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THE LEACHING OF COPPER FROM ANILITE AND THE PRODUCTION OF A METASTABLE COPPER SULFIDE STRUCTURE

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ABSTRACT

Natural leaching of copper sulfides (Goble 1980) results in a mineralogical change from djurleite ($Cu_{1.97}S$) to anilite ($Cu_{1.75}S$) to spionkopite ($Cu_{1.40}S$) to yarrowite ($Cu_{1.12}S$) to covelline (CuS). Anilite specimens leached artificially in a ferric sulfate solution show a compositional change corresponding to the change from anilite to yarrowite but do not develop the hexagonal yarrowite structure. These leached anilite specimens develop a structure similar to the pseudocubic structure of geerite ($Cu_{1.60}S$). The structure of leached anilite, by analogy with other copper sulfide structures, shows dimensional characteristics predicted for compositions of both $Cu_{1.18}S$ and $Cu_{1.60}S$. The artificially leached anilite remains metastably in this structure to compositions approaching covelline. X-ray powder patterns of leached anilite strongly resemble those of the *blaubleibend* covellines, raising questions about the identification of these phases by powder methods.

Keywords: anilite, leaching, copper sulfides, *blaubleibend* covelline.

SOMMAIRE

Dans la nature, le lessivage de sulfures de cuivre (Goble 1980) donne lieu à la transformation minéralogique djurléite $Cu_{1.97}S$ → anilite $Cu_{1.75}S$ → spionkopite $Cu_{1.40}S$ → yarrowite $Cu_{1.12}S$ → covelline CuS. Les échantillons d'anilite lessivés au laboratoire dans une solution de sulfate ferrique montrent un changement de composition allant jusqu'à la yarrowite mais sans apparition de la structure hexagonale de celle-ci. Ces échantillons lessivés ont plutôt la structure pseudocubique de la geerite $Cu_{1.60}S$ et, par analogie aux structures d'autres sulfures de cuivre, montrent les caractéristiques dimensionnelles prévues pour les compositions $Cu_{1.18}S$ et $Cu_{1.60}S$. L'anilite ainsi lessivée artificiellement adopte, de façon métastable, cette structure jusqu'à des compositions voisines de la covelline. Les clichés de poudre de ces produits ressemblent fortement à celui de la covelline *blaubleibend*, rendant douteuse l'identification de ces phases par cette méthode.

(Traduit par la Rédaction)

Mots-clés: anilite, lessivage, sulfures de cuivre, covelline *blaubleibend*.

INTRODUCTION

The structural characteristics of the eight low-temperature copper sulfide minerals identified to date are listed in Table 1. If allowance is made for the presence of covalently bonded sulfur layers such as exist in covelline, these structures can be described to a first approximation in terms of cubic and hexagonal close-packed arrays of spherical sulfur atoms, with the smaller copper atoms occupying interstitial positions. In the ideal cubic and hexagonal close-packed arrays, the distance D between sulfur layers is equal to $2R\sqrt{2/3}$, where R is the radius of the sulfur atoms. Relatively intense reflections from planes with spacings corresponding to both R and D can be identified on X-ray patterns of the copper sulfides. The observed spacings of R and D are plotted as functions of composition in Figures 1A and 1B, respectively; the ideal relationship $R = D/2\sqrt{2/3}$, determined from the data of Figure 1B, is plotted in Figure 1A.

The copper sulfides of Table 1 can be subdivided into three general groups based upon the information summarized in Figure 1A. Group 1 consists of those minerals with approximate cubic close-packing of the sulfur atoms (geerite, anilite, digenite). Group 2 contains those minerals with less copper than Group 1; these are characterized by hexagonal close-packed sulfur layers interspersed with covalently bonded sulfur layers (covelline, yarrowite, spionkopite). Group-3 minerals have more copper than the minerals in Group 1 and are characterized by approximately hexagonal close-packed sulfur layers (djurleite, chalcocite). However, the distance between layers in Group-3 minerals is too great for truly hexagonal close-packing. The structural stability of the sulfur layers is remarkable and permits wide compositional ranges for many of these minerals, even though significant parts of the ranges may be metastable relative to rearrangement of the sulfur framework.

