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M. B. McNeil, J. M. Jones, and B. J. Little

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MINERALOGICAL FINGERPRINTS FOR CORROSION PROCESSES INDUCED BY SULFATE REDUCING BACTERIA

M. B. McNeil
Naval Coastal Systems Center
Panama City, FL 32407-5000

J. M. Jones
Naval Surface Warfare Center
Silver Spring, MD 20903-5000

B. J. Little
Naval Oceanographic and Atmospheric Research Laboratory
Stennis Space Center, MS 39529-5004

ABSTRACT

Mineralogical data, thermodynamic stability (Pourbaix) diagrams, and the simplexity principle for precipitation reactions are used to rationalize corrosion product mineralogy in a variety of situations involving both fresh and saline water and to demonstrate the action of SRB in these cases. Methods for using corrosion product mineralogy as a diagnostic tool for microbiologically influenced corrosion (MIC) are discussed. Many sulfides under near-surface biosphere conditions can only be produced by microbiological action on specific precursor materials such as metals. If a corrosion process can be shown to have taken place in a pH-Eh range typical of near-surface biosphere conditions and no compelling kinetic arguments can be adduced, mineralogical and geochemical data indicate that the presence of these minerals as corrosion products implies that sulfate reducing bacteria (SRB) were active.

INTRODUCTION

The authors have divided MIC into two subsets: microbiologically intermediated and microbiologically induced corrosion. Microbiologically intermediated corrosion refers to corrosion processes in which chemical intermediates have been produced by microorganisms without the microbe directly contacting the metal surface. An example is corrosion attack by microbiologically produced reduced sulfur species in a gas phase. Microbiologically induced corrosion refers to corrosion controlled by

conditions at the biofilm/metal interface where conditions differ from those in the bulk phase. For example, a metal in an oxygenated medium can be covered with a biofilm such that conditions at the biofilm/metal interface are strongly reducing.

The corrosion processes discussed in this paper will be limited to those occurring between -20°C and 35°C in waters less than 10 meters deep or shallow land burial. Peat bogs, volcanic environments, acid mine waters and artificial environments such as chemical process equipment are excluded. It is assumed that either (1) a sulfide has been observed, and its formation must be explained, or (2) no sulfide has been observed and its absence must be explained. The second question is specifically addressed in the case of a corrosion failure where morphological and chemical evidence indicate MIC but no sulfide minerals are detected. Thermodynamic data used in this paper, unless otherwise stated, are taken from the most recent National Bureau of Standards publication.[1]

Figure 1 is a silver-sulfur stability diagram. The upper diagonal line (a) is the oxygen line, above which water is thermodynamically unstable with respect to oxygen generation. The lower diagonal line (b) is the hydrogen line, below which water is thermodynamically unstable with regard to hydrogen evolution. Waters do exist outside these boundaries under special conditions.

Horizontal line c separates the regions in which chloride corrosion of Ag can and cannot take place. The upper hatched area (below line d) approximates the region of effective redox/acidity conditions for near surface waters. Strongly acidic and basic regions are characteristic of ground waters, not seawaters. The effective redox potential of oxygenated water is less than would be calculated thermodynamically from oxygen concentrations because of kinetic effects. The effective redox potential also depends on on water pollutants, temperature, and temperature/pressure history.

The lower, oppositely hatched parallelogram indicates redox/acidity conditions existing in the biosphere but nor characteristic of near surface waters. Conditions outside the parallelograms are found in peat bogs, coal mines and at depths not considered in this paper.

The heavy diagonal line e though the hatched areas indicates redox conditions for a series of waters sampled from a brackish, stagnant pond.[2] The upper levels of this pond were heavily oxygenated because of

temperature effects and the depths contained 40 mg/l H_2S and significant decaying organic material. The hatched regions were generated using pond conditions to define the upper and lower Eh/pH values near neutrality. Eh/pH slopes were assumed to be controlled by oxidation reactions. The pH values were bounded by the highest and lowest literature values, excluding those found in coal mine and peat-bog situations.

In Figure 2, parallelograms have been superimposed on a Pourbaix diagram for iron in water with 10^{-2}M total reduced sulfur content, representative of conditions under a biofilm with active SRB and unlimited sulfate. In Figure 3, the same parallelograms have been superimposed on a Pourbaix diagram for copper in water with 10^{-2}M reduced sulfur. Sulfate content of the waters is important only as a source of sulfate ions for SRB. Copper sulfate minerals cannot form in the presence of water at sulfate concentrations likely to be found in sea service or land burial. Nonbiological conversion of sulfate and other oxidized sulfur species to reduced sulfur species is slow even by geological standards. For example, sulfates in the Permian Basin in Texas have been in contact with reducing waters for tens of millions of years with no detectable conversion of sulfate to sulfide.

Within the context of this paper, the conversion of a metal to a sulfide is defined as MIC. Corrosion conditions in the upper parallelograms of Figures 2 and 3 can result from either microbiologically intermediated or microbiologically induced corrosion. Corrosion conditions in the lower parallelograms are specific for microbiologically induced corrosion. Formation of minerals stable only in the lower parallelogram during corrosion is an indicator that microbiologically induced corrosion has taken place.

BIOGENIC PRODUCTION OF SULFIDES

Conversion of metals to sulfides by SRB has been studied since the late 1800s.[3,4] Attention has been paid to the mechanisms for the formation of sulfide ores. There is a substantial literature addressing the formation of metal sulfides under near-surface conditions (termed supergene sulfides) and the relationship between formation processes and mineral morphology. Baas-Becking and Moore[5] list the sulfides produced with the SRB *Desulfovibrio desulfuricans*, over a large pH range. They produced mackinawite (tetragonal FeS_{1-x}) from iron and iron oxides. Neither pyrite nor marcasite (both FeS_2) were prepared. More recent

work[6] indicates that on continued exposure to SRB the mackinawite alters to greigite (Fe_3S_4) and smythite (Fe_9S_{11}) and finally to pyrrhotite (FeS_{1+x}). SRB in thin biofilms on the surfaces of pottery[7] and silver[8] can produce pyrite films. Framboidal pyrite has been produced microbiologically by reacting mackinawite with elemental sulfur.[9] There is no evidence for the formation of marcasite in the biosphere (microbiologically or otherwise). Abiotic aqueous synthesis of these minerals, with the possible exception of pyrite, requires H_2S pressures higher than those found in the biosphere. Figure 2 (drawn for clarity with pyrite and mackinawite as the only sulfides) shows that the region of stability for pyrite is accessible under severe biosphere conditions. The region of stability of mackinawite is wholly outside the region of normal biosphere conditions, and its presence in corrosion products generally is proof that the corrosion was SRB-induced.

