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

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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 whereas parallel reactions oxidize the sulfide to either elemental sulfur or to sulfate, the reaction that produces elemental sulfur is by far the fastest. The rate of disappearance of ferric iron fits a first-order law, $-dm_{Fe^{3+}}/dt = k(A/M)\, m_{Fe^{3+}}$, where $m_{Fe^{3+}}$ is the molal concentration of uncomplexed ferric iron, k is the rate constant, 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-constant (k) is $7.14 \times 10^{-5}\ s^{-1}$ for *blaubleibender* covellite and $9.4 \times 10^{-6}\ s^{-1}$ for covellite, indicating that under these conditions, *blaubleibender* covellite reacts over one order of magnitude faster than stoichiometric covellite. The activation energy of these reactions, however, is nearly the same over the temperature interval 25 to 50°C: 51.8 ± 6.2 kJ mol^{-1} for *blaubleibender* covellite and 58.3 ± 13.7 kJ mol^{-1} for covellite. This suggests that the rate-limiting step is the same for both reactions. The relatively high activation-energies indicate that surface reactions, at these temperatures, control the rate of oxidation.

Keywords: covellite, kinetics, supergene enrichment, sulfide oxidation, *blaubleibender* covellite.

SOMMAIRE

Les vitesses de réaction d'échantillons pulvérisés (100–200 mesh) de covelline *blaubleibende* et de covelline à 10^{-3} m d'ion ferrique, dans une solution à pH = 2, ont été déterminées à 25, 35 et 50°C. Les concentrations en ion ferreux et cuprique de la solution font penser que des réactions parallèles qui oxydent le sulfure, soit en soufre élémentaire, soit en sulfate, c'est celle qui produit le soufre élémentaire qui est de loin la plus rapide. La vitesse de disparition du fer ferrique est régie par une loi du premier ordre, $-dm_{Fe^{3+}}/dt = k(A/M)\, m_{Fe^{3+}}$. Dans cette équation, $m_{Fe^{3+}}$ est la concentration molaire du fer ferrique non-complexé, k est la constante de la vitesse de disparition de Fe^{3+} et A/M est le rapport de la surface du réactif solide à la masse de la solution. À 25°C la valeur mesurée de la constante k est $7.14 \times 10^{-5}\ s^{-1}$ pour la covelline *blaubleibende* et $9.4 \times 10^{-6}\ s^{-1}$ pour la covelline: dans ces conditions, la covelline *blaubleibende* réagit plus vite que la covelline stoechiométrique de plus d'un ordre de grandeur. Néanmoins l'énergie d'activation de ces deux réactions est presque la même entre 25 et 50°C: 51.8 (± 6.2) et 58.3 (± 13.7) kJ mol^{-1} pour la covelline *blaubleibende* et la covelline stoechiométrique, respectivement. Ce résultat porte à croire que le seuil limite de la vitesse de disparition de Fe^{3+} est le même pour les deux réactions. Les énergies d'activation mises en jeu montrent qu'à ces températures des réactions de surface gouvernent la vitesse d'oxydation.

(Traduit par la Rédaction)

Mots-clés: covelline, cinétique, enrichissement supergène, oxydation de sulfures, covelline *blaubleibende.*

INTRODUCTION

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

This study was designed to evaluate the rates of oxidation of covellite and *blaubleibender* covellite by Fe^{3+} at pH 2 in a batch-reactor system. These data should contribute to our understanding of the geochemical processes involved in second-cycle weathering of enriched zones. Chaffee (1982a, b) discussed the geochemistry of copper deposits and tech-