TABLE 1. COMPOSITION, CRYSTALLOGRAPHY AND STABILITY OF THE EIGHT KNOWN COPPER SULFIDE MINERALS

†MINERAL NAME	COMPOSITION STRUCTURAL	COMPOSITION OBSERVED	CRYSTAL SYSTEM	SPACE GROUP	MAXIMUM THERMAL STABILITY (°C)*	REFERENCES
covelline	$Cu_{1.00}S$	$Cu_{1.00}S$	Hexagonal	$P6_3/mmc$	507	Berry (1954), Kullerud (1965), Potter (1977)
yarrowite	$Cu_{1.12}S$	$Cu_{1.0-1.2}S$	Hexagonal	$P\bar{3}m1$, $P3m1$ or $P321$	157	Moh (1964), Potter (1977), Goble (1980)
spionkopite	$Cu_{1.40}S$	$Cu_{1.3-1.5}S$	Hexagonal	$P\bar{3}m1$, $P3m1$ or $P321$	157	Moh (1964), Potter (1977), Goble (1980)
geerite	$Cu_{1.60}S$	$Cu_{1.5-1.6}S$	(Pseudocubic)	($F\bar{4}3m$)	?	Goble & Robinson (1980)
anilite	$Cu_{1.75}S$	$Cu_{1.75-1.80}S$	Orthorhombic	$Pnma$	70	Morimoto <u>et al.</u> (1969), Morimoto & Koto (1970)
digenite	$Cu_{1.80}S$	$Cu_{1.75-1.80}S$	Cubic	$Fd3m$	83	Morimoto & Kullerud (1963), Roseboom (1966)
djurleite	$Cu_{1.97}S$	$Cu_{1.93-1.97}S$	Orthorhombic	$Pmnm$	93	Morimoto (1962), Roseboom (1966), Potter & Evans (1976)
chalcocite	$Cu_{2.00}S$	$Cu_{1.99-2.00}S$	Monoclinic	$P2_1/c$	103	Roseboom (1966), Evans (1971), Potter (1977)

*only low-temperature forms are listed

†Pseudonyms: covelline ≡ covellite; yarrowite ≡ blaubleibend covelline I ≡ blue-remaining covelline; spionkopite ≡ blaubleibend covelline II ≡ blue-remaining covelline

In a study* of copper sulfides from southwestern Alberta, Goble (1980) noted that natural low-temperature leaching of copper from these sulfides led to the progressive replacement of djurleite by anilite, then spionkopite, yarrowite and finally, covelline. Throughout this replacement, the orientation of the crystallographic planes corresponding to *R* and *D* of Figure 1 remains constant; *D* is readily located perpendicular to the cleavage of all these minerals. *R* and *D* can be observed on X-ray precession photographs by choosing the hexagonal *a* and *c* axes as precession axes. For this reason, orientations will be referred to the hexagonal *a* and *c* axes throughout this paper.

Coupled with the loss of copper from the sulfides, there is a progressive change in cell dimensions as shown in Figure 1 and, for the range $Cu_{1.60}S$ to $Cu_{1.00}S$, a corresponding series of structural changes from the geerite to the spionkopite to the yarrowite to the covelline structure (Goble 1977, in prep.). The present study outlines an attempt to artificially reproduce the replacement of anilite by spionkopite or yarrowite while observing the structural change on the X-ray precession camera.

PROCEDURES

Natural specimens of anilite from the Yarrow Creek – Spionkop Creek area of southwestern Alberta were used for the leaching experiments. Associated minerals are bornite, yarrowite, spionkopite, djurleite, wittichenite and chalcopyrite. One set of anilite precession and Gandolfi films was used as a standard after comparison with the data of Morimoto *et al.* (1969). For the leaching experiments, cleavage fragments of anilite were identified on a polished surface using optical techniques, plucked from the polished surface, mounted on glass fibres and photographed using a 114.6-mm-diameter Gandolfi X-ray camera. The resulting films were compared with the standard anilite film to confirm the optical identification. Each anilite fragment was then transferred to a goniometer head and oriented using a precession camera (Mo radiation) to arrange as precession axes those anilite axes corresponding to the hexagonal *a* and *c* axes of yarrowite, spionkopite and covelline (anilite *b* and [101], respectively). These orientations are parallel and perpendicular, respectively, to the sulfur layers and to the cleavage in covelline, yarrowite, spionkopite, and anilite. Zero-level precession films were prepared and compared with the standard in-

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*Note that on p. 511, in the abstract, and on p. 513, second column, line 26 of that paper, the calculated density is given as 5.13 g/cm³. This applies to the natural material, $Cu_{1.32}S$. The calculated density for spionkopite $Cu_{1.4}S$ should be 5.33 g/cm³.

dexed anilite films. For the specimens used, this comparison revealed minor amounts of oriented djurleite intergrown with the anilite. The grain, still mounted on the goniometer head, was then immersed in an acidic ferric sulfate solution for a set period of time, with experimental conditions as outlined in Table 2. Upon removal from this solution, the grain was washed with distilled water and photographed on the X-ray precession camera. This process was repeated until a structural change was observed, at which time a complete set of X-ray films was prepared.