Digenite (Cu_5S_9), chalcocite (Cu_2S), and covellite (CuS) have been produced by SRB-induced corrosion of copper.[5] Field experience[10] and laboratory experiments[11,12] confirm these minerals as products of SRB-induced corrosion of copper and high-copper alloys. In addition, Macdonald et al.[12] report djurleite ($Cu_{1.96}S$). Djurleite has been identified in the corrosion products of copper alloys in MIC experiments and in archaeological situations though it has never been produced in experiments with pure Cu and abiotic NaCl solutions. Baas-Becking and Moore[5] identified only the low-temperature monoclinic polymorph of chalcocite in their SRB experiments. Other experiments have produced the hexagonal polymorph, which is thermodynamically stable between 103°C and 435°C. In this paper, monoclinic chalcocite will be termed low chalcocite and hexagonal chalcocite will be termed high chalcocite. The simplexity principle[13] states that precipitation of minerals in an environment rich in impurity atoms likely to substitute for atoms of the cation of primary interest leads to preferential precipitation of high-temperature polymorphs with looser structures.

Djurleite is important in SRB-induced corrosion of copper alloys because it reportedly forms a protective sulfide film[10] and because it is difficult to synthesize abiotically at room temperature.[14] Chalcocite is the most characteristic corrosion product in SRB-induced corrosion of copper. Baas-Becking and Moore[5] claim that chalcocite cannot be formed abiotically at room temperature. They further maintain that microbiological formation of chalcocite is as an alteration product of digenite, which they regard as the first product of SRB-induced corrosion

of copper alloys. Phase transformations between chalcocite and digenite have been studied extensively.[14,15,16,17] A study of the kinetics of transformations during dry corrosion has been published.[18] The valence state of Cu in all these minerals is +1[19] though some earlier workers assumed it to be +2.

The effect of SRB for molybdenum alloys is not simply to move conditions from one part of a stability diagram to another but rather to accelerate corrosion directly.[20] SRB in contact with silver produces acanthite (monoclinic Ag_2S).[6] The SRB-influenced production of Cu-containing argentite (cubic Ag_2S) is a complex issue, not fully resolved.[21] SRB-induced corrosion of zinc produces a zinc sulfide conjectured to be sphalerite (ZnS)[6]. SRB attack on lead carbonates produces galena (PbS).[6] Galena has been found more recently as a lead corrosion product in SRB-induced corrosion of Pb-Sn alloys.[7]

Baas-Becking and Moore[5] were unsuccessful in preparing bornite (Cu_5FeS_4) and chalcopyrite ($CuFeS_2$) by adding SRB to mildly basic solutions containing hematite (Fe_2O_3) or lepidocrocite (FeOOH) with oxidized copper minerals because experimental conditions limited transport of iron ions to reaction sites. Chalcopyrite is a common corrosion product for copper objects undergoing SRB-induced corrosion in the presence of iron-rich groundwaters over archaeological time.[3,4,8] The formation of bornite and chalcopyrite in abiotic laboratory corrosion experiments on copper in high-sulfide waters has been shown,[22] but neither compound has been formed in quantity in nonarcheological time periods.

Despite extensive work on sulfide biogeochemistry in recent years, the question of how SRB control corrosion processes remains unanswered.[23] The purpose of the following investigation was to determine mineralogical fingerprints in corrosion products which permit unequivocal identification of SRB-induced MIC.

METHOD AND MATERIALS

Sampling and Maintenance of Cultures

The SRB used in the following experiments were isolated, characterized, and maintained at the Naval Surface Warfare Center. The enrichment medium used to isolate and maintain the mixed, microbial

cultures contained lactate as the electron donor and carbon source for growth.[24] The medium was supplemented with 2.5% (wt/vol) NaCl for enrichment of marine microbes. All cultures were grown anaerobically at room temperature in sealed bottles.

Table 1 shows where the mixed, microbial cultures (obligate and faculatitative anaerobes; SRB and non-sulfate reducers) were originally isolated. Culture I-V were obtained by aseptically scraping 3" x 3" corrosion coupons in a constant immersion flume tank at NAVSWC/Ft. Lauderdale, FL. Culture VI was obtained from fouling deposits in a sea chest (seawater piping system) of a surface ship at Long Beach Naval Station in Long Beach, CA. Culture VII was isolated from moisture trapped under the cargo ramp of a C-130 transport plane. This aircraft was at the Naval Aviation Depot (NADEP) at Cherry Point, NC for corrosion maintenance and the ramp area showed signs of blistering and/or peeling of the protective epoxy/polyurethane coatings. Cultures I-VII were used to inoculate 99Cu, 90Cu:10Ni,and 70Cu:30 Ni 1 cm^2 metal coupons for 4 to 5 months. Cells were fed every 7-10 days.

Initial Characterization of SRB From the Mixed Communities

The salt tolerance test for the SRB pure cultures used Postgate medium B with NaCl added in 0.5% increments (range tested was 0% to 4% NaCl). KCl substitution for NaCl was also used. SRB colony types were tested using the desulfoviridin test.[25] One milliliter of each culture was pelleted in 1.5 ml microfuge tubes, suspended in 100 microliters of growth medium. Cells were lysed by added 50 microliters of 2N NaOH. The tubes were vortexed and the lysate was immediately viewed under longwave UV irradiation (365nm). A red fluorescence indicates the presence of the desulfoviridin pigment and is evidence for the presence of *Desulfuvibrio.*

Single colonies of each SRB were streaked onto Postgate medium B plates supplemented with the following antibiotics: ampicillin, 50 micrograms/ml; tetracycline, 15 micrograms/ml; kanamycin, 50 micrograms/ml; streptomycin, 25 micrograms/ml; and chloramphenicol, 10 micrograms/ml. Growth within 2 days meant the SRB were resistant to that antibiotic. After 5 days, no growth was scored as sensitive to the antibiotic. Ampicillin was purchased from ICN Biochemicals (Cleveland, OH) and the other antibiotics were purchased from USB Corporation (Cleveland, OH).

Additional specimens of 99Cu, 90Cu10Ni, and 70Cu30Ni were placed in sealed flasks containing 100 ml. of estuarine water (less than 1% solids) from a salt marsh pond in St. Andrew's State Park, Bay County, FL., from the Gulf of Mexico at Bay St. Louis, MS., and from a fresh-water pond on the grounds of the Naval Coastal Systems Center, Panama City, FL. The waters were aerated before used to oxidize water-borne sulfides. Two percent Na_2SO_4 and 2% Argo brand corn-starch were added to the waters. A second series of metals were exposed to these naturally-occurring waters without any sulfate or carbon additions. These were termed nutrient-deprived. The pH values of the waters, measured after two weeks, were between 5.5 and 6.8. Tests were terminated after 150 days.

At the end of the exposure periods, surface topography and chemistry were documented using an Electroscan Model E-30 environmental scanning electron microscope and a Tracor Northern Model 5502 energy dispersive x-ray spectrometer (ESEM/EDAX). Coupons were removed from the culture medium, washed through a series of salt water/distilled water washes and examined directly from distilled water.