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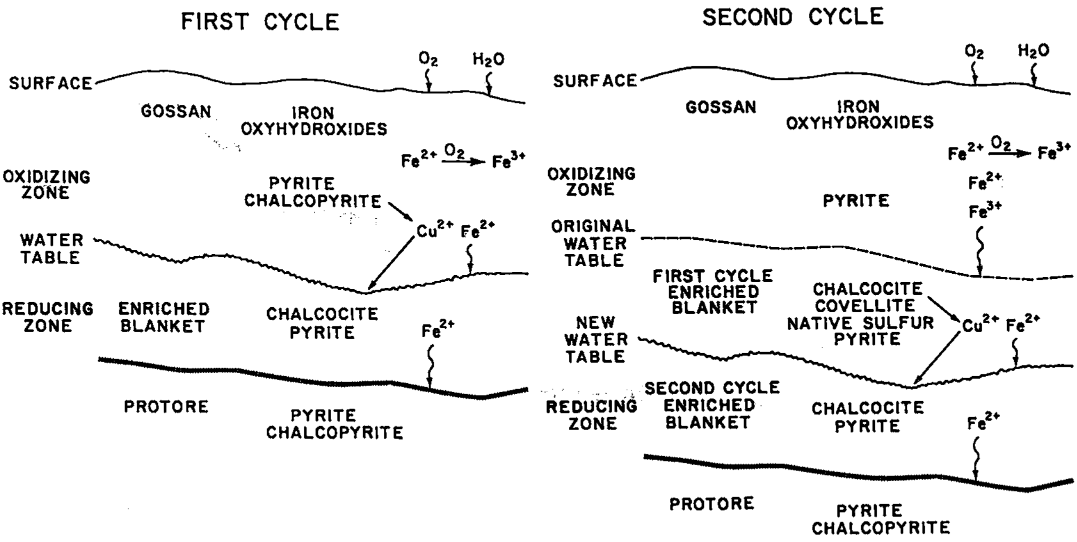

FIG. 1. The first and second cycles of weathering and patterns of enrichment in copper-bearing ore deposits.

niques for prospecting for these. Also, leaching by ferric ion plays an increasingly important role in hydrometallurgy (Dutrizac & MacDonald 1974a), where in many cases it can be an economical alternative to pyrometallurgy.

Second-cycle enrichment

The first cycle of enrichment of porphyry copper deposits (Fig. 1A) is dominated by the oxidation of iron sulfides. Pyrite is commonly the most abundant sulfide mineral in these 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 pH of groundwater (C.A. Anderson 1955, J.A. Anderson 1982). Subsequent oxidation of ferrous iron to ferric iron is catalyzed by *Thiobacillis ferrooxidans* bacteria (Brierley & Brierley 1981):

$$2Fe^{2+} + ½O_2 + 2H^+ = 2Fe^{3+} + H_2O \quad (2)$$

Much of the regenerated Fe^{3+} reacts with more pyrite to generate more Fe^{2+} and sulfuric acid, whereas the remainder reacts with other metal sulfides such as chalcopyrite to release other metals to solution:

$$CuFeS_2 + 16\,Fe^{3+} + 8H_2O = Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

The copper released during this first cycle of enrichment is transported to the reducing zone, below the water table, where it reacts with indigenous sulfides to form an enriched blanket. This process may continue for a considerable time, and may lead to an accumulation of 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 an arid climate could expose the enriched blanket to the oxidizing conditions of the vadose zone (Fig. 1B). The oxidation reactions result in successive leaching of Cu^{2+} from the copper-rich phases such as chalcocite to produce covellite (Blain & Andrew 1977, King *et al.* 1975, Anderson 1955):

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \quad (4)$$

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

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

and

$$CuS + 8Fe^{3+} + 4H_2O = 8Fe^{2+} + Cu^{2+} + SO_4^{2-} + 8H^+ \qquad (6)$$

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 the covellite present can indicate the rate of oxidation of the enriched ore and, perhaps, yield important information about the rate of copper transport to the zone of second-cycle enrichment. For a more detailed discussion of the weathering and enrichment of copper deposits, see Emmons (1917), Blain & Andrew (1977) and Anderson (1982). Similar processes of oxidation and reduction are responsible for the accumulation of copper in redbed copper deposits (Tourtelot & Vine 1976, Berendsen & Lambert 1981, Lambert *et al.* 1981).

Previous studies

There are numerous studies of the rate of oxidation of covellite by ferric ion. Dutrizac & MacDonald (1974a) reviewed many of these. 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 the studies reviewed report essentially first-order kinetics, where the rate is limited by a chemical reaction rather than by diffusion. Most authors contend that Cu^{2+} and S° are the dominant products of this reaction (see equation 6). However, Dutrizac & MacDonald (1974b), along with Thomas & Ingraham (1967), reported the formation of minor amounts of sulfate along with elemental sulfur. The study by Thomas & Ingraham (1967) also showed an initially faster rate of reaction. They suggested 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 both S° and sulfate as products. The oxidation of the *blaubleibender* covellite was found to have a higher activation energy than that reported for chalcocite and to be chemically controlled.