Upon completion of the X-ray analysis, run products were mounted in epoxy and analyzed using an Applied Research Laboratories AMX electron microprobe equipped with a Tracor Northern NS–880 energy-dispersion spectrometer. Fragments of unleached anilite also were analyzed. Operating conditions were: accelerating voltage 15 kV, sample current about 1.5 nA, beam diameter about 2 μm. Standards used were CuS and $Cu_{1.8}S$. Apparent concentrations were corrected for absorption, secondary fluorescence and atomic number effects using a general ZAF program, TAPEEMX2 (Dep. Geol. Sci., Queen's University).

CHEMICAL AND PHYSICAL CHANGES IN LEACHED ANILITE

Only very minor changes in the spacings of the crystallographic planes of anilite were observed as a result of immersion in the acidic ferric sulfate for periods of up to ten hours, whereas immersion for twelve hours produced a major structural change readily observable on precession photographs. Immersion times greater than twelve hours (up to ten days) produced no additional observable structural changes. No attempt was made to correlate the rate of change with concentration of the ferric sulfate solution. Therefore, the times listed indicate the chronology of change for only one particular set of conditions. C. Harlem and L. Whiteside (pers. comm. 1981) produced a

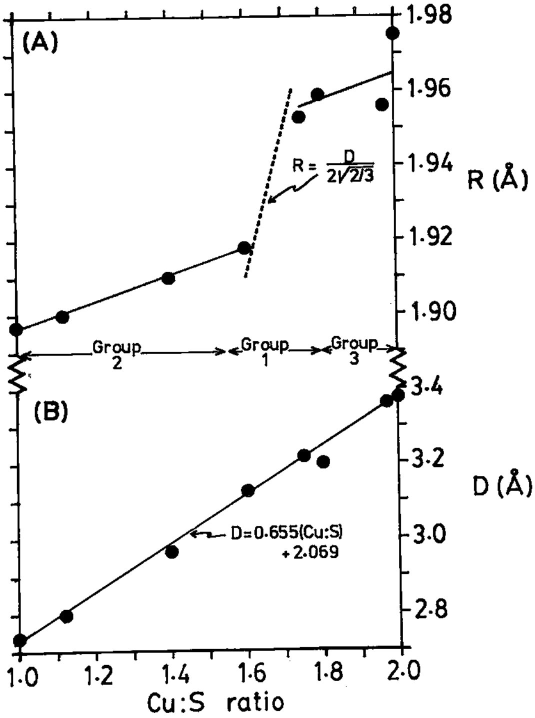

FIG. 1. Variation with composition: (A) of the radius *R* of sulfur atoms in the close-packed layers and (B) of average distance *D* between close-packed layers in the copper sulfides. Ideal structural compositions are used. The ideal relationship for close-packed structures, $R = D/2\sqrt{2/3}$, using *R* from Figure 1B, subdivides the copper sulfides into three groups as shown. *R* is the spacing (110) of covelline, (040) of anilite, (046) of djurleite, (630) of chalcocite (Potter & Evans 1976), (110) of jarrowite, (660) of spionkopite (Goble 1980), (220) of geerite (Goble & Robinson 1980) and (10.10.0) of digenite (Donnay *et al.* 1958). *D* is the spacing (006) of covelline, (202) of anilite, (800) of djurleite, $(\bar{2}04)$ chalcocite (Potter & Evans 1976), (00.24) of yarrowite, (00.14) of spionkopite (Goble 1980), (111) of geerite Goble & Robinson 1980) and (555) of digenite (Donnay *et al.* 1958). Modified from Goble (1977).

TABLE 2. CONDITIONS FOR LEACHING EXPERIMENTS

RUN TIME	TEMPERATURE (°C)	$Fe_2(SO_4)_3 \cdot xH_2O$ SOLUTION pH	concentration	volume	SAMPLE SIZE	STRUCTURAL CHANGE
10 hours	25	~5	~10^{-3} M	~5 ml	~50x100x200 μm	none
12 hours*	25	~5	~10^{-3} M*	~5 ml	~50x100x200 μm	complete
7 days	25	~5	~10^{-3} M	~5 ml	~50x100x200 μm	complete
10 days	25	~5	~10^{-3} M	~5 ml	~100x200x200 μm	complete

*HARLEM & WHITESIDE (pers. comm. 1981) produced a structural change in 12 hours at $Fe_2(SO_4)_3 \cdot xH_2O$ concentrations of 10^{-5} M; the change in structure occurred over a period of 3 - 5 minutes.