Minerals within the corrosion products were identified by X-crystallography at the Naval Coastal Systems Center. Coupons were removed from the culture media and washed in acetone. Corrosion products were scraped onto two-sided tape, mounted on a slide and placed in a Phillips Model x-ray diffraction apparatus and the diffraction pattern scanned from 10°to 90° using copper kα radiation. X-ray diffraction patterns were also measured on other corrosion products ground in a corundum (Al_2O_3) mortar and left for several hours in a dessicator before measurement. The mortar-ground specimens gave the same results as duplicate specimens scraped directly onto slides.

RESULTS AND DISCUSSION

Initial Characterizations of SRB From the Mixed Communities

SRB are found in natural water of all salinities from near zero to saturation. Above 2% NaCl the population is almost always *Desulfovibrio*. Most SRB obtained from the marine environment (cultures I-VI in table 2) have an absolute requirement for 0.5% or greater concentration of NaCl. There were SRB from cultures II and IV that had an absolute requirement for 1.0% or greater concentrations of NaCl. The SRB grew equally well in NaCl concentrations from 1.0 to 4.0%. KCl did not substitute for NaCl for any of the sulfate reducers. From culture VII (non-marine environment),

pure cultures of SRB were obtained that grew on 0% NaCl but grew equally well on seawater concentrations of NaCl (facultative halophile).

From some of the mixed communities, differences in SRB colonies and cell morphologies suggested that different strains and/or species of lactate-utilizing SRB were isolated. Many of the pure culture SRB isolates from mixed cultures I-VII (marine and non-marine) were desulfoviridin-positive. From the desulfoviridin test and salt tolerances, it appears likely that these pure cultures are *Desulfovibrio*. From the non-marine culture (VII, SRB were obtained that showed no fluorescence (desulfoviridin-negative). Further characterization of the SRB (in pure and mixed cultures) will involve the use of fluorescent 16s rRNA probes for SRB. Some of the SRB will be identified using gas chromatography on total fatty acid composition by Microbial ID, Inc. (Newark, DE) or by an in-depth study of the physiology, metabolism, total fatty acid composition and growth optimization by ATCC (Rockville, MD).

For genetic manipulation of SRB, a knowledge of the antibiotic resistances of the bacterial isolates is an important first step. Table 2 shows some of the SRB pure cultures and their resistance/sensitivity to five antibiotics commonly used in microbial genetics studies. Results for the desulfoviridin test is also shown in this table.

Surface Topography and Chemistry

All copper-containing metals exposed to SRB in isolated cultures and in the natural augmented waters were covered with black sulfur-rich deposits (Figure 4). The thickness and tenacity of the surface deposits varied among the metals and cultures. Corrosion products on 99Cu were consistently nonadherent and in some cases sloughed from the surface in the growth medium (Figure 5). Corrosion products on copper alloys were more adherent and in some cases difficult to scrape from the surface. In all cases, bacteria were closely associated with the sulfur-rich deposits (Figure 6). Figure 7 is a typical EDAX spectrum collected from the surface of 99Cu colonized by culture IV. The metal surface under the bacteria was enriched in sulfur and iron (Figure 8). Many of the bacteria were encrusted with deposits of copper sulfides (Figure 9). The corrosion resulting from the SRB will be characterized elsewhere.

Mineralogy

Table 3 lists major corrosion products identified by x-ray crystallography. Blanks and "nutrient-deprived" tests showed no sulfide corrosion products.

Traces of covellite were present in tests using bacterial culture II on 90Cu:10Ni. SRB are known to produce covellite during corrosion of Cu alloys[10-12] and it has been produced in by SRB in laboratory tests.[5] The limited occurrence of covellite in these tests can be rationalized by observing that the formation of covellite in near-neutral solutions requires a high concentration of reduced sulfur. The stability diagram similar to Figure 3 but for total reduced sulfur 10^{-6} M shows a small wedge of covellite stability under acidic conditions. The formation of covellite at pH=4 or greater requires a high local concentration of reduced sulfide.. Such concentrations can be maintained within a biofilm by providing large amounts of reducing, sulfate-rich waters to the biofilm or by limiting the reactions which consume sulfide in the biofilm. In the laboratory synthesis of covellite[5] finely divided copper was produced by in-situ reduction of a copper mineral and then exposed to a sulfate-rich environment containing SRB with limited metal availability. In the experiments described in this paper the mass of the copper specimens was far in excess of any reasonable estimate of the mass of sulfide produced. To maintain adequate levels of sulfide activity at the coupon surface it is necessary to provide a continuous supply of water with a high sulfate content to the microorganisms in the biofilm or to allow sulfide buildup over long periods of time. Covellite is frequently reported in in-service situations in severely polluted waters, in laboratory experiments where continuously renewed harbor waters were used,[11,12] and in archaeological situations. In our experiments the waters were either not renewed at all or renewed on a 10 day cycle.

The results of our corrosion tests confirm that all SRB-induced corrosion of copper and its alloys produce chalcocite. In the absence of oxygenated seawater the sulfide corrosion products (chalcocite or other) are not intergrown with either hydroxychlorides such as paratacamite ($Cu_2(OH)_3Cl$) or cuprite (Cu_2O). In these experiments, as in experiments conducted with polluted seawater[26] both the high-temperature and the low-temperature forms of chalcocite are formed. The high temperature form of chalcocite has not been reported in any abiotic corrosion experiment on a copper alloy.

Digenite was found occasionally in our samples (Table 3). Digenite has never been observed in an abiotic corrosion experiment. Digenite may

be a major component of corrosion products lasting for only a few days, since it is thought to be a precursor to chalcocite.[5]

The strongly adherent corrosion products contained major amounts of djurleite. The prevalence of djurleite in corrosion products on copper-nickel alloys, and its close correlation with adherent corrosion product films, are both of importance. Djurleite has never been observed as a product of abiotic corrosion, and it is a difficult mineral to prepare. The existing data support the argument that djurleite is a mineralogical fingerprint for SRB-induced MIC.. Corrosion products composed principally of djurleite are observed in the corrosion of copper alloys, not of pure copper. Djurleite formation may be promoted by nickel in the same way digenite formation is promoted by iron.[17] The superior adherence of corrosion products containing djurleite as a major component, and the observation that djurleite can form protective coatings on copper alloys suggest that stabilization of djurleite may be a factor in the superior corrosion resistance of copper-nickel alloys to copper in sulfiding corrosion situations in general.

CONCLUSIONS

Djurleite and the high temperature polymorph of chalcocite may be mineralogical fingerprints for the SRB induced corrosion of copper-nickel alloys.

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Figure 1. Thermodynamic Stability Diagram for Ag in Seawater, with Parallelograms Bounding Biosphere Conditions.

Figure 2. Thermodynamic Stability Diagram for Iron in Fresh Water: Total Reduced Sulfide = 10^{-2}M, Total Dissolved Iron = 10^{-6}M with Parallelograms Bounding Biosphere Conditions.

Figure 3. Thermodynamic Stability Diagram for Copper in Fresh Water: Total Reduced Sulfide = 10^{-2}M, Parallelograms Bounding Biosphere Conditions.

