

STRUCTURAL AND COMPOSITIONAL CHANGES IN COPPER SULFIDES DURING LEACHING AND DISSOLUTION

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ABSTRACT

Many recent studies (e.g., Potter 1977, Goble 1980, 1985) deal with the stability of blue-remaining covelline. This study shows that leaching and dissolution of synthetic digenite or anilite, in acidic ferric sulfate solution, produce metastable polymorphs of geerite, yarrowite, spionkopite, covelline and CuS_2 ; the structures contain the sulfur atoms in cubic close-packing. Using X-ray-diffraction patterns, eight stages of transformation have been identified in the leaching of digenite to forms containing less copper. The phases produced do not have the typical optical properties of blue-remaining covelline, nor its hexagonal structure. These transformations were produced at leachate concentrations greater than 10^{-3} M. In weaker leachates, digenite and anilite structures alternate in a constant time-cycle, in which digenite grains first leach to anilite and then quickly return to the digenite structure. Using synthetic chalcocite, at least two leach paths are observed: 1) in weak solutions ($\leq 10^{-2}$ M), chalcocite leaches to tetragonal-phase chalcocite and then to digenite, following the digenite leaching paths from that time onward; 2) in stronger concentrations, synthetic chalcocite leaches directly to djurleite. With continued leaching, the resulting phases have the optical properties and X-ray-diffraction patterns of spionkopite and yarrowite. Under special conditions covelline is formed. Compositions of leached grains, determined by microprobe analysis, show a tendency for copper to be leached at an accelerated rate as leachate concentration is increased. Goble's (1985) composition-structure relationships are confirmed by the addition of new data-points.

Keywords: copper sulfides, leaching, digenite, anilite, geerite, chalcocite, djurleite, yarrowite, spionkopite.

SOMMAIRE

De nombreux travaux récents (par exemple, Potter 1977, Goble 1980, 1985) concernent la stabilité de la covelline *bleubleibende*. Notre étude montre que, par lixiviation et dissolution de digénite synthétique ou d'anilite, dans une solution de sulfate ferrique, on obtient des formes polymorphiques métastables de geerite, yarrowite, spionkopite, covelline et CuS_2 ; toutes leurs structures contiennent les atomes de soufre en paquetage cubique compact. Par diffraction X, nous avons pu identifier huit stades de transformation dans la lixiviation de digénite en formes à teneur moindre en cuivre. Les phases produites ne possèdent ni les propriétés optiques typiques de la covelline *bleubleibende*, ni sa structure hexagonale. Ces transformations se produisent lorsque la concentration de la lessive excède 10^{-3} M. Lorsqu'elle n'atteint pas cette valeur, un cycle

constant s'établit, au cours duquel les grains de digénite sont tout d'abord lixiviés en anilite, mais reviennent ensuite rapidement à la structure de digénite. Avec chalcocose synthétique, on note au moins deux processus de lixiviation: 1) en solution de concentration faible ($\leq 10^{-2}$ M), la chalcocose se transforme en chalcocose tétragonale, puis passe à la digénite, dont elle continue ensuite le processus de lixiviation; 2) en concentration plus forte, la chalcocose synthétique se transforme directement en djurleite. Si l'on continue la lixiviation, les phases résultantes montrent les propriétés optiques et les clichés de diffraction X de la spionkopite et la yarrowite. Dans des conditions spéciales, c'est la covelline qui se forme. La composition des grains lixiviés, déterminée par analyse à la microsonde électronique, indique que la lixiviation du cuivre tend à s'accélérer quand on accroît la concentration de la lessive. Les relations entre composition et structure établies par Goble (1985) sont confirmées par l'addition de données qui ajoutent des points nouveaux à la courbe expérimentale.

Mots-clés: sulfures de cuivre, lixiviation, digénite, anilite, geerite, chalcocose, djurleite, yarrowite, spionkopite.

INTRODUCTION

Blue-remaining (*bleubleibender*) covelline has been recognized for many years in the oxidation zone of ore deposits, where it occurs as an intermediate phase in the alteration of copper and copper-iron sulfides to optically normal covelline. Research by a number of investigators on both natural (Sillitoe & Clark 1969, Ottemann & Frenzel 1971, Goble & Smith 1973, Putnis *et al.* 1977, Goble 1980) and synthetic materials (Frenzel 1959, 1961, Moh 1964, 1971, Rickard 1972, Potter 1977, Putnis *et al.* 1977) has determined the presence of two varieties of blue-remaining covelline, having compositions of approximately $\text{Cu}_{1.1}\text{S}$ and $\text{Cu}_{1.4}\text{S}$.