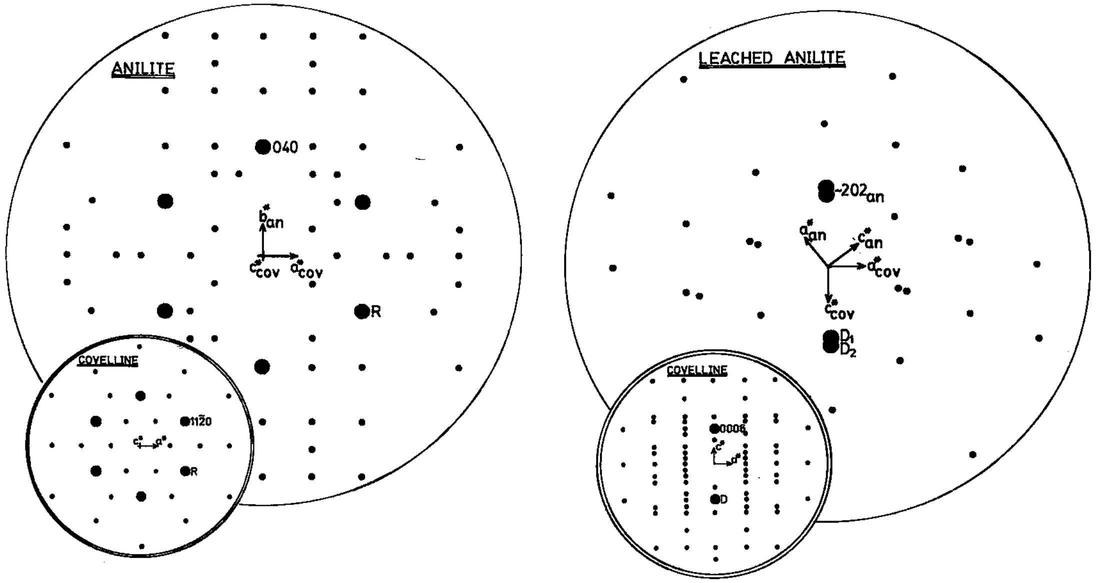

FIG. 2. Observed precession data for anilite: (A) perpendicular to the (101) cleavage and to the sulfur close-packed layers in the structure and (B) parallel to the (101) cleavage and to the sulfur close-packed layers in the structure. The reciprocal lattice of covelline in the equivalent orientations is reproduced on a smaller scale on the lower left of both figures. The positions of the reciprocal axes of anilite and covelline are indicated, as are the *D* and *R* reflections of Figure 1.

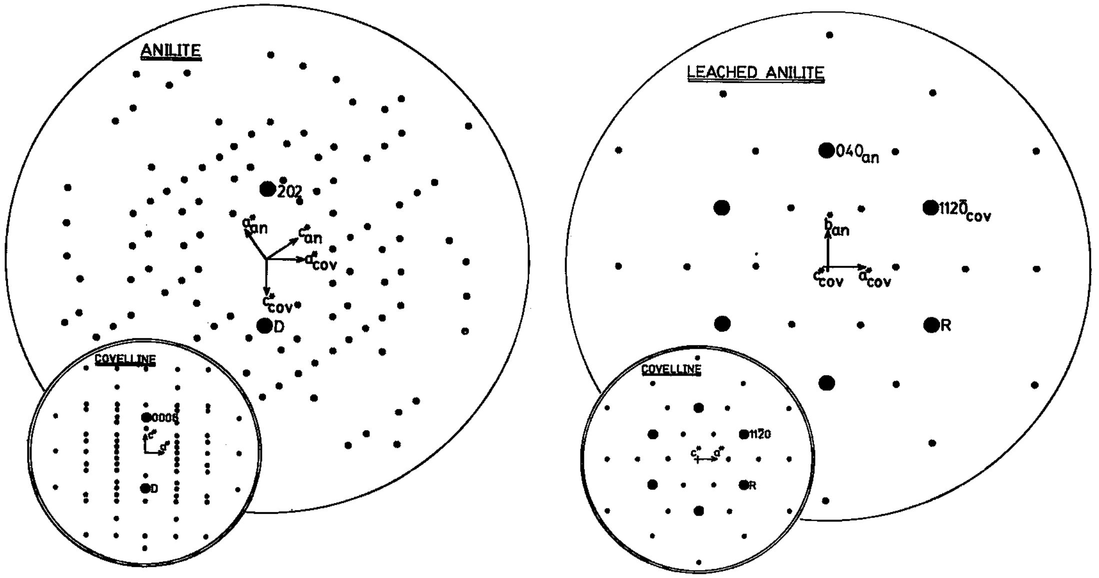

FIG. 3. Observed precession data for anilite leached in acidic ferric sulfate solution for twelve hours. Orientations are the same as in (A) Figure 2A and (B) Figure 2B.

structural change after twelve hours in a similar experiment; the complete change took place over a period of 3 to 5 minutes.