Figure 4. Deposits on 99Cu after four months exposure to cultures I, II, and III.

Figure 5. Surface of 99Cu after four months exposure to culture VI. Corrosion products have sloughed from surface revealing pitting.

Figure 6. Bacteria associated with corrosion products.

a. Culture I
b. Culture II
c. Culture III
d. Culture V

Figure 7. EDAX Spectrum of 99Cu Colonized by Culture IV.

Figure 8. EDAX Spectrum of the 99Cu Metal Surface under Culture IV.

Figure 9. Encrustations of Copper Sulfide along Bacterial Cell.

Figure 10. Stability Diagram for Copper in Fresh Water

Table 1. Summary of Mixed Microbial Cultures Originally Isolated from Corroding Naval Materials in Marine and Non-Marine Environments

CULTURE	METAL	PRIMER	TOPCOAT
I	4140 STEEL	5 STEP IRON PHOSPHATE	NONE
II	4140 STEEL	5 STEP IRON PHOSPHATE	EPOXY
III	4140 STEEL	ZINC	NONE
IV	4140 STEEL	IVD-ALUMINUM	NYLON
V	4140 STEEL	5 STEP IRON PHOSPHATE	NONE
VI	CARBON STEEL	PROPRIETARY	PROPRIETARY
VII	ALUMINUM ALLOY	EPOXY	POLYURETHANE

Table 2. Antibiotic and Desulfoviiridin Screens on Pure Cultures of Marine and Non-Marine Sulfate Reducing Bacteria

CULTURE	Amp[a]	Tet[b]	Kan[c]	Str[d]	Chl[a]	Dsulfoviridin[f]
I	+	+	-	-	-	+
II	+	+	-	-	-	+
III	+	+	-	-	-	+
IV	+	+	+		-	+
V-#1	+	+	+	-	-	+
V-#2	+	+	-	-	-	+
VI	+	-	-	-	-	+
VIIg						
+NaCl #1	+	+	-	+	-	+
+NaCl #2	+	-	-	-	-	+
-NaCl #1	N.D.[h]	N.D.	-	-	-	-
-NaCl #2	N.D.	N.D.	-	+	-	+

[a] Amp, 50 micrograms ampicillin/ml.

[b] Tet, 15 micrograms tetracycline/ml.

[c] Kan, 50 micrograms kanamycin/ml.

[d] Str, 25 micrograms streptomycin/ml.

[e] Chl, 10 micrograms chloramphenicol/ml.

[f] The desulfoviridin test is described in the materials and methods section of this report. +, desulfoviridin-positive result and is evidence for the isolate being *Desulfovibria*; - , desulfoviridin-negative isolate.

[g] + NaCl, SRB isolates that require 0.5% or geater concentrations of NaCl but these isolates also grew without any NaCl added to the medium.

[h] N.D., Not determined

Table 3. Minerals in Corrosion Products

	Bacterial Cultures							Augmented Natural Waters		
	I		III	IV	V	VI	VII	Gulf of Mexico	Lake Water	Salt Marsh
99Cu		Low-Chalcocite Digenite Djurleite*		Low-Chalcocite Digenite* Anilite		Low Chalcocite High Chalcocite*		Low-Chalcocite	Low-Chalcocite	Low-Chalcocite
90Cu 10Ni		Low Chalcocite High Chalcocite Covellite*		Low Chalcocite High Chalcocite Djurleite*			Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*	Low-Chalcocite High Chalcocite Djurleite Digenite*
70Cu 30Ni						Low Chalcocite Djurleite*	Low Chalcocite Djurleite*			

Formulae

Low Chalcocite	Cu_2S
High Chalcocite	Cu_2S
Digenite	Cu_9S_5
Djurleite	$Cu_{1.93}S$-$Cu_{1.97}S$
Anilite	Cu_7S_5
Covellite	CuS

* low concentration

Blanks indicate work that has not been completed

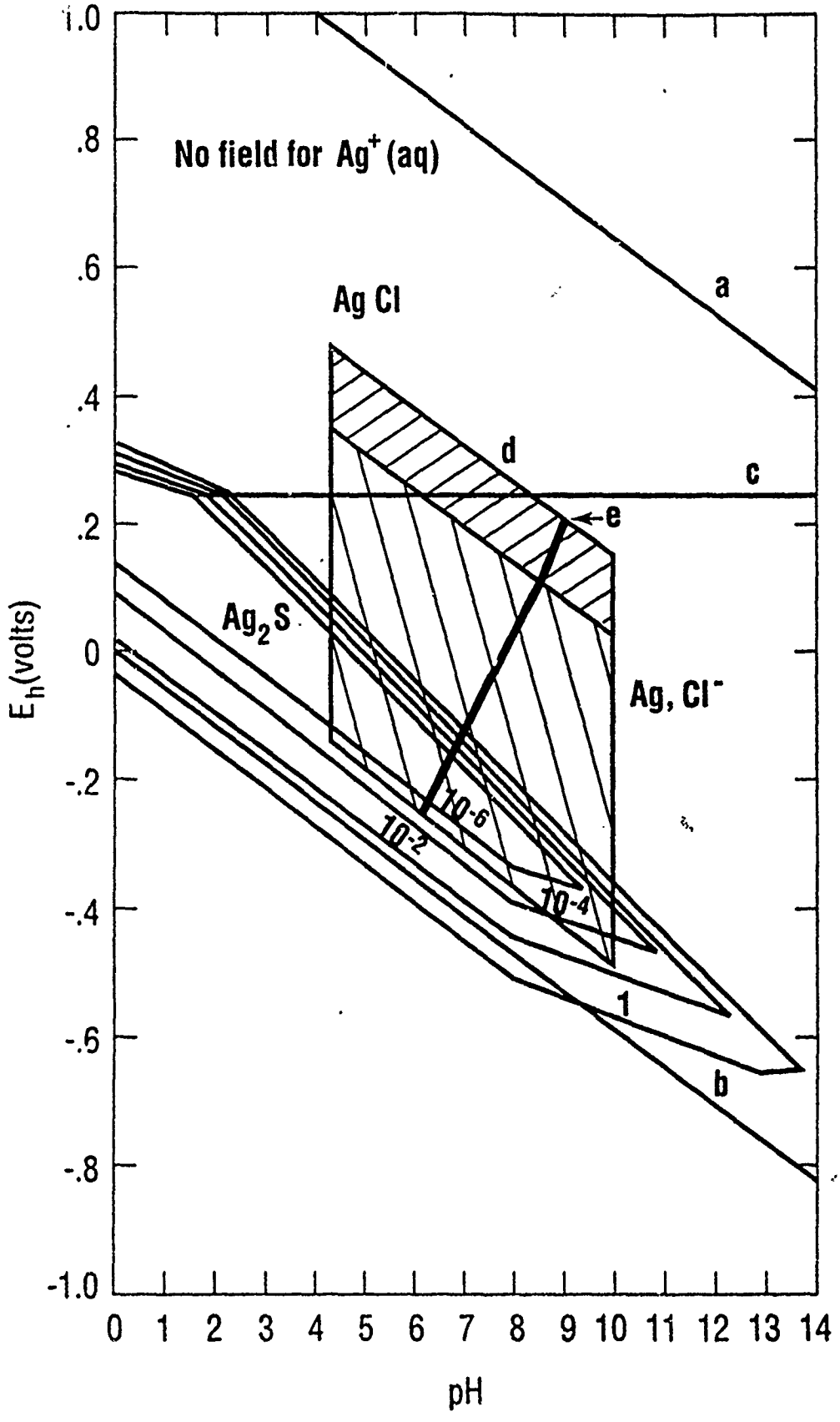

No field for Ag^+ (aq)
Ag Cl
a
d
c
e
Ag_2S
Ag, Cl^-
10^{-6}
10^{-2}
10^{-4}
1
b
E_h(volts)
1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH

