RATES OF REACTION OF COVELLITE AND BLAUBLEIBENDER COVELLITE WITH FERRIC IRON AT PH 2.0

by

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Covellite (CuS), a copper sulfide whose brilliant blue color makes it one of the most easily recognized of all minerals, is a common secondary mineral in the enriched zones of copper-bearing ore deposits. Long believed to be one mineral species, megascopically blue covellite was found by Ramdohr (1969) to include at least one additional, similar compound. He found that some covellites did not display the characteristic deep red-orange anisotropic color when viewed in reflected light, in oil immersion, but instead remained blue; these were called blaubleibender or blue-remaining covellites. Goble (1980) finally sorted out the mineral nomenclature when he defined the chemistry and crystal structure of the two blue-remaining covellites, yarrowite and spionkopite. These minerals have been found in frequent association with normal covellite in the enriched zones of many copper-bearing deposits; in spite of these occurrences the blaubleibender covellite phases are generally believed to be metastable phases in the Cu-S system (Moh 1971, Rickard 1972 and 1973, Potter 1977, and Goble 1980). Covellite and blaubleibender covellites apparently form during second cycle enrichment in copper deposits by the oxidation and successive leaching of copper from more copper rich phases in the primary enrichment blanket, such as digenite and chalcocite (Frenzel, 1959 and 1961).

The purpose of this study was to measure the rates of oxidation of covellite and blaubleibender covellite by Fe^{3+} at pH 2 in a batch reactor system. The data should prove useful for understanding the

geochemical processes involved in second-cycle weathering of enriched zones. This information can be helpful in exploration for copper deposits. Chaffee (1982a,b) discusses the geochemistry of copper deposits and techniques of prospecting for them. Also ferric ion leaching is playing an increasingly important role in hydrometallurgy (Dutrizac and MacDonald 1974a), where in many cases it can be an economic alternative to pyrometallurgy. This study contributes to a better understanding of the chemistry of ferric ion leaching of sulfide minerals.

Second-cycle enrichment

The first cycle of enrichment (Figure 1a) is dominated by the oxidation of iron sulfides. Pyrite is commonly the most abundant mineral in of porphyry copper deposits, (Titley 1982). Upon exposure, pyrite oxidizes according to the overall reaction:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4H^+ + 4SO_4^{-2} \quad (1)$$

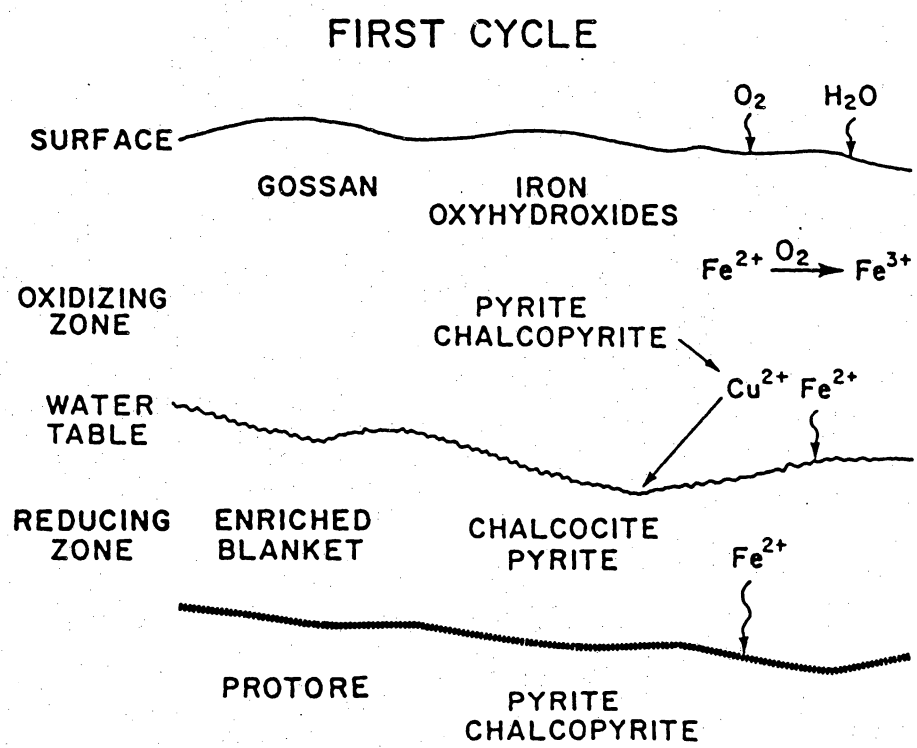
This reaction sustains the weathering process by generating sulfuric acid which lowers the ground water pH, (Anderson 1955, and Anderson 1982). Subsequent oxidation of ferrous iron to ferric iron is catalyzed by ferrooxidians bacteria (Brierley and Brierley 1981):

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{3+} + H_2O \quad (2)$$

Much of the Fe^{3+} reacts with more pyrite (Wiersma and Rimstidt 1984) to generate more Fe^{2+} and sulfuric acid, while the remainder reacts with other metal sulfides such as chalcopyrite to release other metals to solution:

$$CuFeS + 16\ Fe^{3+} + 8H_2O = Cu^{2+} + 17Fe^{2+} + 2SO_4^{-2} + 16H^+ \quad (3)$$

FIG 1a. Diagram of the second cycle of weathering and enrichment of copper-bearing ore deposits.


FIRST CYCLE
O_2
H_2O
SURFACE
GOSSAN
IRON OXYHYDROXIDES
$Fe^{2+} \xrightarrow{O_2} Fe^{3+}$
OXIDIZING ZONE
PYRITE CHALCOPYRITE
Cu^{2+} Fe^{2+}
WATER TABLE
REDUCING ZONE
ENRICHED BLANKET
CHALCOCITE PYRITE
Fe^{2+}
PROTORE
PYRITE CHALCOPYRITE

The copper released during this first enrichment cycle is transported to the reducing zone, below the water table, where it reacts with indigenous sulfides to form an enriched blanket. For example, the copper released in the oxidizing zone might react with chalcopyrite to produce chalcocite:

$$CuFeS + Cu^{2+} = Cu_2S + Fe^{2+} \quad (4)$$

This process may continue for considerable time accumulating large quantities of secondary minerals in the enrichment zone. At a later time, a lowering of water table due to a tectonic event, a lowering of the erosional base level, or the development of a more arid climate could expose the enriched blanket to the oxidizing conditions of the vadose zone (Figure 1b). The oxidation reactions result in successive leaching of Cu^{2+} from the copper-rich phases such as chalcocite to produce covellite, (Blain and Andrew, 1977; Anderson, 1955):

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \quad (5)$$

Chalcocite oxidation to covellite is a relatively rapid process compared to the subsequent oxidation of covellite to give elemental sulfur or sulfate (Dutrizac and MacDonald 1974a):