TABLE 1. ACTIVATION ENERGIES FROM PREVIOUS STUDIES ON COVELLITE

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

The leaching solution was ferric sulfate (from the summary of other studies discussed in Dutrizac & MacDonald 1974a).

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 starting 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. The reader should refer to Berry (1954) for a discussion of the crystal structure of covellite. Goble (1980, 1985) reviewed the crystal structure of the *blaubleibender* covellites and compared their optical properties to those of stoichiometric covellite. He also presented detailed X-ray data for covellite and the *blaubleibender* covellites.

Solutions were prepared and analyzed following the procedure described by Wiersma & Rimstidt (1984). Ferric chloride was used as the source of ferric iron in these experiments, rather than ferric sulfate. This produced solutions with high activity of ferric iron and low ionic strength; ferric sulfate ion pairs are so strong that most of the iron is tied up as ion pairs in ferric sulfate solutions. The solution models (FORTRAN programs) mentioned below used to calculate the distribution of species in the solutions, and the reaction rates were expressed in terms of the concentration of uncomplexed ferric iron. Thus, these results can be applied to ferric sulfate solutions if ion-pair formation is taken into account. All extractions of experimental solutions were filtered through 8-μm filter paper to remove entrained solids.

The redox potential of the 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 & Rimstidt (1984).

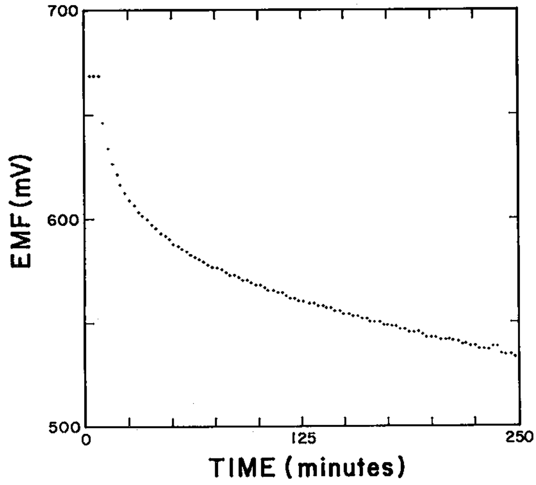

FIG. 2. Emf (measured in mV) *versus* time (in minutes for a typical experiment.

The solutions were thermally equilibrated before the solids were added to begin the reaction. The prepared solids were added to the solution when the potential readings had stabilized, 7.5 to 10 minutes after the experiment had begun. Throughout the course of each experiment, 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 experiment were transferred to an IBM 370 computer for further processing. The FORTRAN computer program, 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, is explained in Wiersma & Rimstidt (1984). The following adjustment was made to the equation relating the measured emf and Eh. According to Langmuir (1971):

$$\text{Eh} = \text{emf (measured)} + \text{Es}' \qquad (7)$$

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

$$\text{Es}' = \text{Ec} + \text{Ej} \qquad (8)$$

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

$$\text{AgCl (s)} + e^- = \text{Ag (s)} + \text{Cl}^- \qquad (9)$$

Zobell's solution was used as a redox-potential buffer to check for the correct function and to calibrate the combination Eh electrode. Nordstrom (1977) gave an equation for the Eh of Zobell's solution relative to the standard hydrogen electrode. Using this equation and equation (7), the half-cell correction (Es′) can be calculated:

$$\text{Eh(z)} - \text{emf(z)} = \text{Es}'(25°\text{C}) = 0.19883 \qquad (10)$$

Wiersma & Rimstidt (1984) noted a constant difference in potential of 0.004 volts from the values calculated by Nordstrom (1977). In this study there was a constant difference in potential of 0.00495 volts, giving an Es′ of 0.19388 at 25°C. From this difference, the Eh values were adjusted as:

$$\text{Eh(v)} = \text{emf (measured, v)} + 0.19388\ (25°\text{C}) \qquad (11)$$

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. The extent of reaction was so small that there was no significant change in the surface area of the solids over the course of the experiments.