FIGURE 1

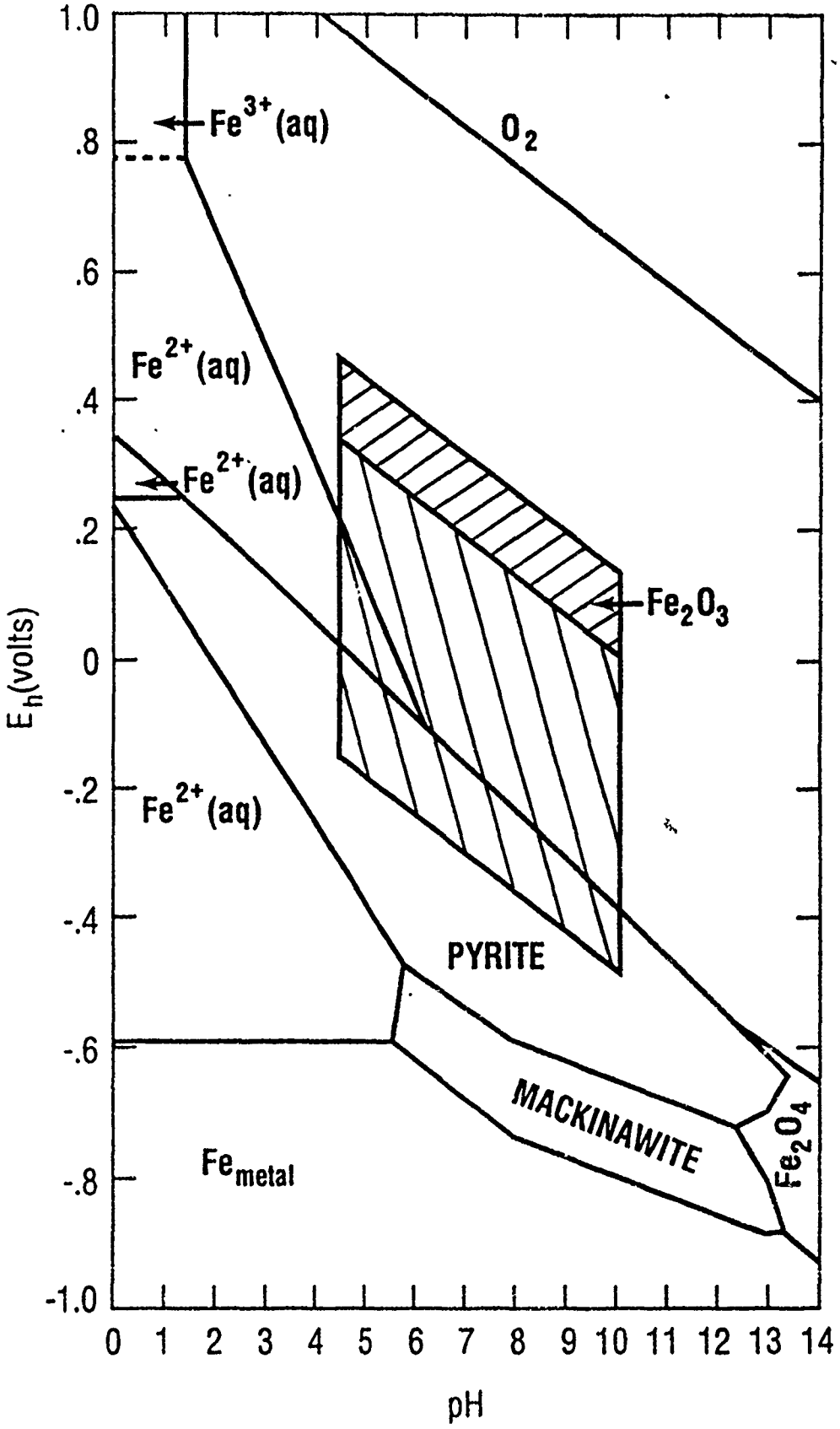

1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1.0
E_h(volts)
Fe^{3+}(aq)
O_2
Fe^{2+}(aq)
Fe^{2+}(aq)
Fe^{2+}(aq)
Fe_2O_3
PYRITE
MACKINAWITE
Fe_3O_4
Fe_{metal}
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH

FIGURE 2

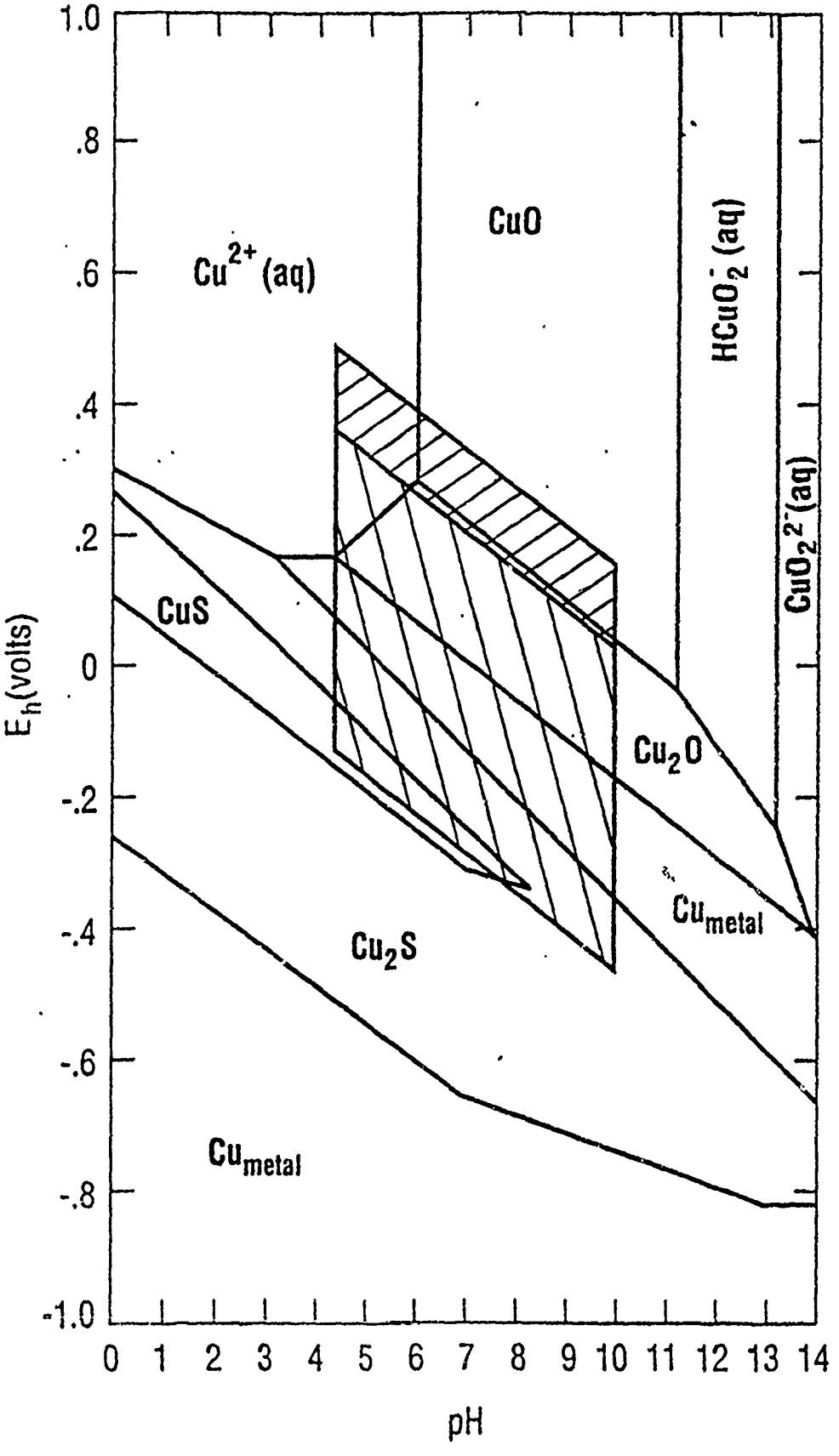

1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1.0
E_h(volts)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
pH
Cu^{2+}(aq)
CuO
$HCuO_2^-$(aq)
CuO_2^{2-}(aq)
CuS
Cu_2O
Cu_{metal}
Cu_2S
Cu_{metal}

FIGURE 3

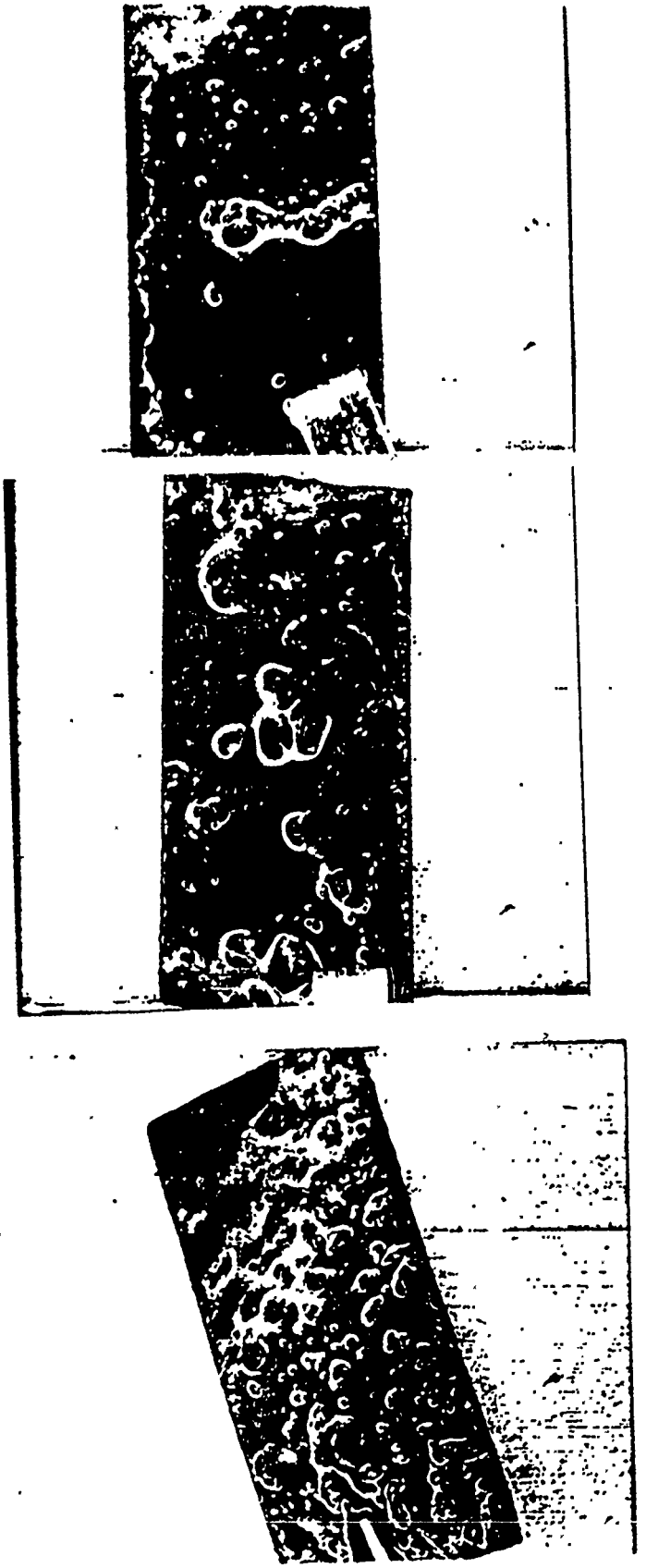
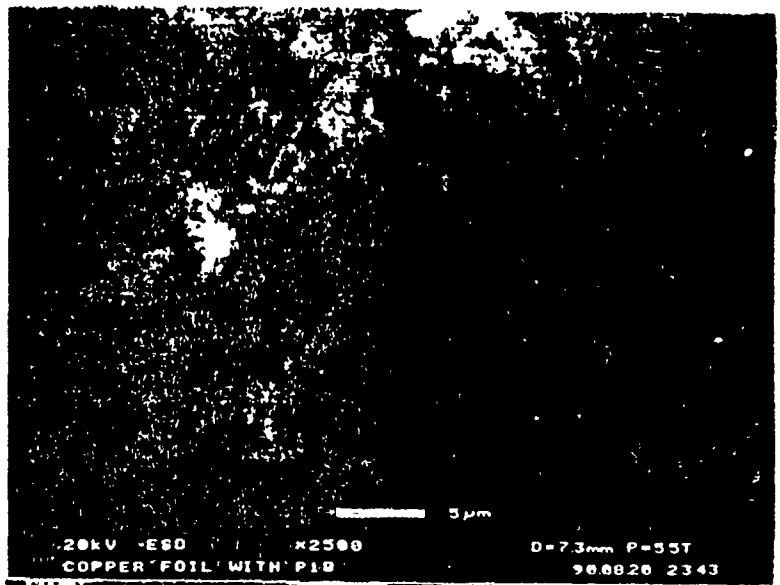
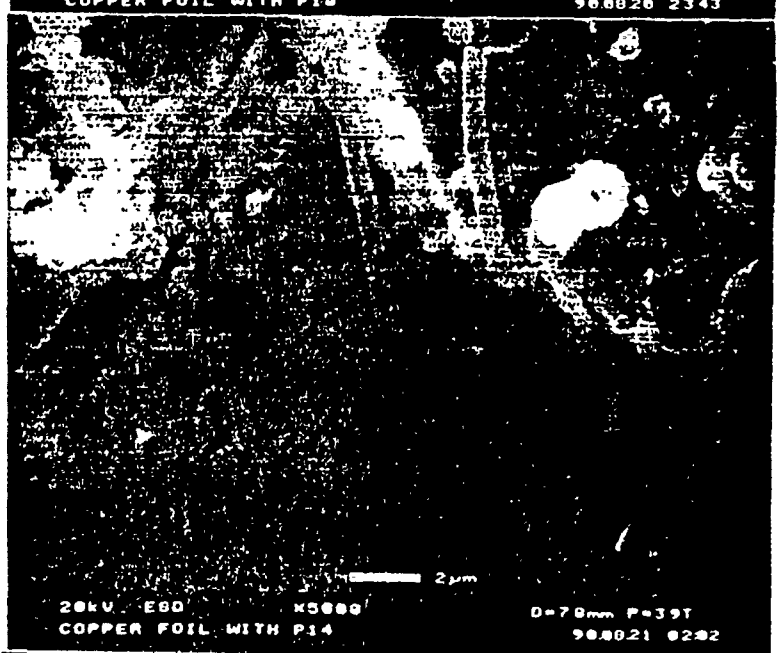


