with products that were found to include lead oxide as well as a mixed carbonate/ hydroxide complex. The ultimate series of oxidation products of galena also included $PbSO_4$; these results found in this study were in excellent agreement with previous surface studies directed at the oxidation of lead sulfide and galena (14,15). The only oxidation product observed for sphalerite was ZnO, both before and after the reaction with copper(II) in solution.

Fig. 2 depicts the sulfur $2p_{3/2,1/2}$ doublet and the lead $4f_{7/2,5/2}$ photoelectron line profiles for galena and its surface products formed upon reacting with aqueous $CuSO_4 \cdot 5H_2O$. Fig. 2a shows clean, unreacted galena, while Fig. 2b shows galena that had been oxidized in air at 25 °C. When this same oxidized sample is rinsed with boiling, distilled water, the spectra (Fig. 2c) show a surface that is unoxidized and essentially identical to the original galena surface; this result has been reported previously (8). Fig. 2d, however, depicts by far most of the spectra observed for copper-reacted galena. Obvious broadening is observed in the sulfur 2p line, indicating the presence of a second sulfide species involving the copper. Finally, Fig. 2e shows galena that has been reacted at a low pH range of 1-3. As observed, the lead 4f lines have split into doublets, indicating the presence of both lead sulfide and lead sulfate that have been incorporated into the surface products. While this lead sulfate can be removed by aqueous solutions before the reaction with copper(II), it cannot be removed afterwards.

Both the galena and sphalerite that had been reacted with copper(II) exhibited spectra indicative of a copper(I) sulfide complex, confirming that the operable process of copper attachment to the mineral surfaces involved reductive adsorption of the copper ion with the concomitant oxidation of the lattice sulfide ion to sulfate. Fig. 3 shows the spin-orbit split doublet copper $2p_{3/2,1/2}$ spectra for the two cases observed in the present study. In Fig. 3a, only a slight trace of "shake-up" structure (16) between the main lines is observed, indicative of a diamagnetic d^{10} copper(I) species; this general type of spectrum was seen for almost all cases. The intensity of the "shake-up" slightly increased, however, in Fig. 3b, indicating some copper(II) to be on the reacted surface. Since there is no true copper(II) sulfide (17), this species was probably either CuO, $Cu(OH)_2$, or $CuSO_4$ chemisorbed onto the initial reaction products from the reaction solution. While previous

studies (18) have expressed concern that the copper(I) surface species results from x-ray induced photoreduction, there was no evidence in the present study for this process. No photoreduction was observed for even the reagent standard copper(II) salts, even though extended irradiation under an x-ray beam can effect it. No beam reduction for copper(II) salts has been observed in previous studies (19,20) under average operating conditions (such as length of time) for obtaining spectra.

The copper sulfide species that formed on the surface of the reacted galena and sphalerite was extensively studied in the present work. While previous research (21) has indicated that this principal surface product might be covellite, the present research does not corroborate that finding. Instead, after comparing the surface data with well-documented standards, the data strongly suggest (although do not unequivocally prove) that the copper sulfide is chalocite, or Cu_2S. The binding energies and other spectral data for copper and sulfur shown in Tables I and II for both the galena and sphalerite reaction systems agree with those shown in Table I for chalcocite. Additionally, the difference in binding energies for the Cu $2p_{3/2}$ and S $2p_{3/2}$ photoelectron lines obtained from the reacted surfaces was also in excellent agreement with that of chalcocite. The Auger parameter (22), α^*, shown for copper in Tables I and II for the reacted surface of galena and sphalerite, was also identical to the value for chalcocite. The atomic ratio of Cu:S was found to be almost exactly 2:1, or Cu_2S. Finally, larger dipyramidal particles that form at 100 °C in the galena/Cu(II) reaction are compatible with chalcocite. While all these data are in strong agreement with chalcocite, one should not accept them as unequivocal proof. This is especially true in light of the extreme complexity of the copper-sulfur mineral systems (17).