DISCUSSION OF RESULTS

The experimental data were to fit to a first-order rate law:

$$-dm_{Fe^{3+}}/dt = k(A/M)m_{Fe^{3+}} \qquad (12)$$

(where $m_{Fe^{3+}}$ is the concentration of *uncomplexed* ferric iron in the solution and A/M is the ratio of surface area of solids to mass of solution). 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:

$$\log k_{Fe^{3+}} = -2.303\ (k't) + \log m°_{Fe^{3+}} \qquad (13)$$

where $m°_{Fe^{3+}}$ is the initial concentration of ferric iron. According to this equation, a plot of log

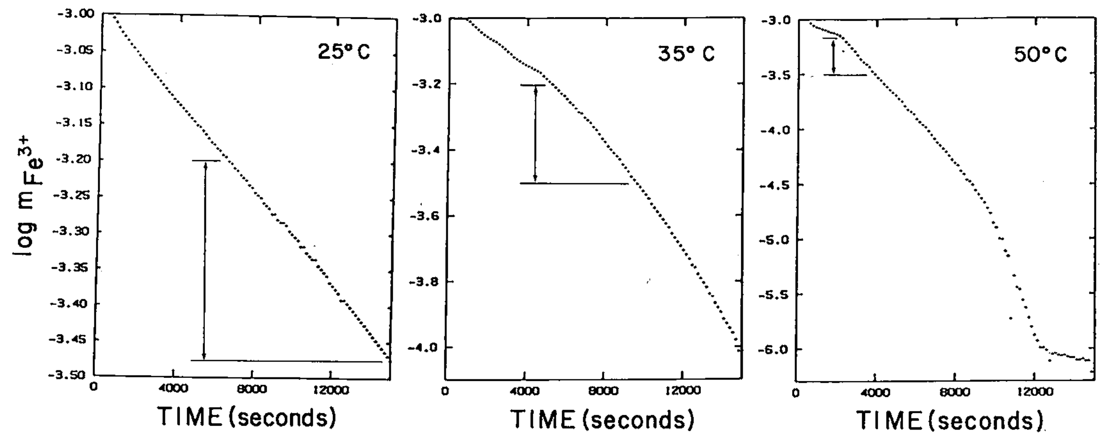

FIG. 3. Value of log $m_{Fe^{3+}}$ *versus* time (seconds) for *blaubleibender* covellite. The change in slope of these lines (especially for the 50°C experiments) suggests that the reaction mechanism changes with Eh. This might explain the wide variation of reported values of activation energy (see Table 1). The rate constants reported here were calculated over relatively narrow ranges of Eh (ferric iron activities corresponding to these ranges are indicated by arrows) considered to be representative of those expected in the zone of weathering.

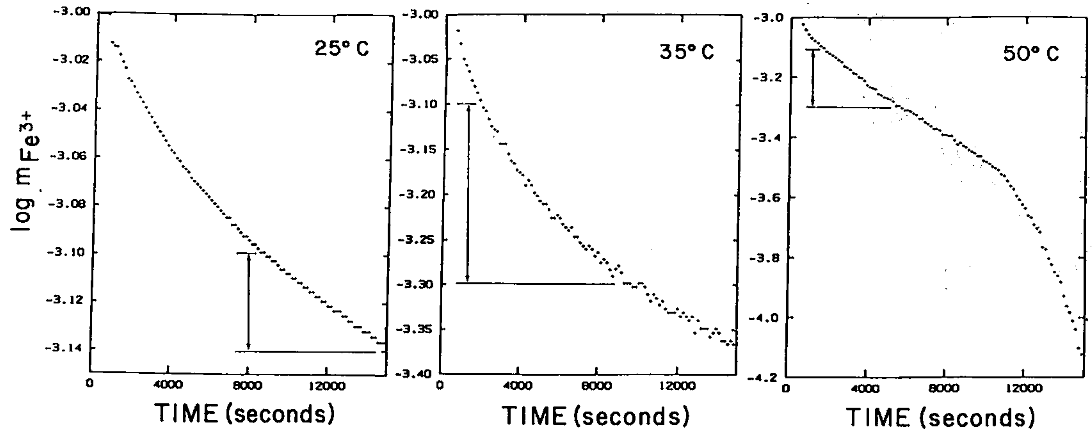

FIG. 4. Value of log $m_{Fe^{3+}}$ *versus* time (seconds) for covellite. The change in slope of these lines (especially for the 50°C experiments) suggests that the reaction mechanism changes with Eh. This might explain the wide variation of reported values of activation energy (see Table 1). The rate constants reported here were calculated over relatively narrow ranges of Eh (ferric iron activities corresponding to these ranges are indicated by arrows) considered to be representative of those expected in the zone of weathering.