Figure 4

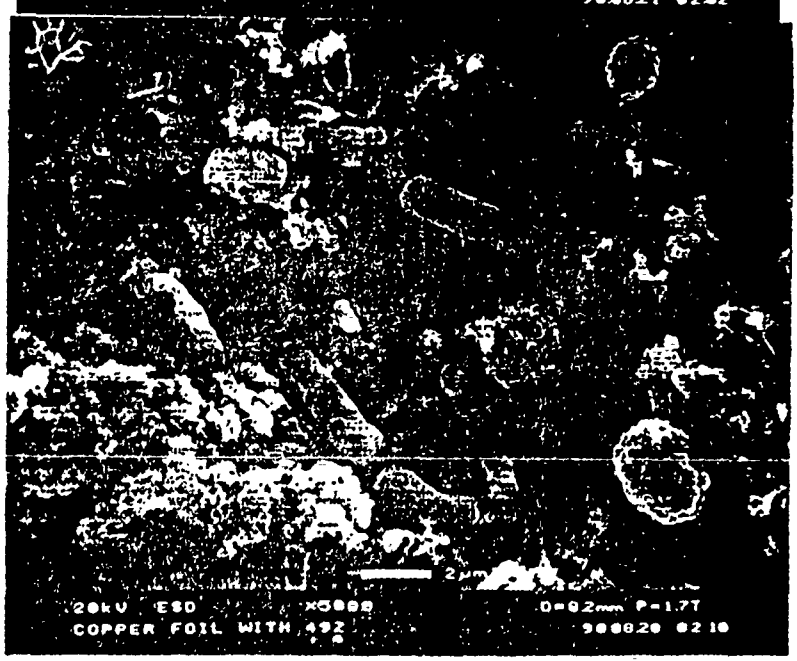
a


5μm
20kV ESD ×2500 D=7.3mm P=55T
COPPER FOIL WITH P18 90.08.26 23:43

b

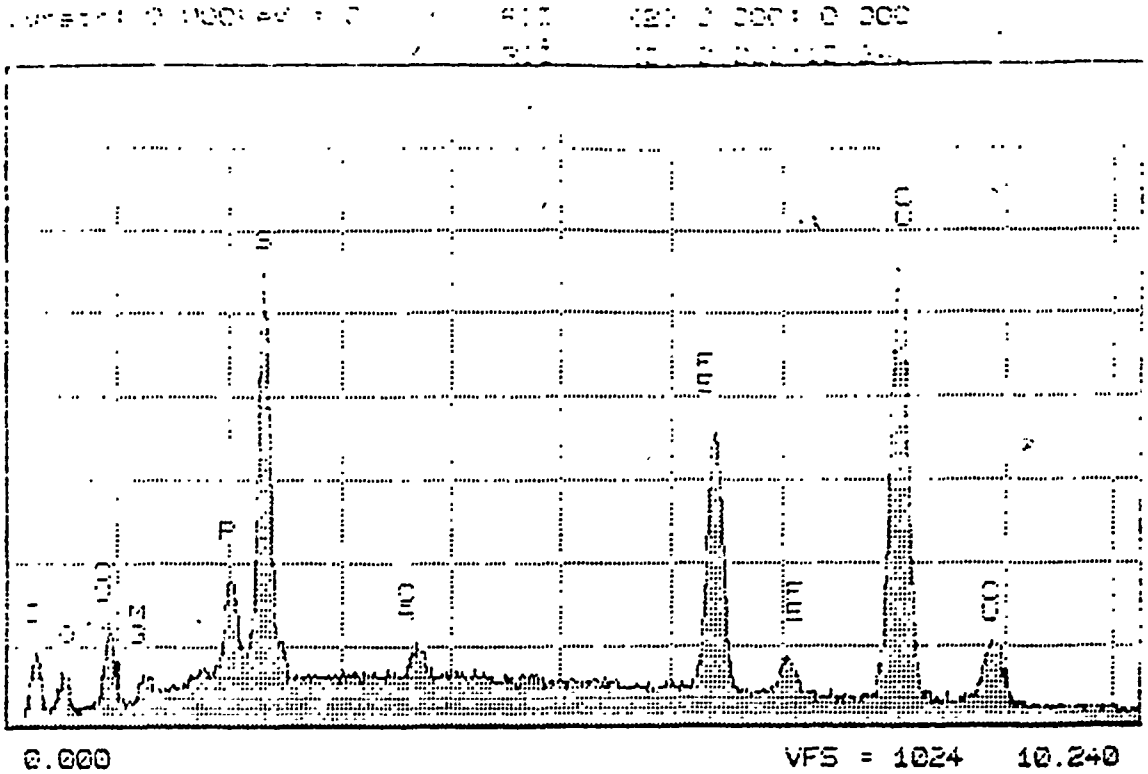

2μm
20kV ESD ×5000 D=7.8mm P=39T
COPPER FOIL WITH P14 90.08.21 02:02

c


2μm
20kV ESD ×5000 D=8.2mm P=1.7T
COPPER FOIL WITH 492 90.08.26 02:10

d


5μm
20kV ESD ×4950 D=7.8mm P=23T
CU FOIL <DUAL COLOR> WITH P31 90081I 13:18



100 COPPER FOIL WITH I14 FLAT TOP LAYER

SO: QUANTIFY

COPPER FOIL WITH I14 FLAT TOP LAYER
Standardless Analysis
20.0 KV 62.0 Degrees

Chi-sqd = 1.02

Element	Rel. K-ratio	Net Counts
Cu-L	0.01801 +/- 0.00113	1214 +/- 76
Mg-K	0.00345 +/- 0.00093	333 +/- 90
P -K	0.02056 +/- 0.00203	2204 +/- 218
S -K	0.09776 +/- 0.00284	9663 +/- 281
Ca-K	0.01003 +/- 0.00198	822 +/- 162
Fe-K	0.19403 +/- 0.00568	7521 +/- 220
Cu-K	0.65616 +/- 0.01292	14625 +/- 288