Scanning electron microscopy and Auger electron spectroscopic point analyses yielded even more information concerning both the chemical and morphological conditions of the copper(II)-reacted mineral surfaces. The scanning electron micrograph in Fig. 4 shows the surface of unoxidized galena which had been reacted with 100 ppm $CuSO_4 \cdot 5H_2O$ at 25 °C for 15 min. In addition to the layer of copper sulfide and other oxidation products totally covering the surface, small particles were also observed. When one examined the initial surface, the result is shown in the top spectrum of Fig. 4; this spectrum is the same regardless of where the point analysis (the electron beam width is approximately 2μ) is conducted on the surface, including on or off the individual particles. The spectrum clearly indicates a copper sulfide coating as well as other products such as

lead oxide, hydroxide, and carbonate. On sputtering the
surface with argon ions, however, some copper sulfide
was still left (middle spectrum) but much of the carbon and
oxygen (indicative of a carbonate that might possibly have
formed by chemisorption of CO_2 from either the air or the
aqueous reaction medium) had been removed. The amount of
copper was greatly reduced. After sputtering, the analysis
of one of the particles (bottom spectrum) showed that the
particle was indeed enriched in copper--more so than the flat
area of the surface. Because the width of the electron beam
was greater than that of the individual particles and the
particles were closer together than the width of the beam,
one cannot point analyze only a flat region or a particle;
each spectrum out of necessity will represent a slight
component of the area not wanted in the analysis, no matter
how well the electron beam is centered. Elemental mapping of
the surface, using scanning Auger microscopy in conjunction
with argon ion sputtering, however, yielded exactly the
same results as the Auger point analyses shown here.

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TABLE I. Binding Energies (eV) – Galena Reaction System

	Pb $4f_{7/2}$	S $2p_{3/2}$	O 1s	Cu $2p_{3/2}$	Cu L_3VV[b]	$\alpha*$[c]	Δ[d]
PbS[e]	137.7	160.9					
PbS(ox)[f]	138.9	168.4	531.7/529.8				
PbSO$_4$[g]	139.5	168.7	531.9				
PbSO$_3$[g]	138.8	166.8	531.2				
PbS$_2$O$_3$[g]	138.7	167.7/162.0	531.5				
PbS/CuSO$_4$[h]	137.7	161.7		932.6	917.3	1849.9	770.9
PbS/CuSO$_4$[i]	139.5	168.7	531.9	932.6	917.3	1849.9	
Cu$_2$S[j]		161.7		932.6	917.3	1849.9	770.9
CuS[k]		162.5		932.4	917.9	1850.3	769.9