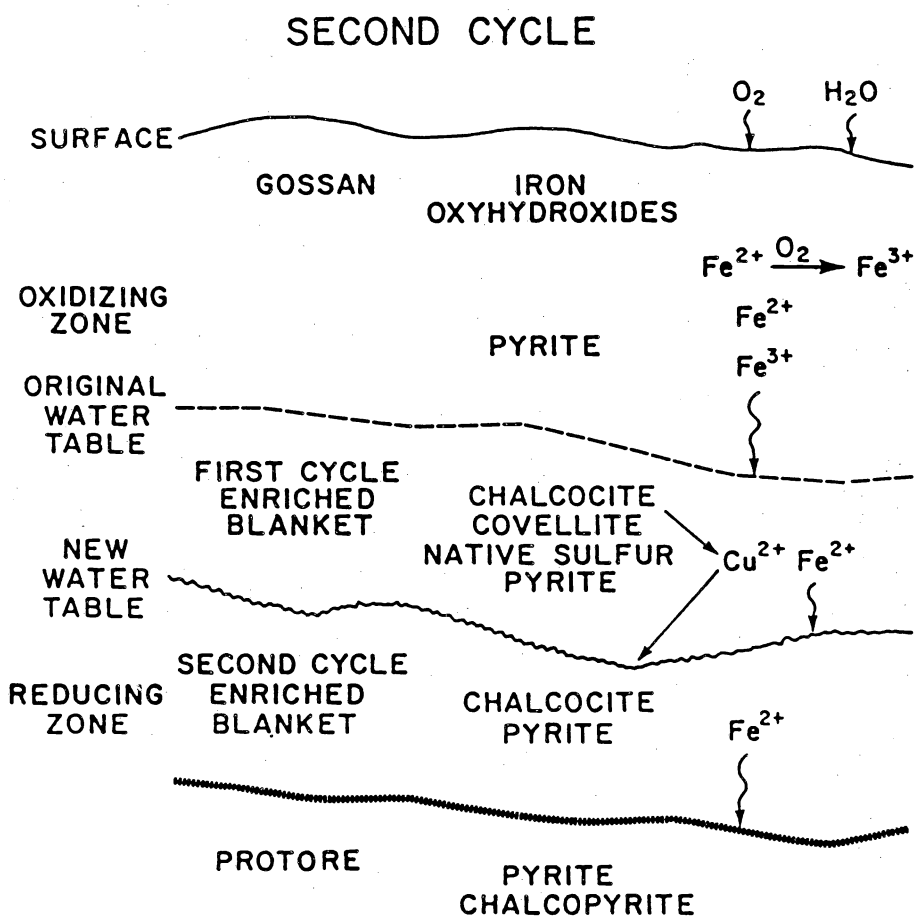
$$CuS + 2Fe^{3+} = 2Fe^{2+} + Cu^{2+} + S^{\circ} \quad (6)$$

and

$$CuS + 8Fe^{3+} + 4H_2O = 8Fe^{2+} + Cu^{2+} + SO_4^{-2} + 8H^{+} \quad (7)$$

Therefore, the oxidation of covellite appears to be the rate controlling step in the second-cycle leaching of copper from the enriched zones. The amount and composition of covellite present can indicate the rate of oxidation of the enriched ore, and perhaps, yield important information

FIG 1b. Diagram of the second cycle of weathering and enrichment of copper-bearing ore deposits.


SECOND CYCLE
O_2
H_2O
SURFACE
GOSSAN
IRON OXYHYDROXIDES
$Fe^{2+} \xrightarrow{O_2} Fe^{3+}$
OXIDIZING ZONE
Fe^{2+}
PYRITE
Fe^{3+}
ORIGINAL WATER TABLE
FIRST CYCLE ENRICHED BLANKET
CHALCOCITE
COVELLITE
NATIVE SULFUR
PYRITE
Cu^{2+}
Fe^{2+}
NEW WATER TABLE
SECOND CYCLE ENRICHED BLANKET
REDUCING ZONE
CHALCOCITE
PYRITE
Fe^{2+}
PROTORE
PYRITE
CHALCOPYRITE

about the rate of accumulation of the second-cycle enrichment zone. For a more detailed discussion of the weathering and enrichment of copper deposits see Emmons (1917), Blain and Andrew (1977), and Anderson (1982). Similar oxidation and reduction processes are responsible for the copper accumulation in redbed copper deposits, (Tourtelot and Vine, 1976; Beendsen and Lambert, 1981; and Lambert et al., 1981).

Previous studies

Numerous authors have studied the rate of oxidation of covellite with ferric ion. Dutrizac and MacDonald (1974a) have reviewed many of these studies. The reported activation energies range from 33 to 92 kJ mol^{-1} (8 to 22 kcal mol^{-1}) (see Table 1). This wide range of values suggests that the reaction of covellite with Fe^{3+} is not well defined by these studies. However, all of the studies reviewed report essentially first order kinetics where the rate is limited by a chemical reaction rather than by diffusion. Most authors feel that Cu^{2+} and S° are the dominant products of this reaction (see equation 6). However, Dutrizac and MacDonald (1974b) along with Thomas and Ingraham (1967) report the formation of minor amounts of sulfate along with elemental sulfur. The study by Thomas and Ingraham (1967) also showed an initial faster reaction rate. They suggest a dual mechanism for covellite dissolution over the temperature range of 25 to 80° C.

Thomas, et al. (1967) oxidized chalcocite and digenite with ferric sulfate to form blaubleibender covellite. They found that the blaubleibender covellite reacted with Fe^{3+} at an appreciable rate to give

Table 1. Activation energies from previous studies on covellite. The leaching solution was ferric sulfate (from the summary of other studies discussed in Dutrizac and MacDonald, 1974a).

Type of Material	Temp Range (°C)	Activation Energy kJ mol^{-1}
Synthetic	<60	92.0
	60-80	33.5
Natural Crystals	40-70	58.6
Synthetic Powder	30-90	83.7
Pure Synthetic; Natural Crystals	15-95	75.0
Nonstoichiometric CuS	20-80	104.6

both S^{o} and sulfate as products. The oxidation of the blaubleibender covellite had a higher activation energy than that reported for chalcocite and was chemically controlled.

EXPERIMENTAL

Blaubleibender covellite ($Cu_{1+x}S$), prepared according to the procedure given in Appendix I, and covellite (Fisher Scientific certified cupric sulfide, CuS) were used as run materials. The covellite material, already in powder form, was dry sieved to isolate the 100-200 mesh size fraction. A 1.2500 ± 0.0005 g sample of the sized material was acid etched according to steps 2 through 5 of the procedure outlined in Appendix I to remove any oxidized material from the surface of the grains. The remaining solids, 1.000 ± 0.001 g of covellite, or 0.900 ± 0.001 g of blaubleibender covellite were used as run material. The average composition of the blaubleibender covellite, $Cu_{1.3}S$, was determined by electron microprobe analysis.

These materials were examined by powder X-ray diffraction and in polished section with reflected light microscopy to determine their suitability for experiments. Refer to Berry (1954) for a discussion of the crystal structure of covellite. Goble (1980) reviews the crystal structure of the blaubleibender covellites and compares their optical properties to stoichiometric covellite. He also presents detailed X-ray data for covellite and the blaubleibender covellites.