$m_{Fe^{3+}}$ *versus* time should yield a straight line of slope of *k'* and intercept of log $m°_{Fe^{3+}}$. The log $m_{Fe^{3+}}$ values were calculated from the experimentally derived emf values following the procedure reported in Wiersma & Rimstidt (1984) using a FORTRAN computer program.

Figures 3 and 4 show log $m_{Fe^{3+}}$ *versus* time for 25, 35 and 50°C experiments with *blaubleibender* covellite. The 50°C experiments show that the mechanism of these reactions changes as they proceed to lower Eh conditions so that the plots of log $m_{Fe^{3+}}$ *versus* time are composed of a series of linear segments. The lower-temperature experiments did not attain as large an extent of reaction and, consequently, show only two segments. The data from the segments between the arrows were used to find the k' reported here. The correlation coefficient (r^2) is greater than 0.99 for all covellite data and greater than 0.96 for *blaubleibender* covellite data, indicating that a linear model is appropriate for this reaction interval. Thus the rate constants reported here (Table 2) are based on restricted portions of the

TABLE 2. EXPERIMENTAL VALUES FOR THE RATE CONSTANTS

Run Number	T°C	k'x10^5	kx10^5	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

$m^o_{Fe^{3+}} = 10^{-3}$ and pH 2.0. k' = slope of the log $m_{Fe^{3+}}$ versus time plot. k = rate constants in units of s^{-1}

TABLE 3. AVERAGE EXPERIMENTAL VALUES FOR THE RATE CONSTANTS

Temperature	A	A/M	k×10^5*	Temperature	A	A/M	k×10^5*
Blaubleibender covellite				Covellite			
25°C	0.270	0.54	7.14	25°C	0.526	1.05	0.94
35			11.21	35			2.33
50			35.46	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° = 1 m^2 and M° = 1 kg, as defined by Rimstidt & Barnes (1980). Coefficient of determination r^2: blaubleibender covellite ≥ 0.994, covellite ≥ 0.961. Mean standard error for the fit of k': blaubleibender covellite 1.5×10^{-6}%, covellite 4.2×10^{-5}%.

TABLE 4. EXPERIMENTAL VALUES FOR Cu^{2+} CONCENTRATIONS OF SOLUTIONS AND Fe^{2+}/Cu^{2+} MOLAR RATIO

T (°C)	Run No.	Elapsed Time, min	Cu^{2+} (ppm)	$m_{Fe^{2+}}/m_{Cu^{2+}}$
	BLAUBLEIBENDER COVELLITE			
25	26	0.0	0.45	
		145.0	11.80	3.95
		250.0	17.65	3.11
35	27	0.0	0.54	
		75.0	11.55	2.87
		130.0	14.94	2.86
		177.5	17.65	2.73
		250.0	21.60	2.47
50	32	0.0	0.15	
		52.2	21.1	2.11
		90.0	24.8	2.31
		182.5	29.3	2.16
		250.0	27.8	2.28
		COVELLITE		
25	25	0.0	0.64	
		135.0	8.1	3.20
		250.0	11.25	2.84
25	28	0.0	0.65	
		75.0	8.45	2.40
		97.5	9.25	2.46
		182.5	13.95	2.15
		250.0	12.05	
50	24	0.0	2.2	
		147.5	23.0	1.73
		250.0	40.0	1.48

curves where the reaction mechanisms and stoichiometries appear to correlate. The other portions of the graph reflect different mechanisms of reaction. For *blaubleibender* covellite, k' was calculated for the range of ferric iron concentrations between 6.31×10^{-4} and 3.16×10^{-4} m. For covellite, the reported rate-constants are based on a range of ferric iron concentrations between 7.94×10^{-4} and 5.01×10^{-4} m. The rate constants are summarized in Table 3.