(a) All spectra referenced to C 1s at 285.0 eV.
(b) Kinetic energies for the Auger lines were determined from their apparent
    binding energies (KE = hv−BE).
(c) Modified Auger parameter (see Wagner et al., Anal. Chem., 51, 466(1979)) for copper.
(d) The differences in binding energies between the Cu $2p_{3/2}$ and S $2p_{3/2}$ photoelectron lines.
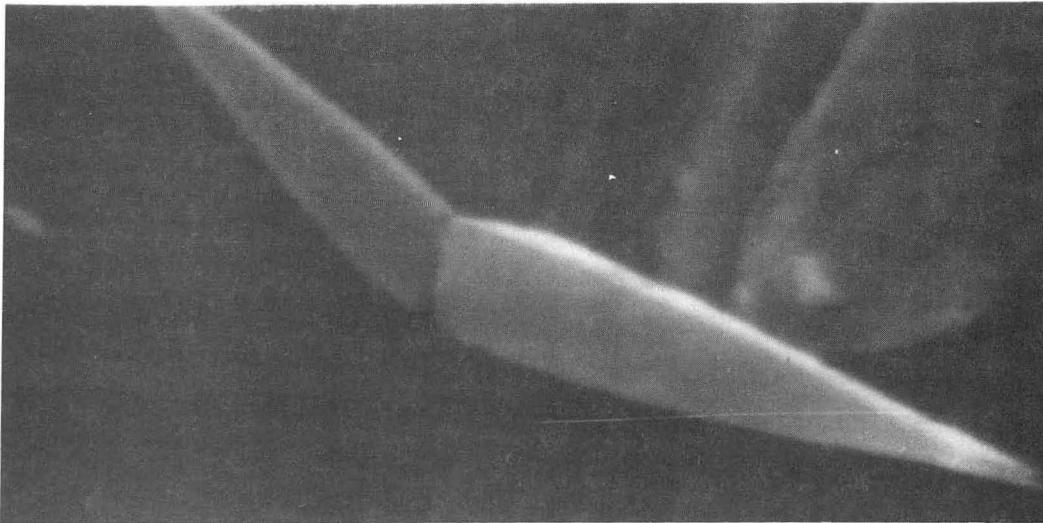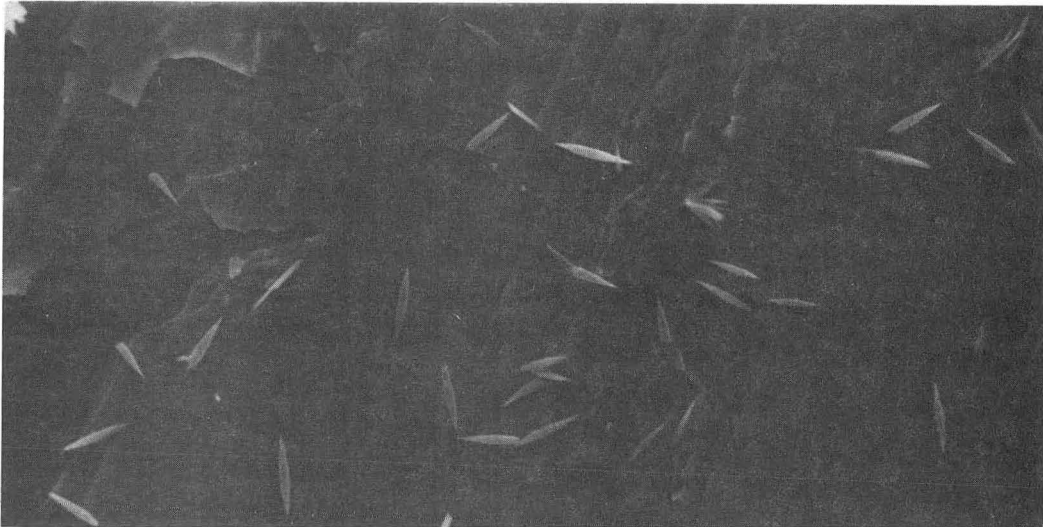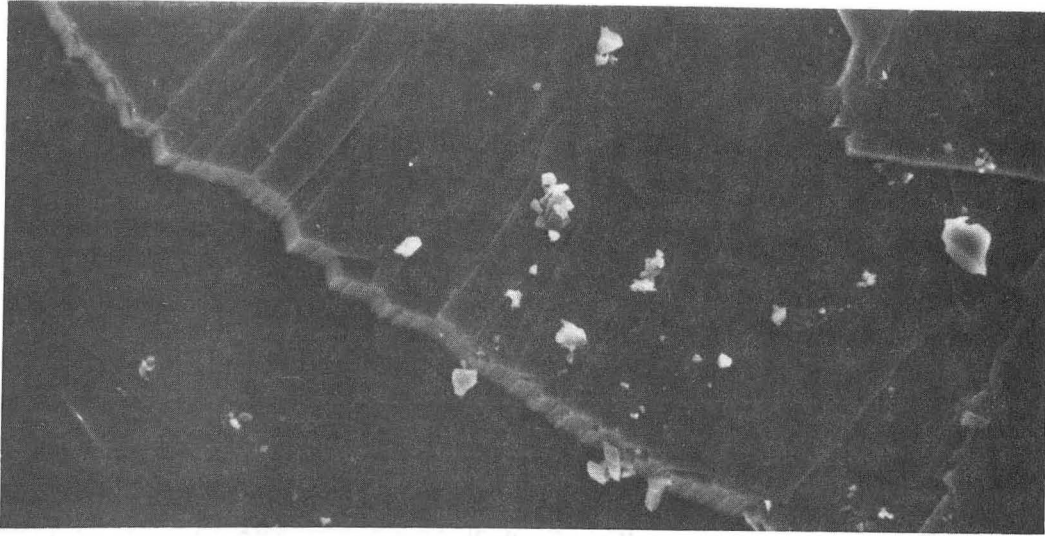(e) Galena, air cleaved.
(f) Freshly cleaved galena exposed to air for one day.
(g) Powdered, reagent grade standard.
(h) PbS exposed to CuSO$_4$·5H$_2$O solution; see Fig. 2d.
(i) PbS exposed to solution pH <7.0; sometimes showed PbSO$_4$ incorporation; see Fig. 2e.
(j) Freshly crushed chalcocite.
(k) Freshly crushed covellite.