The reciprocal lattice of anilite as seen on precession photographs (precession axes $c_{\text{hexagonal}}$, $a_{\text{hexagonal}}$) is reproduced in Figures 2A and 2B. The reciprocal lattice of the leached product after immersion in acidic ferric sulfate solution for twelve hours, using the same orientations, is shown in Figures 3A and 3B. For comparison purposes, the reciprocal lattice of the hexagonal sulfide covelline in the equivalent positions is shown on a smaller scale in the lower left corner of both figures. The reciprocal lattices of yarrowite and spionkopite are similar to that of covelline (Goble 1980).

Using $c_{\text{hexagonal}}$ as a precession axis, the reciprocal lattices of anilite (Fig. 2A) and leached anilite (Fig. 3A) are very similar. However, the spacing of the *R* plane (110 covelline, 040 anilite) decreases from 1.958 to 1.902 Å, the spacings of other planes decrease by a corresponding amount, and the diffraction symmetry changes from twofold to sixfold. The reciprocal lattice of leached anilite is virtually identical to that of covelline in this orientation.

Using $a_{\text{hexagonal}}$ as a precession axis, the reciprocal lattices of anilite (Fig. 2B) and leached anilite (Fig. 3B) are again somewhat similar, but there has been a loss of numerous anilite reflections and an addition of some reflections of leached anilite; the spacings of the remaining anilite reflections have changed. The reciprocal lattice of leached anilite does not, however, resemble the reciprocal lattice of covelline or the similar reciprocal lattices of yarrowite and spionkopite, as was expected from the observed replacement sequence in natural specimens. It does strongly resemble a geerite (and sphalerite) reciprocal lattice in this orientation; the reciprocal lattices of leached anilite and geerite are shown at the same scale in Figure 4. One striking difference between the reciprocal lattices of leached anilite and geerite in this orientation is the doubling of some reflections on the former, the most important doublet being two reflections corresponding to the *D* spacing (111 geerite, ~202 anilite). The spacings for this doublet are 3.11 Å (D_1) and 2.82 Å (D_2) as compared with 3.128 Å for geerite.

Gandolfi simulated powder patterns were prepared for the leached anilite; lines on the patterns are diffuse and difficult to measure accurately, similar to reflections commonly ob-

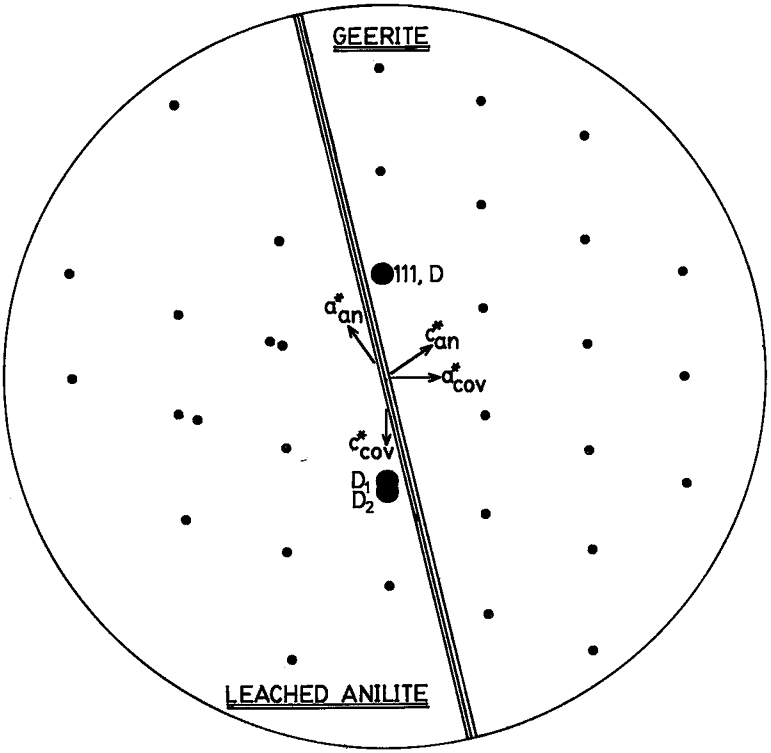

FIG. 4. Observed precession data for geerite (right) and leached anilite (left) in the same orientations as in Figures 2B and 3B.