The values of the ratio $m_{Cu^{2+}}/m_{Fe^{2+}}$ listed in Table 4 suggest that the sulfide sulfur in the mineral is oxidized to elemental sulfur by the ferric iron. If sulfate were the final product of oxidation of the sulfide sulfur, the reaction would proceed according to equation (6) and the ratio of ferrous iron to copper in the final solution would be 8:1. If the sulfide were only oxidized to elemental sulfur, the reaction would follow equation (5) and the ferrous iron to copper ratio in solution would be 2:1. Table 4 shows that predominant reaction produced elemental sulfur as values of the $m_{Fe^{2+}}/m_{Cu^{2+}}$ ratio are always near two. Values of $m_{Fe^{2+}}/m_{Cu^{2+}}$ greater than two suggest that some of the sulfur was oxidized all the way to sulfate (equation 7). The values of the ratio listed in Table 4 range from 3.95 at high Eh values, where sulfate formed most readily, to 2.11 within the ranges of ferric iron concentration ranges examined. Dutrizac & MacDonald (1974b) and Thomas & Ingraham (1967) reported the formation of both elemental sulfur and sulfate during ferric ion leaching of covellite. However, sulfate comprised less that 10% of the sulfur products in their experiments. No sulfur was detected in the solid product of these experiments. However, a surface layer of only 4×10^{-8} cm thickness would have been formed if reaction 6 dominated throughout the four-hour experiments. The first-order rate observed here is thus a synthesis of these two first-order reactions.

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. One gram of covellite was added to 500 mL of pH 2 HCl solution, and the reaction was followed using a 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. 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 experiments (Fig. 4). The lack of subsequent leaching of copper suggests that the simple, nonoxidative dissolution-reaction is unimportant under the conditions of the oxidation experiments.

Activation energy

Figure 5 shows the temperature dependence of the reaction rates of the *blaubleibender* covellite and covellite. According to the Arrhenius equation,

$$\log k = 2.303(-E_a/R)(1/T) + \log(A') \qquad (14)$$

The activation energy for the reaction of Fe^{3+} with *blaubleibender* covellite is 51.8 ± 6.2 kJ mol^{-1} (12.4 ± 1.5 kcal mol^{-1}) and is 58.3 ± 13.7 kJ mol^{-1} (13.9 ± 3.3 kcal mol^{-1}) for the reaction of Fe^{3+} with covellite. These high activation-energies indicate that over the ranges of temperature and Fe^{3+} concentration examined in this study, a surface reaction or reactions control the overall rate (diffusion-limited reactions have $E_a < 20$ kJ mol^{-1}: Lasaga 1981). Furthermore, the similarity of the activation energies suggest that the rate-limiting step for both reactions may be the same.

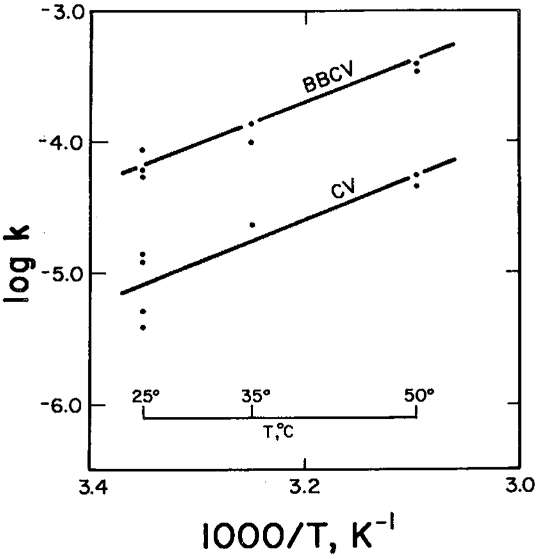

FIG. 5. Arrhenius plot for experiments on covellite and *blaubleibender* covellite. Solid lines are best-fit lines obtained by linear regression of the data.