TABLE II. Binding Energies (eV) – Sphalerite Reaction System

	Zn 2p$_{3/2}$ [a]	Zn L$_3$M$_{45}$M$_{45}$ [b]	α* [c]	S 2p$_{3/2}$	Cu 2p$_{3/2}$	Cu L$_3$VV [b]	α* [d]	Δ [e]
ZnS [f]	1022.0	989.5	2011.5	161.7				
ZnS/CuSO$_4$ [g]	1022.0	989.5	2011.5	161.7	932.6	917.3	1849.9	770.9
ZnO [h]	1022.1	989.3	2011.4					

(a) All spectra referenced to C 1s at 285.0 eV.

(b) Kinetic energies for the Auger lines were determined from their apparent binding energies (KE = hν−BE).

(c) Modified Auger parameter (see Wagner et al., Anal. Chem., 51, 466(1979)) for zinc.

(d) Modified Auger parameter (see Wagner et al., Anal. Chem., 51, 466(1979)) for copper.

(e) The differences in binding energies between the Cu 2p$_{3/2}$ and S 2p$_{3/2}$ photoelectron lines.

(f) Air cleaved sphalerite.

(g) Freshly cleaved sphalerite exposed to CuSO$_4$·5H$_2$O solution; binding energies did not vary with solution parameters.
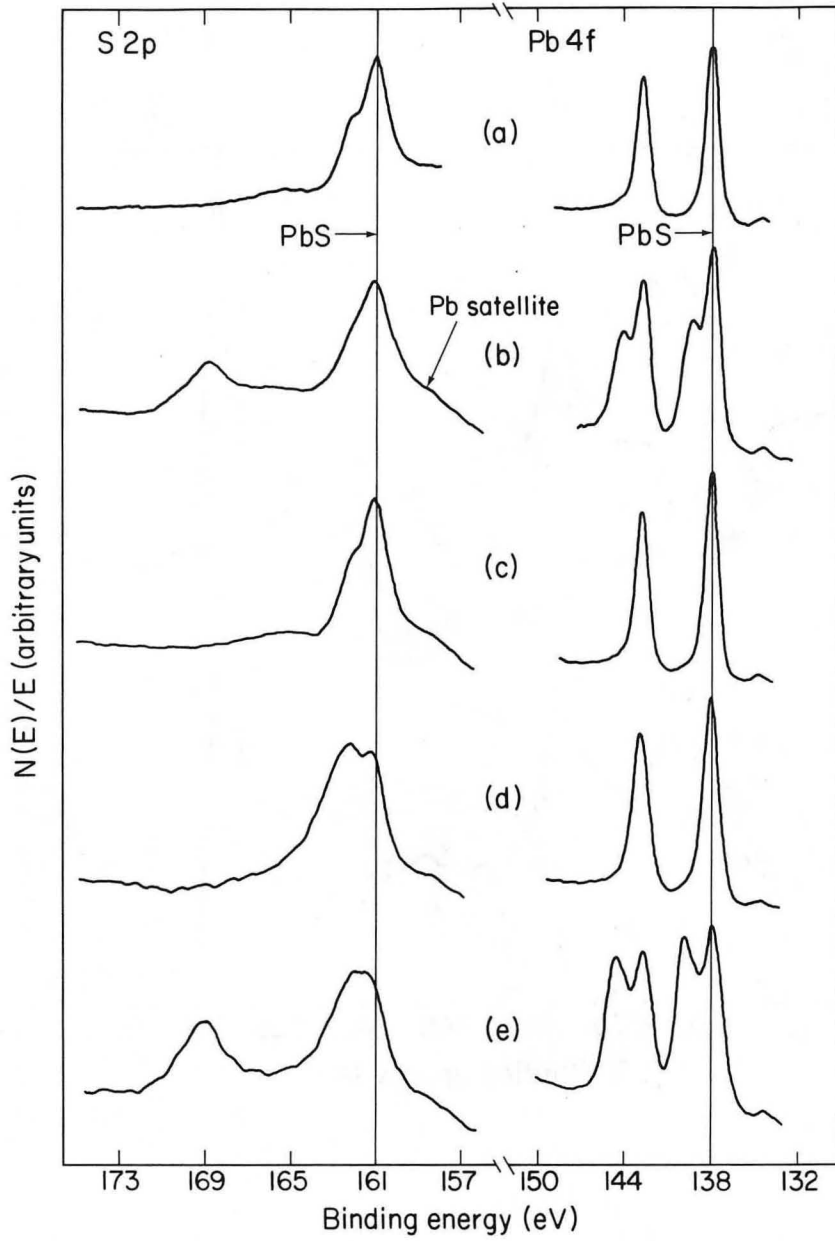
(h) Powdered, reagent grade standard.