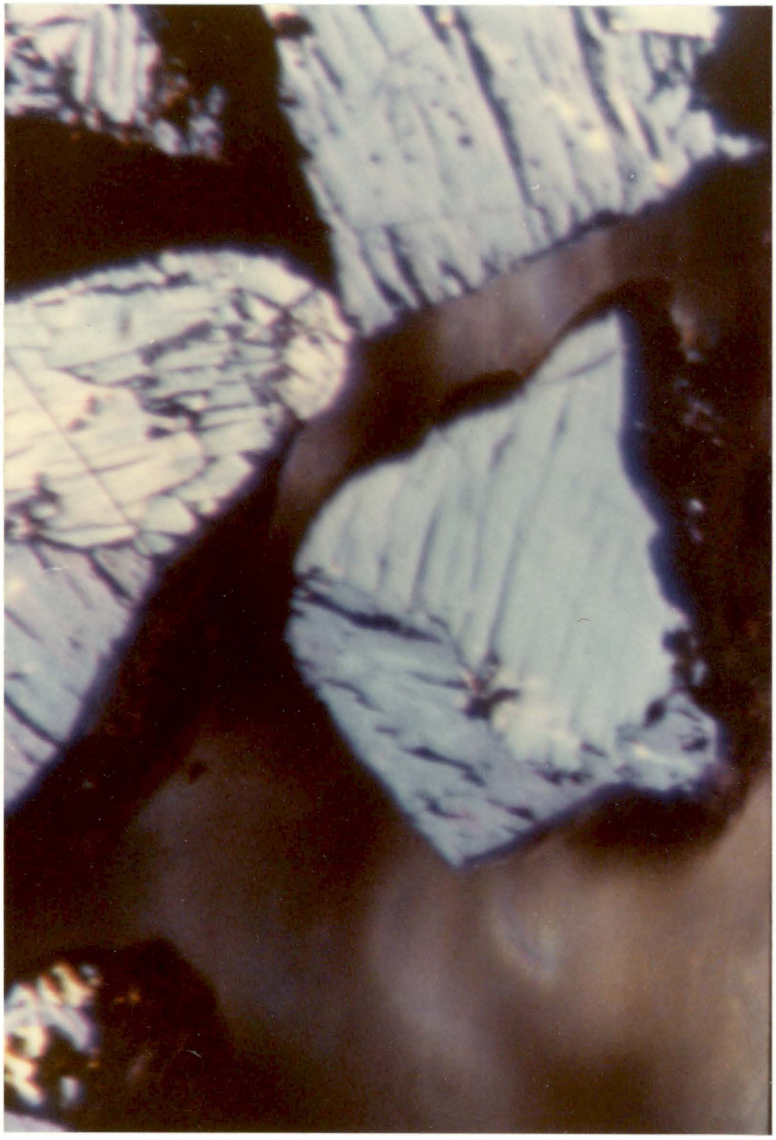
Run solutions were prepared fresh for each experiment by combining 0.25 ml of Fisher Scientific reagent solution $FeCl_3 \cdot 6H_2O$ with 1.0 liter distilled/deionized H_2O which had been acidified to pH 2.00± 0.02 with 1.5 ml concentrated HCl. The solution pH was checked preceding and following each run using a Model 811 ORION Research Microprocessor pH/millivolt meter, and a Fisher Scientific Micro-

Combination pH electrode. The initial and final pH values agreed within 0.06 pH units.

Spectrophotometric determinations for ferrous and total iron were carried out on all pre-run solutions using the 1,10 phenanthroline procedure of Harvey, et al. (1955) with minor modifications outlined by Wiersma (1982). Ferric ion concentrations were determined from the difference in the total iron and ferrous ion concentrations. Blaubleibender covellite run solutions were also assayed at the end of each run to determine if any iron had been leached from the minor amounts of chalcopyrite ($CuFeS_2$), present in the samples, (see Appendix I). All run solution extractions were filtered through 8 micron filter paper to separate run solids from the solution. No incease in the total iron concentration was detected for any of the blaubleibender covellite runs; the assay was sensitive to approximately 0.1 ppm. This indicates that less than 0.01 g of chalcopyrite dissolved for every 1.0 g of blaubleibender covellite dissolved during the course of the experiment. This was confirmed by examination of the post-run solids by reflected light microscopy, which showed no evidence that the chalcopyrite had reacted (see Plate 3).

Cupric ion and total copper concentrations were measured at various times during several of the experiments. Cupric ion concentrations were determined using an ORION Cupric electrode, Model 94-29. The ferric ion in the solution interfered with the function of the cupric electrode and prevented continuous use of this electrode throughout the runs. The solutions were assayed for Cu^{2+} at various

Plate 3. Post-run blaubleibender covellite and chalcopyrite.



intervals during the runs by extracting 5 ml and filtering solutions through 8 micron filter paper. Ferric ion interference was eliminated by diluting 5 ml of the run solution to 25 ml with 0.01 molal NaF solution along with one-half milliliter of 5 molar $NaNO_3$ which was added to give a constant ionic strength. Fisher Atomic Absorption copper standard (1000 ppm Cu) was used to prepare a standard curve. The slope of the standard curve was approximately 29.5 mv/decade at 25°C. Total copper concentrations were determined using a Perkin-Elmer Atomic Absorption Spectrophotometer Model 560.

The experiments were carried out in a Colora ultra-thermostat constant temperature bath. A 500 ml Kimax reaction kettle contained the run solutions. The solutions were stirred by an overhead glass assembly rotated by a Richards variable speed motor. A stirring rate of 800 rpm was used for all experimental runs. This rate created a vortex of the solution and suspended all of the solids. The redox potential of the run solutions was measured using a Fisher combination platinum/saturated KCl/Ag-AgCl electrode monitored by an Apple II Plus Microcomputer and Disk II Operating System via an Adalab interface card as described in Wiersma and Rimstidt (1984).

The run solutions were thermally equilibrated before the solids were added to begin the reaction. One hundred emf readings were taken at 0.1 minute intervals prior to the beginning of each run to demonstrate the function and stability of the electrode. The prepared solids were added to the run solution when the potential readings had stabilized, 7.5 to 10 minutes after the experiment had begun.

Throughout the course of each run 100 emf readings were taken at 2.5 minute intervals; see Figure 2 for an example of typical results. The potential readings for individual runs were recorded on diskettes and a hard copy was provided by an Epson MX-80 printer. The 100 emf values collected from each run were transfered to an IBM 370 computer for further processing. A FORTRAN computer program was written to calculate the Eh values relative to the standard hydrogen electrode from the potentials measured by the platinum/saturated KCl/Ag-AgCl reference electrode. Wiersma and Rimstidt (1984) explain these calculations. The following adjustment was made to the equation relating the measured emf and the Eh.

According to Langmuir (1971):

$$Eh = emf\ (measured) + Es' \qquad (8)$$

Es' is the half cell potential of the reference electrode and is defined by Langmuir (1971) as:

$$Es' = Ec + Ej \qquad (9)$$

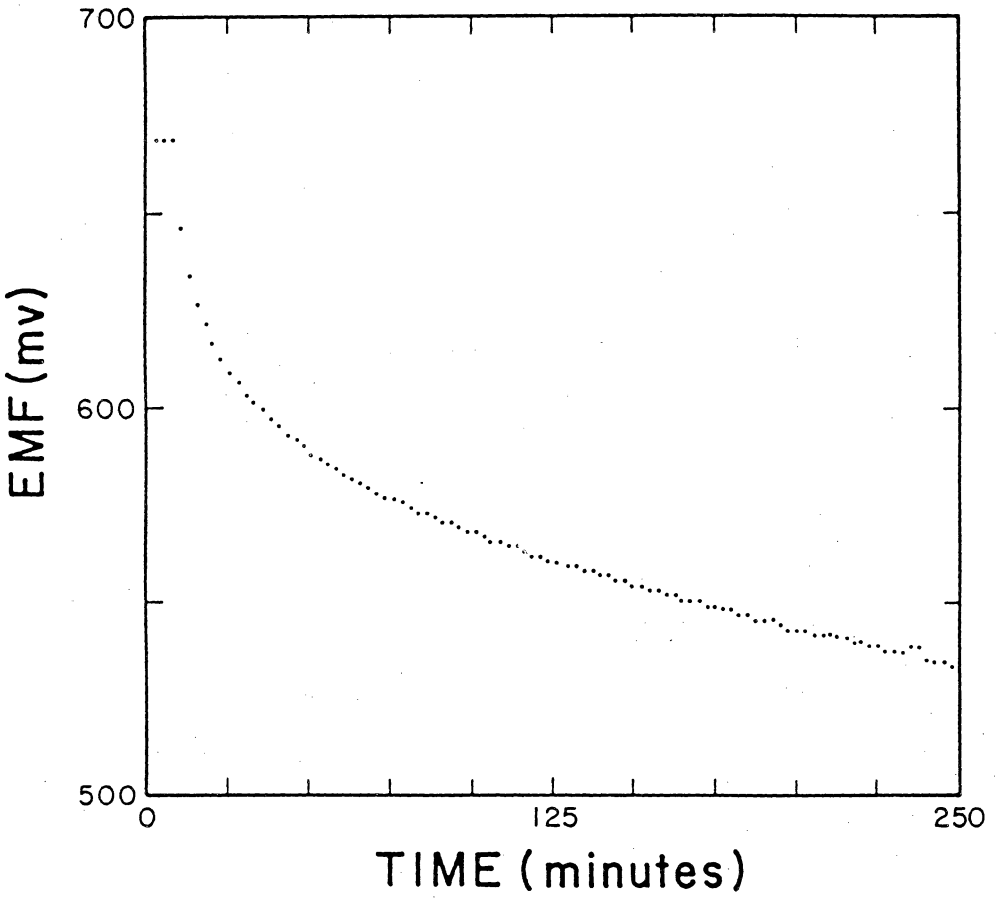
where Ej is the liquid junction potential and Ec is the potential due to the reference half cell reaction:

$$AgCl\ (s) + e- = Ag\ (s) + Cl^- \qquad (10)$$

Zobell's solution was used as a redox potential buffer to check for correct function and to calibrate the combination Eh electrode. Nordstrom (1977), gives an equation for the Eh of Zobell's solution relative to the standard hydrogen electrode. Using this equation and equation (5) the half cell correction (Es') can be calculated as such:

$$Eh(z) - emf(z) = Es'(25°C) = 0.19883 \qquad (11)$$

FIG 2. Plot of emf (measured in mv) versus time (in minutes) for a typical run.


700
600
500
EMF (mv)
0
125
250
TIME (minutes)

Wiersma and Rimstidt (1984) noted a constant potential difference of 0.004 volts from the values calculated by Nordstrom (1977). This author noted a constant potential difference of 0.00495 volts giving an Es' of 0.19388 at 25°C. From this difference the Eh values were adjusted as:

$$Eh(v) = emf\ (measured,\ v) + 0.19388\ (25°C) \qquad (12)$$

The specific surface areas of acid etched pre-run samples were determined by Quantachrome Corporation, of Syosset New York, using the multipoint BET method. The initial degassing, of the 2.25-2.35 g samples, was carried out at 75°C for 2-3 hours. The blaubleibender covellite samples had a specific surface area of 0.300 (±1%) m^2/g and the covellite had a specific surface area of 0.526 (±1%) m^2/g.

DISCUSSION OF RESULTS

The rate constants for the reaction of Fe^{3+} with blaubleibender covellite and covellite calculated by linear regression of the experimental data, at 25, 35, and 50°C, are listied in Table 2. The experimental data were best fit by a first order rate law:

$$-dm_{Fe^{3+}}/dt = k(A/M)m_{Fe^{3+}} \quad (13)$$

discussed by Wiersma and Rimstidt (1984). If the constants k and (A/M) are combined to give an apparent rate constant, k', the integrated form of the rate law can be written as:

$$\log m_{Fe^{3+}} = -2.303(k't) + \log m^{o}_{Fe^{3+}} \quad (14)$$

where $m^{o}_{Fe^{3+}}$ is the initial ferric iron concentration. According to this equation a plot of $\log m_{Fe^{3+}}$ versus time should yield a straight line with a slope of k' and an intercept of $\log m^{o}_{Fe^{3+}}$. The $\log m_{Fe^{3+}}$ values were calculated from the experimentally derived emf values following the procedure reported in Wiersma and Rimstidt (1984) using a FORTRAN computer program.

Figures 3 and 4 show $\log m_{Fe^{3+}}$ versus time for 25, 35, and 50°C runs of blaubleibender covellite and covellite. The data from the segments between the arrows were used to find k'. The steep initial slopes were discarded because they are likely due to one or more of the following (Wiersma and Rimstidt, 1984):

1.) Dissolution of a very reactive surface layer produced by the acid treatment.

2.) Rapid adsorption of ferric ion onto reactive sites at the solid surface.

Table 2. Experimental values for the rate constants, $m^{o}_{Fe3+} = 10^{-3}$ and pH 2.0. k' = slope of the log m_{Fe3+} versus time plot. k = rate constants in units of sec^{-1}.

Run Number	T°C	$k' \times 10^5$	$k \times 10^5$	log k
BBCV 16	25	3.34	6.18	-4.21
BBCV 18	25	3.26	6.04	-4.22
BBCV 20	25	4.97	9.20	-4.04
BBCV 17	35	6.85	12.68	-3.89
BBCV 27	35	5.26	9.74	-4.01
BBCV 29	50	19.9	36.85	-3.43
BBCV 32	50	18.4	34.07	-3.47
CV 19	25	0.61	0.58	-5.24
CV 21	25	0.43	0.41	-5.39
CV 25	25	1.39	1.32	-4.88
CV 28	25	1.55	1.47	-4.83
CV 22	35	2.45	2.33	-4.63
CV 23	50	5.61	5.33	-4.27
CV 24	50	4.99	4.74	-4.32

FIG 3. Plots of log $m_{Fe^{3+}}$ versus time (seconds) for blaubleibender covellite. Rate constants were were calculated over the ranges indicated by the arrows.