TABLE 3. X-RAY POWDER DATA FOR LEACHED ANILITE AND SELECTED NATURAL AND SYNTHETIC BLAUBLEIBEND COVELLINES

LEACHED ANILITE		BLAUBLEIBEND COVELLINE							
		natural (yarrowite) (Goble 1980)			synthetic (Rickard 1972)			synthetic (Frenzel 1959)	
I_{obs}	d_{obs} (Å)	I_{obs}	d_{obs} (Å)	hkℓ	I_{obs}	d_{obs} (Å)	hkℓ	I_{obs}	d_{obs} (Å)
25	3.273	<5	3.293	100	5	3.28	100		
10	3.108	8	3.215	104	20	3.22	101	vw	3.24
50	3.041	55	3.061	108	70	3.05	102	s	3.07
15	2.844	20	2.796	00.24	40	2.81	103	m/s	2.85
20	2.730	35	2.767	10.13	30	2.75	006	m	2.73
		8	2.075	(10.25)	5	2.09	106		
					5	2.06	008		
100	1.888	100	1.899	110	100	1.896	107	vs	1.896
								vw	1.800
<5	1.761	15	1.731	10.33	5	1.741	108	vw	1.728
5	1.637	5	1.639	204				vw	1.620
40	1.567	15	1.572	11.24	5	1.558	116	m	1.567

All reflections on the leached anilite powder photograph are very diffuse. Measurement of spacings on precession photographs of leached anilite determines values of 2.82 and 3.11 Å for the doublet reflections equivalent to (006) of covelline, and 1.902 Å for the reflection equivalent to (110) of covelline.

TABLE 4. ELECTRON-MICROPROBE ANALYSES OF ANILITE AND ANILITE LEACHED IN ACIDIC FERRIC SULFATE

Time Leached	% Cu	% S	Σ %	Cu:S	Comments
unleached An	79.52	22.06	101.58	1.82	32% Dj, 68% An
unleached An	80.37	22.04	102.41	1.84	41% Dj, 59% An
12 hours	69.33	32.37	101.70	1.08	
12 hours	69.04	29.91	98.95	1.16	
12 hours	68.2	29.9	98.1	1.15	average = 1.15
12 hours	67.1	28.1	95.1	1.20	
7 days	67.31	31.58	98.89	1.08	
7 days	69.4	31.9	101.3	1.10	
7 days	69.9	31.8	101.7	1.11	average = 1.10
7 days	69.8	31.5	101.2	1.12	
10 days	68.43	32.58	101.01	1.06	
10 days	67.22	33.36	100.58	1.02	
10 days	70.15	34.79	104.94	1.02	average = 1.04
10 days	70.80	33.14	103.94	1.08	

Percentages of anilite (An) and djurleite (Dj) are calculated based upon ideal stoichiometric compositions of $Cu_{1.75}S$ and $Cu_{1.97}S$, respectively; X-ray precession films suggest that much less djurleite is in fact present. Standards used are CuS and $Cu_{1.8}S$ for Cu and S. ZAF corrections applied.

served in the *blaubleibend* covellines. Table 3 lists the powder data for leached anilite and shows comparable data for *blaubleibend* covellines presented by earlier workers (Frenzel 1959, Rickard 1972, Goble 1980). The powder pattern of leached anilite is very similar to the pattern of yarrowite (Goble 1980) and is virtually indistinguishable from the *blaubleibend* covelline patterns presented by Rickard (1972) and Frenzel (1959).

Results of microprobe analyses of some of the anilite used in the experiment and of anilite grains leached in ferric sulfate solutions for periods of twelve hours, seven days and ten days are shown in Table 4. The starting material shows an excess of copper compared with that present in stoichiometric anilite ($Cu_{1.75}S$). Faint djurleite reflections are present on the precession photographs; this intergrown djurleite probably accounts for some of the excess. Microprobe analyses of the associated djurleite show traces of iron (up to 0.4%) and silver. No components other than copper and sulfur were detected in the anilite fragments used. After immersion in acidic ferric sulfate for twelve hours, the anilite composition changed from $Cu_{1.83\pm0.01}S$ to $Cu_{1.14\pm0.06}S$, after seven days to $Cu_{1.10\pm0.02}S$ and after ten days to $Cu_{1.05\pm0.03}S$. No evidence of compositional zoning was noted on X-ray patterns or in microprobe analyses, nor was there evidence of detectable quantities of iron entering the structure. The "ideal" composition of leached anilite can be determined using the spacings of those planes corresponding to *D* and *R* and the structural–compositional relationships of Figures 5A and 5B, respectively. Precession photographs were used to determine the spacings because the reflections were sharper than on the Gandolfi photographs. The *R* reflection has a spacing of 1.902 Å, corresponding to an "ideal" composition of $Cu_{1.18}S$: the *D* reflection is a doublet with spacings of 3.11 and 2.82 Å, corresponding to "ideal" compositions of $Cu_{1.60}S$ and $Cu_{1.16}S$, respectively.

The specimens of leached anilite used in the microprobe analyses were examined using the reflected-light microscope. In air the material is bireflectant in blue and bluish white; in oil these colors are slightly darker, and the blue takes on a violet tint similar to that observed in yarrowite. Under crossed nicols the leached material is strongly anisotropic in orange. The extinction positions are oblique to the anilite cleavage, in contrast to natural *blaubleibend* covellines, which show extinction positions parallel and perpendicular to this cleavage when in replacement of anilite.