Figure Captions

Figure 1. Scanning electron microscopic (SEM) image of sphalerite reacted with $CuSO_4 \cdot 5H_2O$ at 25 °C (top) and 100 °C middle and bottom). Scales: 1.01 kX (top); 1.04 kX (middle); 13.9 kX (bottom).

Figure 2. The sulfur $2p_{3/2,1/2}$ and lead $4f_{7/2,5/2}$ photoelectron lines for a) air cleaved galena, b) galena air-oxidized for 3 weeks, c) sample b) rinsed in boiling water, d) most typical example of galena exposed to $CuSO_4 \cdot 5H_2O$ solutions, and e) oxidized galena exposed to low pH (less than 7) solutions of $CuSO_4 \cdot 5H_2O$ (sometimes showing $PbSO_4$ incorporated into the Cu_2S surface film).

Figure 3. Copper $2p_{3/2,1/2}$ photoelectron lines typical of those observed for galena and sphalerite after exposure to $CuSO_4 \cdot 5H_2O$ solutions; a) was seen in most cases, but copper(II) was also seen sometimes as in b).

Figure 4. Auger point analyses of the particles and flat surface resulting from the reaction of oxidized galena with $CuSO_4 \cdot 5H_2O$ at 25 °C. The top spectrum represents the unsputtered surface layer (at all points on the surface), the middle spectrum a point analysis of the clear region (after sputtering), and the bottom spectrum a point analysis of a particle after sputtering. SEM magnification: 20 kX.
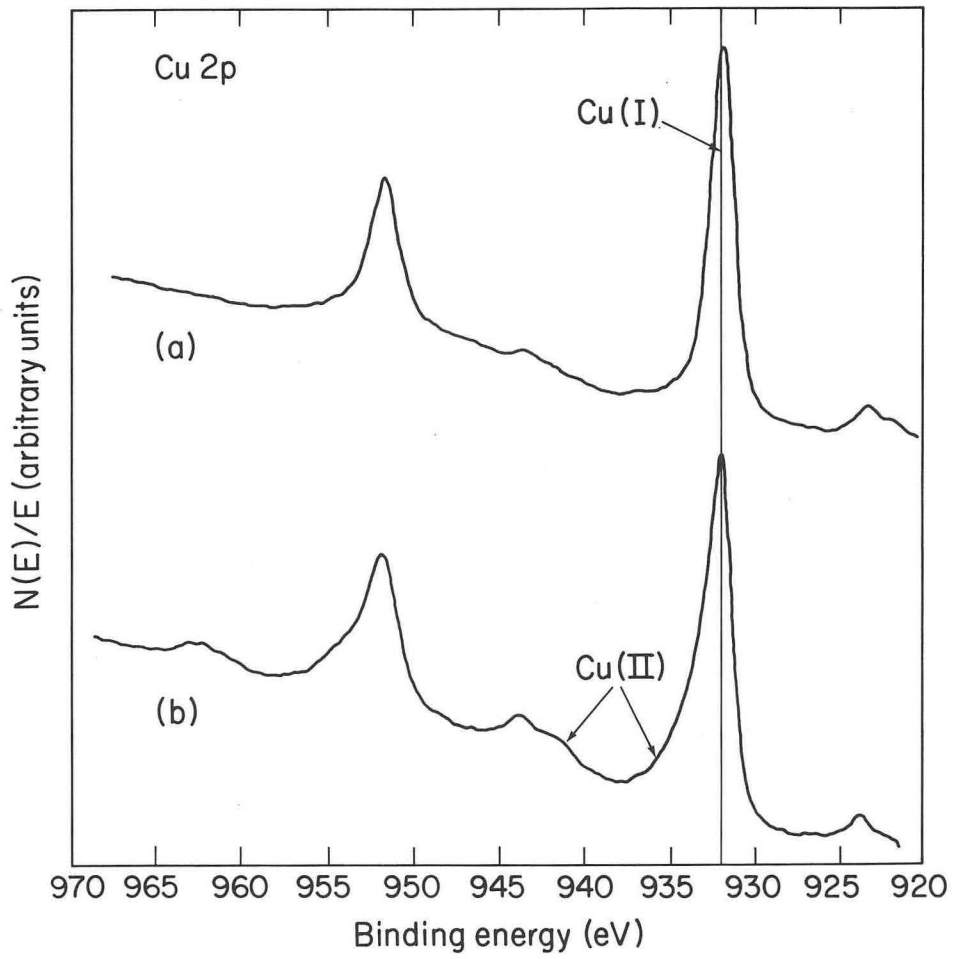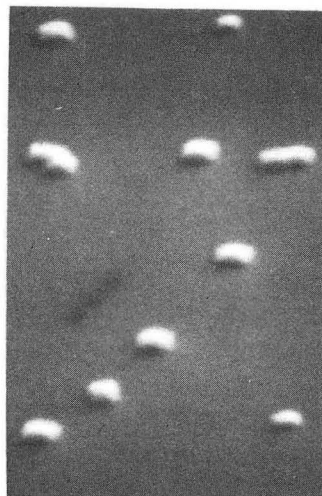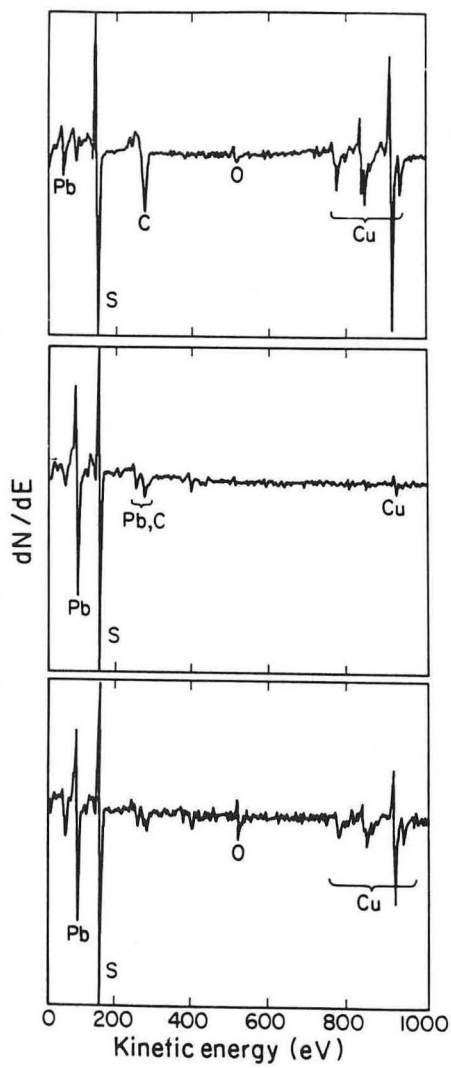
Figure 1.

XBB 845-3732

14

Figure 2.

S 2p

Pb 4f

(a)

PbS →

Pb satellite

(b)

PbS →

(c)

(d)

N(E)/E (arbitrary units)

(e)

173   169   165   161   157   150   144   138   132

Binding energy (eV)

XBL 844-9764

Figure 3.

Cu 2p

Cu(I)

(a)

N(E)/E (arbitrary units)

(b)

Cu(II)

Binding energy (eV)

970 965 960 955 950 945 940 935 930 925 920

XBL 844-9765

16

Figure 4.

XBB 845-3733

17