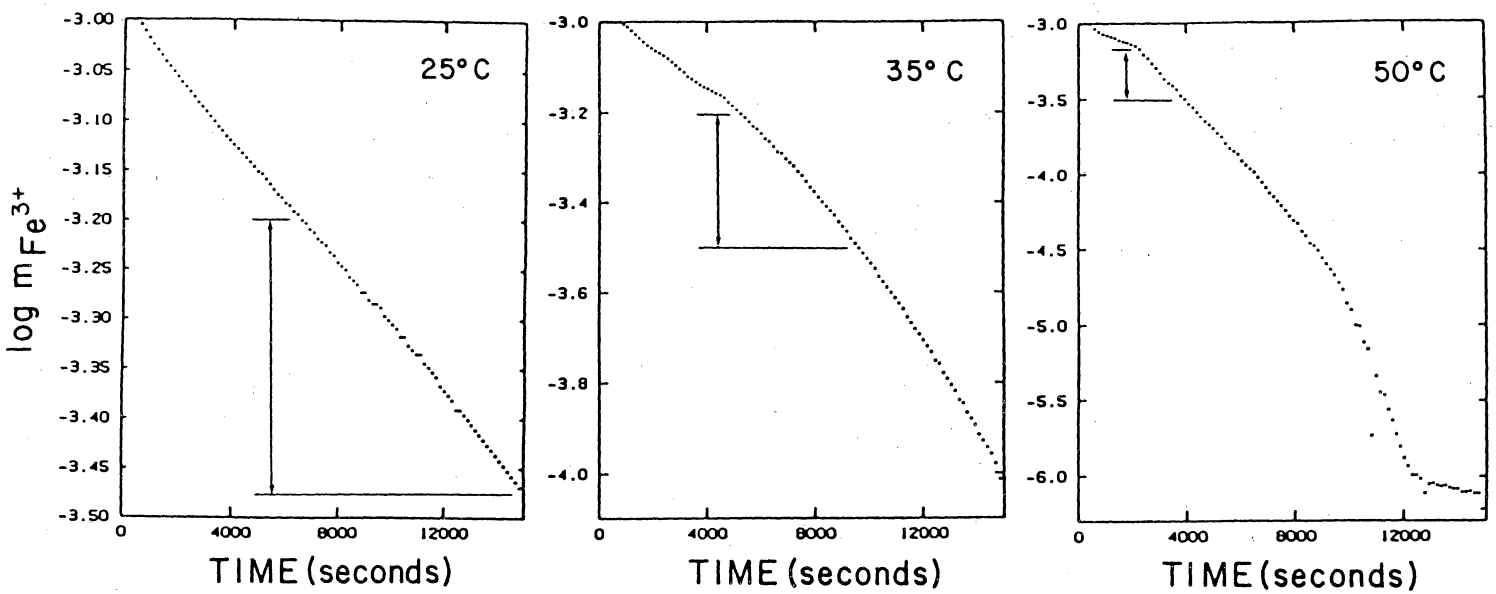
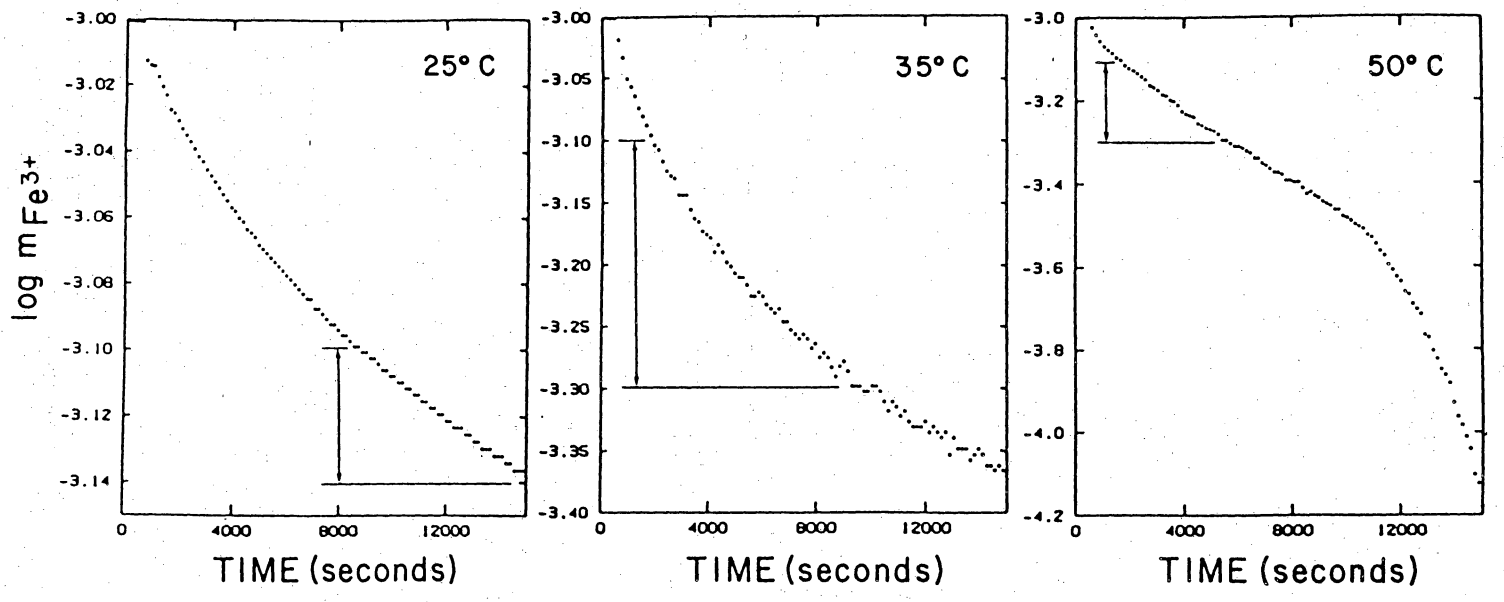

log m Fe^{3+}
-3.00
-3.05
-3.10
-3.15
-3.20
-3.25
-3.30
-3.35
-3.40
-3.45
-3.50
25° C
0
4000
8000
12000
TIME (seconds)
-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
35° C
0
4000
8000
12000
TIME (seconds)
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
50° C
0
4000
8000
12000
TIME (seconds)

FIG 4. Plots of log $m_{Fe^{3+}}$ versus time (in seconds) for covellite. Rate constants calculated over the ranges indicated by the arrows.


log m Fe3+
25° C
35° C
50° C
TIME (seconds)
TIME (seconds)
TIME (seconds)
-3.00
-3.02
-3.04
-3.06
-3.08
-3.10
-3.12
-3.14
-3.00
-3.05
-3.10
-3.15
-3.20
-3.25
-3.30
-3.35
-3.40
-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
0
4000
8000
12000

3.) A rapid decrease and disappearance of a streaming potential at the platinum electrode, produced by the relative movement of the electrode and solution due to stirring.

At greater extents of reaction, the mechanism changes, resulting in a steeper slope for the log $m_{Fe^{3+}}$ versus t function. The Cu^{2+}/Fe^{2+} ratios listed in Table 4 suggest that at least two different reactions occurred simultaneously throughout these experiments. The apparent reaction rate changed as the predominant reaction changed over various Eh intervals. Thus, in order to ensure internally consistent results, k' was calculated using a range of $m_{Fe^{3+}}$ of 6.31 - 3.16 x 10^{-4} for blaubleibender covellite and 7.94 - 5.01 x 10^{-4} for covellite. Dividing the apparent rate constant, k', by A/M. Where A is the surface area of the solid and M is the mass of solution (see Rimstidt and Barnes, 1980) gives the rate constants (k sec^{-1}) for a standard system with 1 m^2 solid surface area per kilograms of solution. The mean values of k for blaubleibender covellite and covellite, 25, 35, and 50°C are listed in Table 3. The overall error in the rate constants, resulting mostly from the error on A, is ± 1%.

The rate of dissolution of covellite in an acid solution at 25°C, in the absence of Fe^{3+}, was tested to determine if the dissolution reaction could take place without an oxidizing agent. The prepared solids were added to 500 ml HCl solution, pH 2, and the reaction was followed using the cupric electrode and the Apple II Plus system. Addition of the solids caused an immediate jump in Cu^{2+} concentration; then over the next 237 minutes the Cu^{2+} concentration remained essentially constant.

Table 3. Average experimental values for the rate constants.

Temp (°C)	A	A/M	Average $kx10^5$
BLAUBLEIBENDER COVELLITE			
25			7.14
35	0.270	0.54	11.21
50			35.46
COVELLITE			
25			0.94
35	0.526	1.05	2.33
50			5.03

A = BET measured surface area in units of m^2g^{-1}.
A/M = Surface area to mass of solution ratio where $A° = 1m^2$ and $M° = 1$ kg, as defined by Rimstidt and Barnes (1980).
Coefficient of determination r^2: blaubleibender covellite ≥ 0.994, covellite ≥ 0.961.
Mean standard error on k': blaubleibender covellite = $1.5x10^{-4}$%, covellite = $4.2x10^{-5}$%.

Table 4. Experimental values for Cu^{2+} concentrations of solutions at various points of the runs, and Fe^{2+}/Cu^{2+} molar ratios calculated from the experimental data.

T, (°C)	Run No.	Elapsed Time, min	Cu^{2+} (ppm)	Fe^{2+}/Cu^{2+}
		BLAUBLEIBENDER COVELLITE		
		0.0	0.45	
25	26	145.0	11.80	3.95
		250.0	17.65	3.11
		0.0	0.54	
		75.0	11.55	2.87
35	27	130.0	14.94	2.86
		177.5	17.65	2.73
		250.0	21.60	2.47
		0.0	0.15	
		52.2	21.1	2.11
50	32	90.0	24.8	2.31
		182.5	29.3	2.16
		250.0	27.8	2.28
		COVELLITE		
		0.0	0.645	
25	25	135.0	8.1	3.20
		250.0	11.25	2.84
		0.0	0.65	
		75.0	8.45	2.40
25	28	97.5	9.25	2.46
		182.5	13.95	2.15
		250.0	12.05	
		0.0	2.2	
50	24	147.5	23.0	1.73
		250.0	40.0	1.48

These results indicate rapid initial dissolution of a very reactive surface on the covellite grains, which may account for the steep initial slopes seen in the covellite runs (Figure 4). The lack of subsequent leaching of copper suggests that the simple dissolution reaction is unimportant in the oxidation of covellite by Fe^{3+}.