Most investigators (e.g., Frenzel 1959, Rickard 1972) have interpreted X-ray patterns of blue-remaining covelline based upon a covelline-like unit cell. Some (e.g., Frenzel 1959, Moh 1971, Potter 1977) have noted a resemblance between the X-ray pattern of one of the blue-remaining covellines ($\text{Cu}_{1.4}\text{S}$) and that of digenite ($\text{Cu}_{1.8}\text{S}$). Using single-crystal X-ray data, Goble (1980) has shown that two of the natural blue-remaining covellines (yarrowite Cu_9S_8 or $\text{Cu}_{1.12}\text{S}$, spionkopite $\text{Cu}_{39}\text{S}_{28}$ or $\text{Cu}_{1.39}\text{S}$) have hexagonal symmetry and structures distinctly different from those of covelline and digenite. These

structures are based upon a combination of hexagonal close-packing of sulfur atoms and covalent bonding of sulfur atomic layers (Goble 1985).

Geerite (Cu_8S_5 or $\text{Cu}_{1.6}\text{S}$) is a recently described copper sulfide (Goble & Robinson 1980) that occurs in epitactic replacement of sphalerite. The structure of geerite is based upon cubic close-packing of sulfur atoms and is believed to be similar to the structure of digenite (Goble 1985); the dimensions of the close-packed network closely approximate those of the host sphalerite.

The two methods commonly used for synthesizing blue-remaining covelline consist of (1) leaching copper or copper-iron sulfides under oxidizing conditions in acidic aqueous solutions or (2) sulfurizing digenite or chalcocite under reducing conditions in organic solvents and in aqueous solutions (Moh 1971); X-ray powder patterns of the products resemble those of natural yarrowite and spionkopite (Goble 1980). Electrochemical investigations of the products of the second type of synthesis were interpreted by Potter (1977) as proof that blue-remaining covellines of compositions $\text{Cu}_{1.1}\text{S}$ and $\text{Cu}_{1.4}\text{S}$ are metastable phases in the Cu-S system. Goble (1981) has shown that with anilite ($\text{Cu}_{1.75}\text{S}$) as starting material, the first type of synthesis produces a material with a metastable structure similar to that of geerite but with a composition of $\text{Cu}_{1.11 \pm 0.09}\text{S}$. X-ray powder patterns of this material strongly resemble those of blue-remaining covelline synthesized by Frenzel (1959) and Moh (1971); these patterns are also similar to those of yarrowite, although the structure, as revealed by X-ray single-crystal patterns, is distinctly different from that of yarrowite (Goble 1985). Optical properties of the leached phase can be used to distinguish it from yarrowite provided that twinning is absent and that extinction can be determined as oblique to cleavage traces (Goble 1981). If twinning is present, the leached phase is optically indistinguishable from yarrowite. Therefore, whereas optical properties can be used to disprove the existence of yarrowite (and spionkopite) in synthetic material, they cannot be used to prove its existence. Inasmuch as Potter's (1977) identification of blue-remaining covelline was based upon X-ray powder diffraction, optical properties and microprobe data, the possibility exists that he was in fact looking at varieties of the metastable geerite (or leached anilite-type) structure detected by Goble (1981) rather than at yarrowite and spionkopite. Therefore, his conclusion that blue-remaining covellines of compositions $\text{Cu}_{1.1}\text{S}$ and $\text{Cu}_{1.4}\text{S}$ are metastable phases in the system copper-sulfur needs to be tested further, for one may reasonably postulate that yarrowite ($\text{Cu}_{1.12}\text{S}$) and spionkopite ($\text{Cu}_{1.40}\text{S}$) may be stable phases in the system copper-sulfur, whereas the geerite-type synthetic phases ($\text{Cu}_{1.1}\text{S}$ and $\text{Cu}_{1.4}\text{S}$) are metastable.

In summary, the unresolved problems in the sys-

tem copper-sulfur can be directly related to uncertainties in differentiating natural and synthetic phases. Many of the eight copper sulfide minerals have similar optical properties. The geerite structure can be maintained during synthetic leaching over a compositional range extending from geerite $\text{Cu}_{1.6}\text{S}$ to spionkopite $\text{Cu}_{1.4}\text{S}$ to yarrowite $\text{Cu}_{1.1}\text{S}$. If twinning is present, this material cannot be distinguished from the natural polymorphs using optical properties and X-ray powder patterns. Because previous workers relied on these to identify synthetic phases, uncertainties remain as to the validity of their conclusions.