DISCUSSION

The material produced by leaching anilite in acidic ferric sulfate solution has a structure approximately the same as that of geerite $Cu_{1.6}S$. In fact, one reflection of the *D* doublet (D_1 in Fig. 3B) has a spacing corresponding to an ideal structural composition of $Cu_{1.6}S$. This structure represents the lowest possible Cu:S ratio that still retains the cubic close-packing of sulfur atoms characteristic of Group-1 copper sulfides (Goble 1977, in prep.). This reflection in the doublet has a spacing consistent with the majority of reflections in this orientation of the reciprocal lattice. The spacing of the second reflection of the *D* doublet (D_2 in Fig. 3B) is anomalous in this orientation, but is consistent with the *R* reflection in indicating a composition of $Cu_{1.16-1.18}S$, very close to the analyzed composition of $Cu_{1.01-1.20}S$. Natural material in this compositional range has the hexagonal structure of yarrowite $Cu_{1.12}S$, a structure distinctly different from that of geerite.

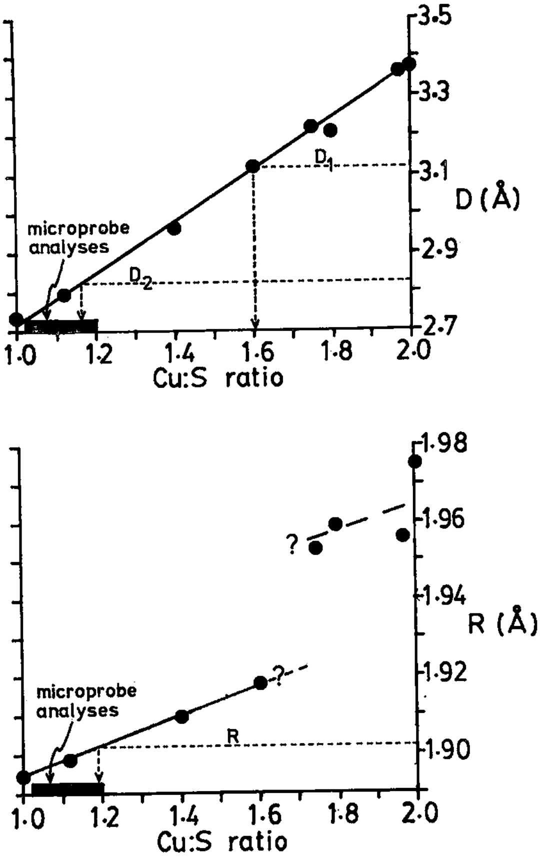

FIG. 5. Variation with composition: (A) of distance *D* and (B) of radius R for the copper sulfides. The spacings of the *D* doublet and of the *R* reflection of leached anilite are shown with the compositions determined for the structure from these spacings. The compositional range determined for the leached anilite by microprobe analysis is indicated on the composition axis. Sources of data are as in Figure 1.

For leached anilite, the sulfur-to-sulfur spacing in the close-packed layers (*R*) and one of the spacings between these layers (D_2) are consistent with the analyzed composition. However, the overall average spacing between the sulfur layers (D_1) is not consistent with this analyzed composition. The most probable explanation for these observed changes in the anilite structure is that anilite, upon loss of copper through artificial leaching, changes into a material having the geerite structure. With further removal of copper from the material, sulfur-to-sulfur distance (*R*) in this structure decrease, but the material remains metastably in the geerite structure. Some formation of covalent sulfur–sulfur bonds such as those observed in covelline, yarrowite and spionkopite may occur, but these covalently bonded sulfur-sulfur pairs are not sufficiently ordered into planes parallel to one another to form the hexagonal structures observed in these minerals. Therefore, the spacings of the *R* reflection and one of the *D* doublet (D_2) accurately reflect the actual composition of the material, whereas the spacing of the other reflection of the *D* doublet (D_1) reflects the ideal composition of the structure of the material. This interpretation is reinforced by the observation of Goble (1977, in prep.) that the analyzed compositions of spionkopite and geerite vary from the structural compositions determined using Figure 5 and other structural data.