Activation Energy

The Arrhenius equation:

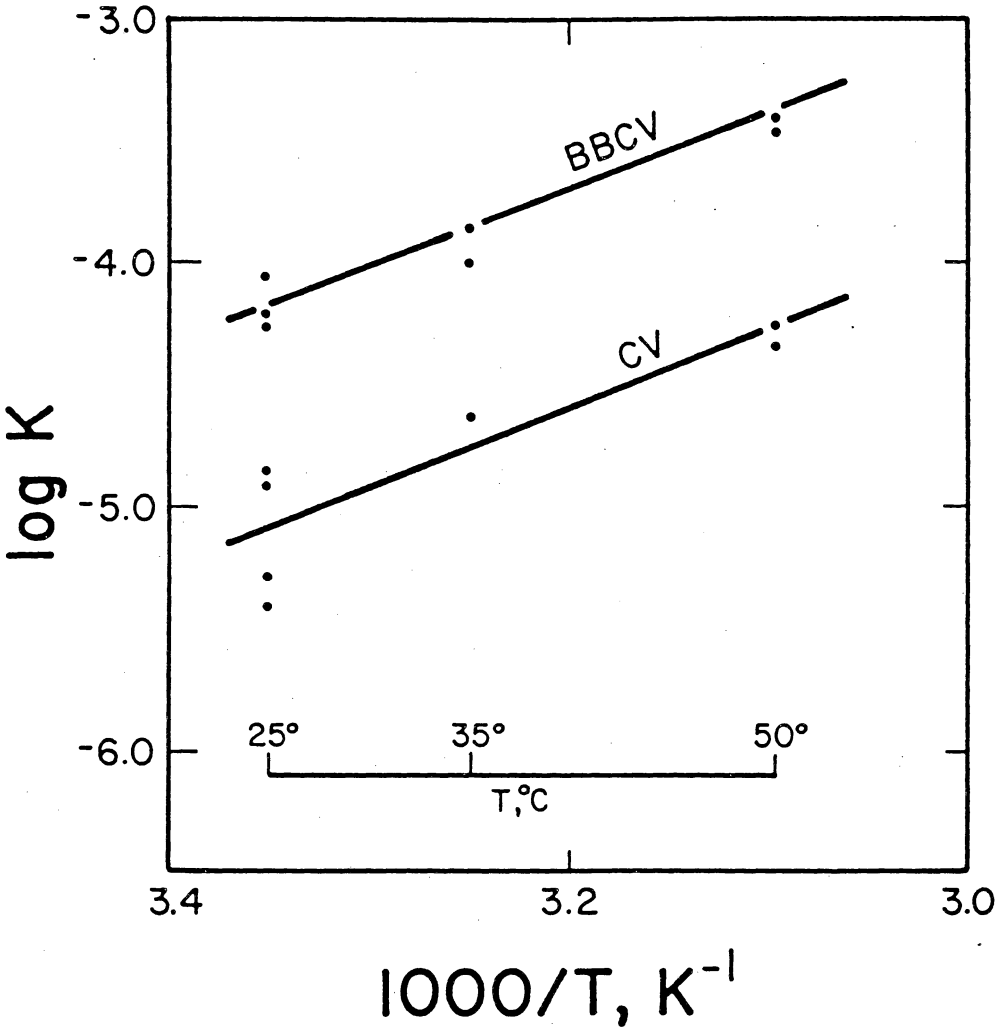
$$k = (A') \exp(-E_a/RT) \tag{15}$$

gives the temperature dependence of the reaction rate constant. A' can have a slight temperature dependence, but over the temperature range examined in this study it may be considered a constant. E_a is the activation energy of the reaction. The Arrhenius equation may also be written:

$$\log k = 2.303(-E_a/R)(1/T) + \log(A') \tag{16}$$

Thus, a plot of log k versus 1/T should yield a straight line with a slope of $-E_a/R$, provided the reaction mechanism does not change over the temperature range examined. Figure 5 is an Arrhenius plot showing the temperature dependence of the rates of the blaubleibender covellite and covellite reactions. The slopes (E_a/R) of the best fit lines, shown on the figure, for blaubleibender covellite and covellite, were found by linear regression. The calculated activation energy for the reaction of Fe^{3+} with blaubleibender covellite equals 51.80 ±6.2 kJ mol^{-1} (12.38 ± 1.48 kcal mol^{-1}) and 58.29 ±13.7 kJ mol^{-1} (13.93 ± 3.27 kcal mol^{-1}) for the reaction of Fe^{3+} with covellite. These high activation energies indicate that over the temperature and Fe^{3+}

FIG 5. Arrhenius plot for covellite and blaubleibender covellite runs, $m^{o}_{Fe^{3+}} = 10^{-3}$, pH 2.0. Solid lines are best fit lines by linear regression of the data.


-3.0
-4.0
-5.0
-6.0
log K
BBCV
CV
25°
35°
50°
T,°C
3.4
3.2
3.0
1000/T, K⁻¹

concentration ranges examined in this study, a surface reaction or reactions control the overall rate (diffusion limited reactions give E_a < 20 kJ mol^{-1}; Lasaga, 1981). Furthermore, the similarity of the activation energies suggest that the rate limiting step for both reactions is the same.

CONCLUSIONS

The relative reactivities of covellite and blaubleibender covellite with Fe^{3+} in acidic ferric chloride solutions can be appreciated by comparing the values for the experimental first-order rate constants. At 25°C they are: 7.14×10^{-5} ±5% sec^{-1} for blaubleibender covellite and 9.4×10^{-4} ±5% sec^{-1} for covellite. These results show that blaubleibender covellite reacts almost an order of magnitude faster than stoichiometric covellite. Where as the blaubleibender covellites are naturally occurring phases, often reported as secondary weathering products of copper deposits (Ramdohr 1969, and Goble 1980), they are actually metastable phases in the Cu-S system (Moh 1971, Rickard 1972,1973, Potter 1977, and Goble 1980). The more rapid oxidation of blaubleibender covellite than stoichiometric covellite is consistent with this. On the other hand, the activation energies for these two reactions are the same within the reported error, 51.8 ±6.2 kJ mol^{-1} for blaubleibender covellite and 58.29 ±13.7 kJ mol^{-1} for covellite. These values suggest that the rate limiting step is the same for the reaction of both minerals with Fe^{3+}. The high activation energies reported for the conditions of this study indicate the rate limiting step to be a surface reaction rather than an aqueous diffusion limited process. A comparison of the Fe^{2+} to Cu^{2+} concentrations in the run solutions shows that two parallel reactions occured. The most important reaction produced Cu^{2+} and elemental sulfur as products (equation 6). This reaction has a ratio of Fe^{2+}/Cu^{2+} of 2:1 on the right side of the equation. Some of the sulfur was oxidized all the way to sulfate