ZAF Correction 20.00 kV 61.96 deg
No.of Iterations = 3

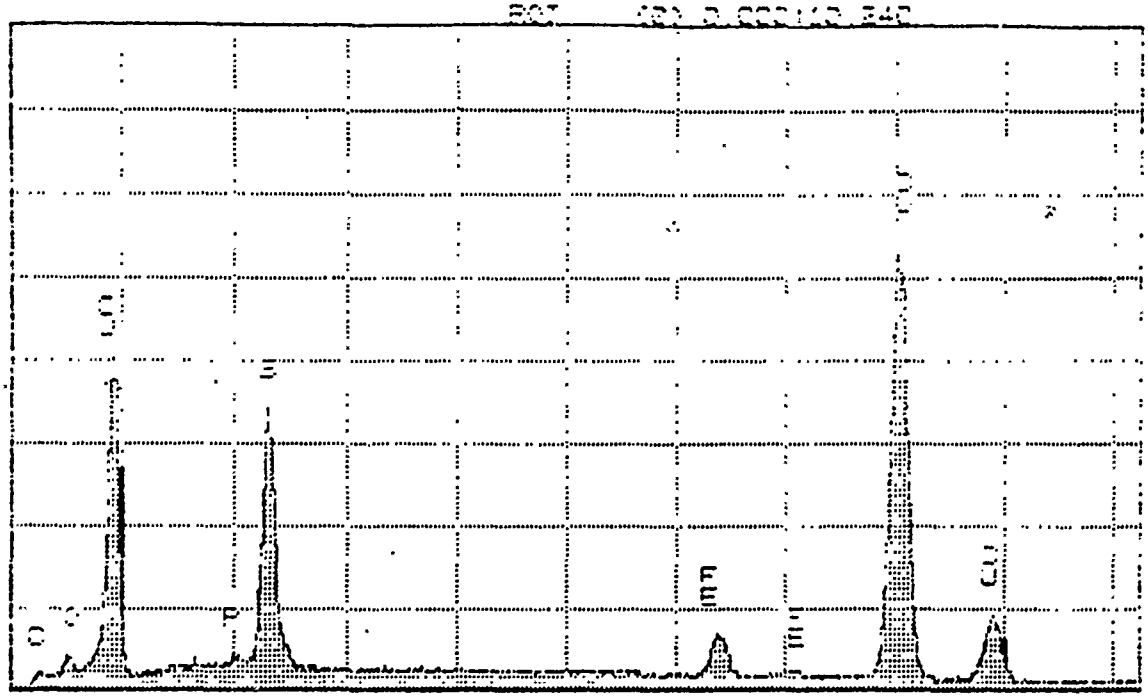
Element	K-ratio	Z	A	F	Atom%	Wt%
Mg-K	0.003	0.909	3.484	0.999	2.31	1.05
P -K	0.020	0.938	1.586	0.994	5.03	2.93
S -K	0.094	0.913	1.407	0.998	20.06	12.10
Ca-K	0.010	0.919	1.109	0.965	1.29	0.97
Fe-K	0.187	1.002	1.011	0.884	15.95	16.76
Cu-K	0.633	1.031	1.014	1.000	55.37	66.18
					Total=	100.00%

...: SETUP DEFINITIONS

University of Southern Mississippi TUE 21-AUG-90 08:48

Cursor: 0.000keV = 0 ROI (2) 0.000:0.000

ROI (3) 0.000:10.240



0.000 VFS = 2048 10.240

100 COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER

SO: QUANTIFY

COPPER FOIL WITH I14 GRANULAR BOTTOM LAYER
Standardless Analysis
20.0 kV 62.0 Degrees

Chi-sqd = 1.16

Element	Rel. K-ratio	Net Counts
Cu-L	0.09590 +/- 0.00160	10367 +/- 173
O -K	0.00259 +/- 0.00111	446 +/- 190
P -K	0.07927 +/- 0.00179	12581 +/- 283
Fe-K	0.04034 +/- 0.00261	2508 +/- 162
Cu-K	0.78179 +/- 0.00968	27941 +/- 346

ZAF Correction 20.00 kV 61.96 deg
No.of Iterations = 3

Element	K-ratio	Z	A	F	Atom%	Wt%
O -K	0.003	0.929	1.650	0.995	0.77	0.47
P -K	0.085	0.905	1.430	1.000	19.38	19.42
Fe-K	0.042	0.991	1.011	0.010	3.59	3.52
Cu-K	0.802	1.019	1.004	1.000	76.26	85.14
					Total=	100.00%

SO: SETUP DEFINITIONS

Sample 8

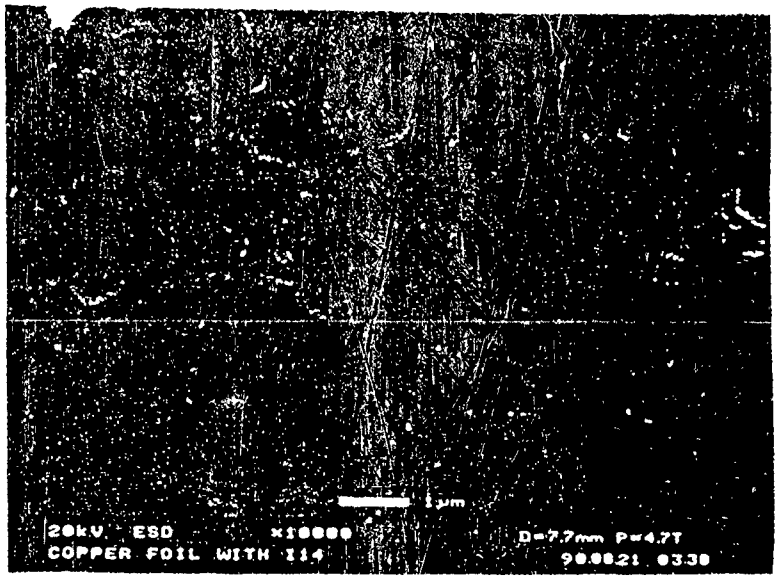

1μm
20kV ESD ×10000 D=7.7mm P=4.7T
COPPER FOIL WITH 114
90.08.21 03:38

Fig. 9