Examination of the X-ray powder data presented in Table 3 reveals one other very important feature about the structure of leached anilite. Powder patterns of leached anilite are very similar to the powder patterns of yarrowite and of synthetic *blaubleibend* covellines prepared by such workers as Rickard (1972) and Frenzel (1959). Goble (1980) has shown that yarrowite, one type of *blaubleibend* covelline, has a structure distinctly different from that shown here for leached anilite. Judging from the powder data of Table 3 alone, it is difficult to say whether in fact these previous workers synthesized material having a structure similar to leached anilite or to yarrowite, particularly with the characteristically weak and diffuse reflections observed in these phases. An important consequence is that powder patterns alone are not sufficient to identify synthetic *blaubleibend* covellines. Two possible methods of positive identification are suggested: 1) single-crystal X-ray patterns of *blaubleibend* covellines will exhibit hexagonal symmetry, whereas leached anilite-type phases will not unless they are twinned; (2) on polished sections, *blaubleibend* covellines have extinction parallel to the cleavage, whereas leached anilite-type phases will not unless they are twinned. For fine grained, artificially precipitated material such as that produced by the method of Rickard (1972), differentiation of *blaubleibend* covelline and the leached anilite-type phase will be particularly difficult, if not impossible.

This uncertainty in the structural identification of synthetic analogues of the *blaubleibend* covellines is of particular interest when applied to the work of Potter (1977). Potter showed the synthetic material of compositions $Cu_{1.1}S$ and $Cu_{1.4}S$, corresponding compositionally to the minerals yarrowite and spionkopite of Goble (1980), to be metastable. Inasmuch as Potter's identification of these phases was based upon X-ray powder-diffraction and microprobe analyses, the possibility exists that he was in fact looking at varieties of the metastable structure of geerite (or of leached anilite) detected in this investigation rather than at yarrowite and spionkopite. [Potter recognized that one of his *blaubleibend* covellines had a digenite-like structure and suggested that *blaubleibend* covellines form because of the difficulty in nucleating normal covelline with its hexagonal close-packed structure.] Therefore, his conclusion that *blaubleibend* covellines of compositions $Cu_{1.1}S$ and $Cu_{1.4}S$ are metastable phases in the system copper–sulfur becomes ambiguous; one may reasonably postulate that yarrowite $Cu_{1.12}S$ and spionkopite $Cu_{1.4}S$ are stable phases in the system copper–sulfur, whereas the leached anilite-type synthetic phases $Cu_{1.1}S$ and $Cu_{1.4}S$ are metastable.

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REFERENCES

BERRY, L.G. (1954): The crystal structure of covelline, CuS, and klockmannite, CuSe. *Amer. Mineral.* **39**, 504-509.

DONNAY, G., DONNAY, J.D.H. & KULLERUD, G. (1958): Crystal and twin structure of digenite, Cu_9S_5. *Amer. Mineral.* **43**, 228-242.

EVANS, H.T., JR. (1971): Crystal structure of low chalcocite. *Nature* **232**, 69-70.

FRENZEL, G. (1959): Idait und "blaubleibender Covellin". *Neues Jahrb. Mineral. Abh.* **93**, 87-132.

GOBLE, R.J. (1977): *The Mineralogy, Composition, and Crystal Structure of Selected Copper Sulphides from the Belt–Purcell Supergroup, Southwest Alberta, Canada.* Ph.D. thesis, Queen's Univ., Kingston, Ontario.

——— (1980): Copper sulfides from Alberta: yarrowite Cu_9S_8 and spionkopite $Cu_{39}S_{28}$. *Can. Mineral.* **18**, 511-518.

——— & ROBINSON, G. (1980): Geerite, $Cu_{1.60}S$, a new copper sulfide from deKalb Township, New York. *Can. Mineral.* **18**, 519-523.

KULLERUD, G. (1965): Covellite stability relations in the Cu–S system. *Freiberger Forschungshefte* **C186**, 145-160.

MOH, G.H. (1964): Blaubleibender covellite. *Carnegie Inst. Wash. Year Book* **63**, 208-209.

MORIMOTO, N. & KOTO, K. (1970): Phase relations of the Cu–S system at low temperatures: stability of anilite. *Amer. Mineral.* **55**, 106-117.

———, ——— & SHIMAZAKI, Y. (1969): Anilite, Cu_7S_4, a new mineral. *Amer. Mineral.* **54**, 1256-1268.

——— & KULLERUD, G. (1963): Polymorphism in digenite. *Amer. Mineral.* **48**, 110-123.

POTTER, R.W. II (1977): An electrochemical investigation of the system copper–sulfur. *Econ. Geol.* **72**, 1524-1542.

——— & EVANS, H.T., JR. (1976): Definitive X-ray power data for covellite, anilite, djurleite, and chalcocite. *J. Res. U. S. Geol. Surv.* **4**, 205-212.

RICKARD, D.T. (1972): Covellite formation in low temperature aqueous solutions. *Mineral. Deposita* **7**, 180-188.

ROSEBOOM, E.H., JR. (1966): An investigation of the system Cu–S and some natural copper sulfides between 25° and 700°C. *Econ. Geol.* **61**, 641-672.

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