(equation 7) giving a Fe^{2+}/Cu^{2+} ratio of 8:1. The ratios listed in Table 4 range from 3.95 at high Eh values where sulfate formed most readily to 2.11 within the ferric iron concentration ranges examined. Dutrizac and MacDonald (1974b) and Thomas and Ingraham (1967) report the formation of both elemental sulfur and sulfate during ferric ion leaching of covellite. Sulfate comprised less than 10% of the sulfur products in their experiments. No sulfur was detected in the post run solids in these experiments. However, it was calculated that a surface layer of only 4×10^{-8} cm thickness would be formed if reaction 6 dominated throughout the four hour runs. The first order rate observed here is thus a synthesis of these two first order reactions. The combination of two first order reactions produces a rate law that is still first order with respect to Fe^{3+}:

$$dm_{Fe^{3+}}/dt = -(k_1' m_{Fe^{3+}} + k_2' m_{Fe^{3+}}) \qquad (16)$$

This simplifies to:

$$dm_{Fe^{3+}}/dt = -(k_1' + k_2') m_{Fe^{3+}} \qquad (17)$$

and can be integrated to give:

$$\log m_{Fe^{3+}} = -2.303(k_1' + k_2')(t) + \log m^{o}_{Fe^{3+}} \qquad (18)$$

which would give a linear relationship of $\log m_{Fe^{3+}}$ versus time plot as seen from the experimental data. To be consistent and to minimize variation related to these mixed kinetics, rate constants were reported for rather narrow ranges of ferric ion concentrations.

The results presented above and the examination of covellite dissolution in HCl indicate that the reaction is not a simple acid leaching of copper from the minerals but rather a redox reaction involving the

ferric/ferrous couple. The experimental data show that parallel reactions occurred where the relative contribution of each reaction changed as the Eh of the solution changed.

Compared to pyrite (Wiersma and Rimstidt, 1984) covellite oxidizes quite rapidly and therefore, covellite weathering is difficult to observe in nature. However, it is important in second cycle remobilization of secondary enriched zones in copper-bearing ore deposits where chalcocite is quickly oxidized to covellite:

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \qquad (19)$$

(Dutrizac and MacDonald 1974a). The covellite then reacts more slowly to give up more copper and produce SO_4^{2-} and S° (reactions 6 and 7). Copper-rich and sulfur-poor solutions which are produced percolate downward to the new water table to form a second cycle enrichment blanket with a higher copper content (Anderson 1982). Elemental sulfur is produced in reaction 6. The fate of this S° is not clear, but it may be left behind in the oxidized zone of the deposit (Emmons 1917 and Ramdohr 1969), or remobilized by recharge waters which periodically flush the oxidized zone. Sulfur oxidizing bacteria probably oxidize the sulfur to a soluble form that subsequently moves downward through the reducing zone (Brierley and Brierley 1981). Thus, second cycle oxidation of enriched blankets in porphyry copper deposits occurs via:

1.) Rapid conversion of chalcocite to blaubleibender covellite and/or covellite.

2.) Relatively slow oxidation of covellite to Cu^{2+}, S°,

and SO_4^{2-} while blaubleibender covellite oxidizes somewhat more rapidly.

3.) Slow oxidation of S^o and any remaining pyrite.

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APPENDIX I

Preparation of Blaubleibender Covellite

Blaubleibender covellite has been synthesized by numerous authors, among them Frenzel (1959, 1961), Moh (1971), and Potter (1977). For this study blaubleibender covellite was synthesized by reacting chalcocite with concentrated nitric acid at 25°C according to the following:

$$Cu_2S + 2HNO_3 \rightarrow (1-x)Cu^+ + Cu_{1+x}S + (1-x)NO_2(g) + (1-x)NO_3^- + (1-x)H_2O \quad (20)$$

1. Chalcocite samples from Butte, Montana were pulverized in a Tekmar Model A10 Analytical Mill. Iron fillings, from the mill blade, present in the material after grinding were removed with a magnet.

2. The material was dry-sieved to recover the 100-200 mesh (75-150 micron) size fraction used for the experiments.

3. 1.2500 ±0.0005 g of the sized material was added to 10 ml concentrated nitric acid and stirred vigorously for two minutes. NO_2 gas was evolved (perform this step in a fume hood), and the solution became green (color of Cu^+ ion).

4. The solution was diluted to 50 ml with distilled/deionized H_2O.

5. The solids were separated from the solution by filtering

through 8 micron filter paper.

The original chalcocite contained minor amounts of bornite (Cu_5FeS_4), see Plate 1. Upon addition of the nitric acid the bornite reacted to produce blaubleibender covellite and chalcopyrite, following the path indicated on Figure 6. Plate 2 shows the intergrowth of these minerals and the resulting textures after the acid treatment. The composition of the blaubleibender covellite phase after the acid treatment was $Cu_{1.3}S$, determined from electron microprobe analysis. The reaction path of the initial chalcocite is also indicated on Figure 6.

Plate 1. Original chalcocite with minor amounts of bornite.

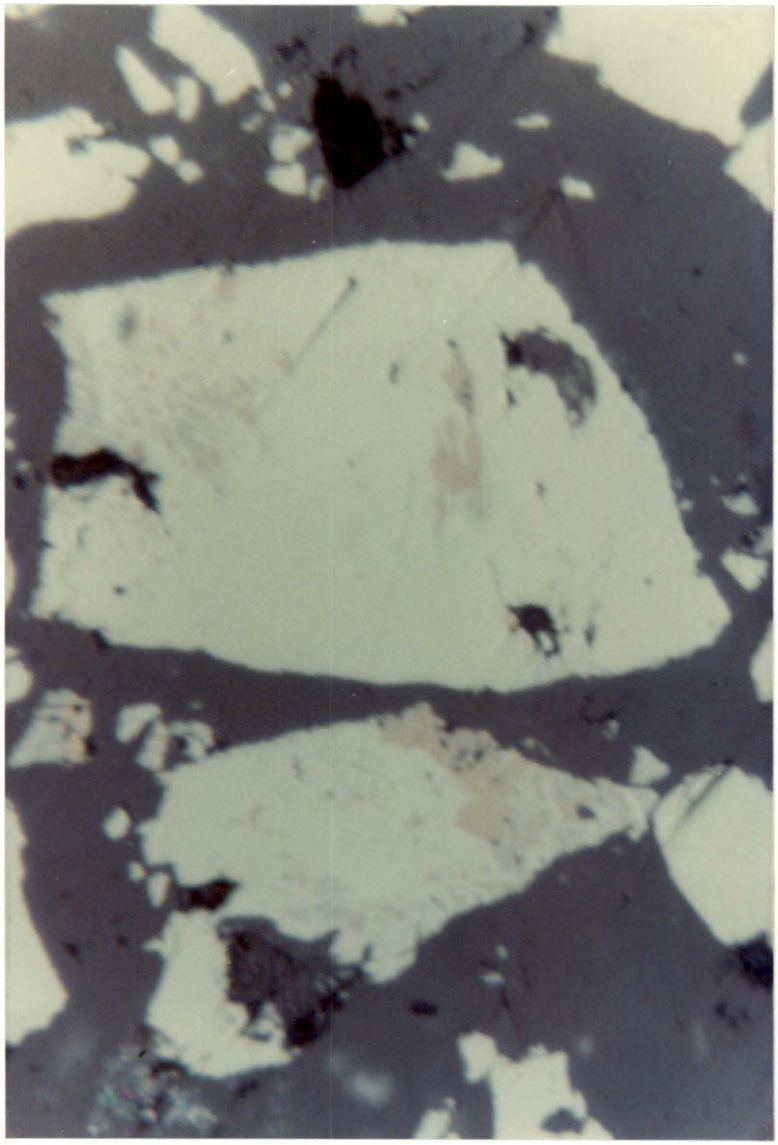

FIG 6. Central portion of Cu-Fe-S phase diagram indicating the reaction paths of bornite (1) and chalcocite (2) during the acid etching procedure.