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} s^{-1} for *blaubleibender* covellite and 9.4×10^{-6} s^{-1} for covellite. These results show that *blaubleibender* covellite reacts almost an order of magnitude faster than stoichiometric covellite. This is consistent with the fact that whereas the *blaubleibender* covellites are naturally occuring phases, commonly reported as products of secondary weathering of copper deposits (Ramdohr 1969, Goble 1980), they are actually metastable phases in the system Cu–S (Moh 1971, Rickard 1972, 1973, Potter 1977, Goble 1980). 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 58.3 ± 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+} and Cu^{2+} concentrations in the solutions after the experiment shows that the most important reaction produced Cu^{2+} and elemental sulfur as products (equation 6). This reaction has a ratio $m_{Fe^{2+}}/m_{Cu^{2+}}$ of 2:1 on the right side of the equation. To be consistent and to minimize variation related to mixed kinetics, rate constants were reported for rather narrow ranges of concentration of ferric ion.

The results presented above and 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 a ferric–ferrous couple. The experimental data show that a parallel reaction, which oxidized sulfide to sulfate, occurred to a minor extent. Furthermore, the contribution of this reaction declined as the Eh of the solution decreased.

Compared to pyrite (Wiersma & 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-enrichment zones in copper-bearing ore deposits, where chalcocite is quickly oxidized to covellite.

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \qquad (15)$$

(Dutrizac & 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 that are produced percolate downward to the new water-table to form a second-cycle enrichment blanket with an even higher copper content (Anderson 1982). The fate of the elemental sulfur produced by reaction 6 is not clear, but some can be left behind in the oxidized zone of the deposit (Emmons 1917, Ramdohr 1969), whereas some is remobilized by recharge waters that periodically flush the oxidized zone. Sulfur-oxidizing bacteria probably convert the sulfur to a soluble form

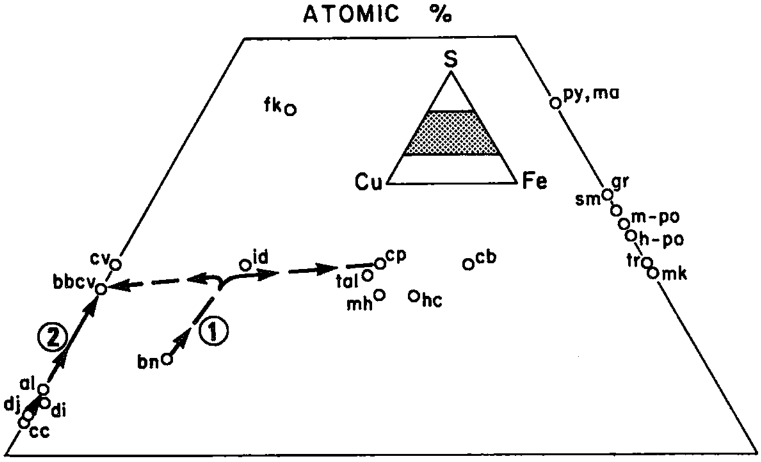

FIG. 6. Central portion of the phase diagram for the system Cu–Fe–S, indicating the reaction paths of bornite (1) and chalcocite (2) during the acid-etching procedure.

that subsequently moves downward through the reducing zone (Brierley & Brierley 1981). Thus the second-cycle oxidation of enriched blankets in porphyry copper deposits occurs *via*:

1) rapid conversion of chalcocite to *blaubleibender* covellite or covellite (or both),
2) relatively slow oxidation of covellite to Cu^{2+} and S°, whereas *blaubleibender* covellite oxidizes somewhat more rapidly.
3) slow oxidation of S° 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:

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

1. Chalcocite samples from Butte, Montana were pulverized in a Tekmar Model A10 Analytical Mill. Iron fillings, from the mill blade, were removed with a magnet.
2. The material was dry-sieved to recover the 100–200 mesh (75–150 μm) 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.
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-μm filter paper.

The original chalcocite contained minor amounts of bornite Cu_5FeS_4. Upon addition of the nitric acid, the bornite reacted to produce *blaubleibender* covellite and chalcopyrite, following the path indicated on Figure 6. The composition of the *blaubleibender* covellite phase after the acid treatment was $Cu_{1.3}S$, determined by electron-microprobe analysis. The reaction path of the initial chalcocite is also indicated on Figure 6.