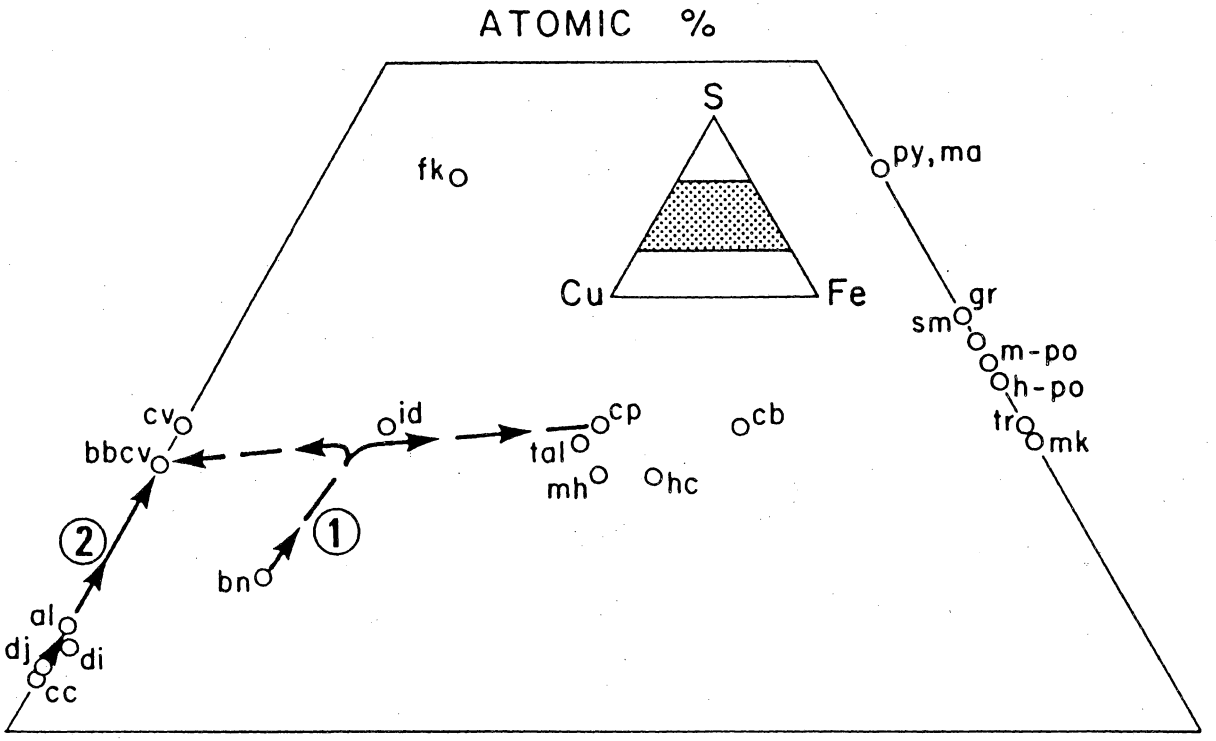
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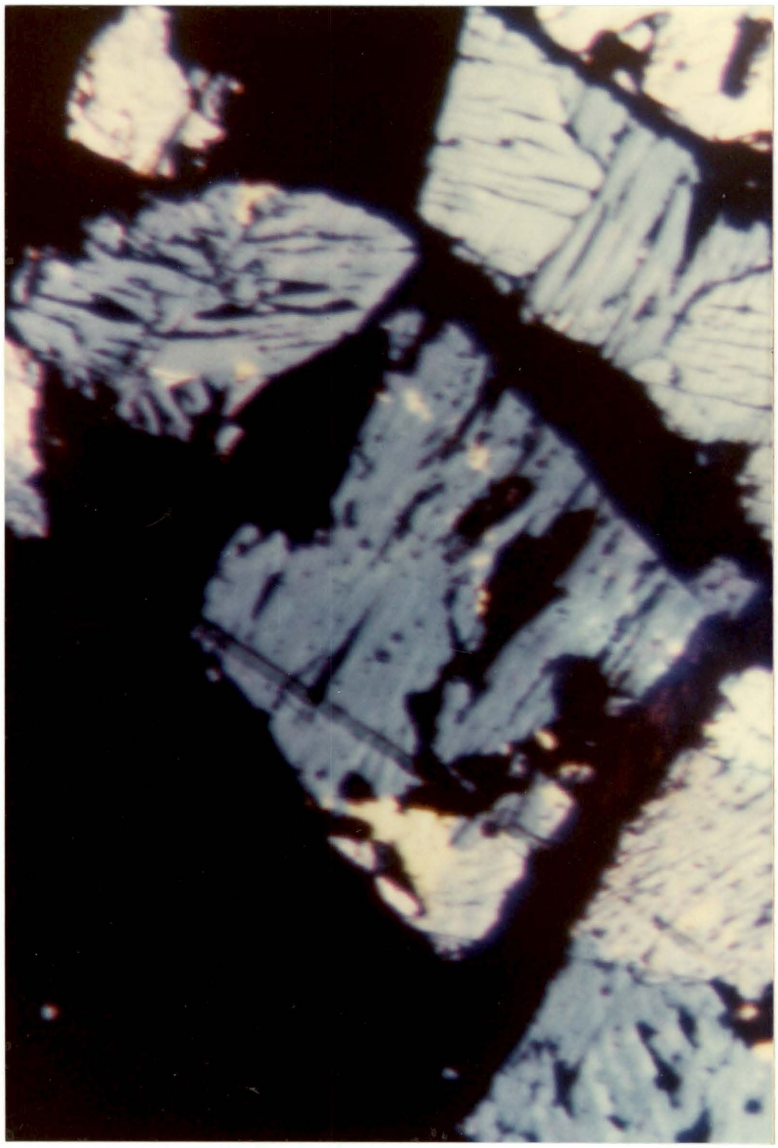
Plate 2. Acid etched chalcocite and bornite reacted to blaubleibender covellite and chalcopyrite.



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RATES OF REACTION OF COVELLITE AND BLAUBLEIBENDER COVELLITE WITH FERRIC IRON AT PH 2.0

by

Carol Ann Walsh

(ABSTRACT)

The rates of reaction of pulverized samples (100-200 mesh) of blaubleibender covellite and covellite with 10^{-3} m ferric iron in a pH 2 solution were determined at 25, 35, and 50°C. Ferrous and cupric ion concentrations of the run solutions suggest that parallel reactions oxidized the sulfur to either elemental sulfur or to sulfate. The reaction that produces elemental sulfur is by far the fastest. The disappearance of ferric iron follows a first-order rate law which is a combination of the two first-order reactions:

$$-dm_{Fe^{3+}}/dt = (k_1 + k_2)(A/M)\ m_{Fe^{3+}}$$

where $m_{Fe^{3+}}$ is the molal concentration of uncomplexed ferric iron, k_1 and k_2 are the rate constants and A/M is the ratio of the surface area of the reacting solid to the mass of the solution.

At 25°C the measured rate constants are $7.14 \times 10^{-5} \pm 1\%\ sec^{-1}$ for blaubleibender covellite and $9.4 \times 10^{-4} \pm 1\%\ sec^{-1}$ for covellite indicating that blaubleibender covellite reacts almost an order of magnitude faster than stoichiometric covellite under these conditions.

However, the activation energies for these reactions, over the temperature interval 25 to 50°C, are the same, within the range of the reported error: 51.8 ± 6.2 kJ mol^{-1} for blaubleibender covellite and 58.29 ± 13.7 kJ mol^{-1} for covellite. This suggests that the rate limiting step for both reactions is the same. The relatively high activation energies indicate surface reactions control the rate of oxidation at these temperatures.