The principal objective of this study was to determine the sequence of structural and compositional changes produced in leaching chalcocite, digenite and anilite as a function of time and leachate concentration. Once this information is quantified, it should be possible to test the validity of Potter's (1977) conclusions on the stability of blue-remaining covelline. An inherent part of the study is the relationship between the material produced and natural blue-remaining covelline and other copper sulfides. One long-range goal is to identify the stable assemblages and to establish a hierarchy of metastabilities among the others. Another is to understand the circumstances under which various paths of evolution and transition of metastable phases can be predicted and by which the genetic processes operating can be interpreted from the character of the final product.

EXPERIMENTAL METHODS AND PROCEDURES

Synthesis

Synthetic digenite and chalcocite were prepared using the standard techniques of synthesis described by Morimoto *et al.* (1969), Morimoto & Koto (1970) and Moh (1971). Weighed samples of research-grade copper and sulfur powder were sealed in evacuated silica tubes, heated in tube furnaces and then quenched. Evacuated conditions were maintained until leaching was to commence. Synthesized material had a sintered appearance, with numerous well-formed macroscopic crystals. The sintered portion was gently crushed between the fingers to avoid mechanical alteration of the structure from digenite to anilite, and sorted by sieving so that investigated grains were between 150 and 250 micrometres in diameter. Optical studies of polished sections show that these grains are an aggregate of many smaller grains, generally less than 50 micrometres in diameter.

Apparatus

Leaching was done by immersing sulfide grains and a quartz standard into a solution containing a

TABLE 1. COMPOSITION OF LEACHED GRAINS OF DIGENITE AS A FUNCTION OF CONCENTRATION OF FERRIC SULFATE LEACHATE AND DURATION OF THE LEACHING PROCESS

Leaching Time (min)	10^{-5} M Ferric Sulfate				10^{-2} M Ferric Sulfate				10^{-1} M Ferric Sulfate				1 M Ferric Sulfate				2 M Ferric Sulfate			
	wt % Cu	wt % S	Total Cu:S ratio	Cu:S	wt % Cu	wt % S	Total Cu:S ratio	Cu:S	wt % Cu	wt % S	Total Cu:S ratio	Cu:S	wt % Cu	wt % S	Total Cu:S ratio	Cu:S	wt % Cu	wt % S	Total Cu:S ratio	Cu:S
0	78.1	21.9	100.0	1.80	77.1	21.6	98.7	1.80	78.4	22.0	100.4	1.80	79.1	22.2	101.3	1.80	78.4	21.9	100.3	1.81
1	79.1	22.1	101.2	1.80	77.8	21.8	99.6	1.80	76.8	21.9	98.7	1.77	77.5	22.1	99.6	1.77	77.4	22.2	99.6	1.76
					77.3	22.1	99.4	1.77	78.1	22.1	100.2	1.78	78.6	22.7	101.3	1.75	78.1	23.8	101.9	1.66
					79.0	22.6	101.6	1.76	78.6	22.1	100.7	1.79	78.9	22.7	101.6	1.75	77.3	23.3	100.6	1.67
									78.2	22.3	101.0	1.76								
2	79.6	22.3	101.9	1.80	78.4	22.5	100.9	1.76	78.2	22.6	100.8	1.75	76.7	22.0	98.7	1.76	76.6	22.3	98.9	1.74
					77.9	22.4	100.3	1.76	78.5	22.8	101.3	1.74	77.8	22.5	100.3	1.75	77.6	22.7	100.3	1.73
					77.0	22.2	99.2	1.75					77.3	24.6	101.9	1.59	75.7	23.9	99.6	1.60
3	78.4	22.1	100.5	1.79	77.5	22.3	99.8	1.76	77.1	22.5	99.6	1.73	75.1	22.7	97.8	1.67	77.2	24.4	101.6	1.62
					78.6	22.8	101.4	1.74	75.8	23.4	99.2	1.63	77.0	24.3	101.3	1.63	74.4	23.6	98.0	1.59
					75.6	22.0	97.6	1.73	77.3	24.2	101.5	1.61	77.4	24.1	101.5	1.62	76.7	25.6	102.3	1.51
3.5	77.0	21.7	98.7	1.80	77.7	23.3	101.0	1.68	76.7	24.2	100.9	1.60	75.3	23.7	99.0	1.60	73.5	26.1	99.6	1.42
									75.4	23.8	99.2	1.59	74.7	24.9	99.6	1.51	73.1	26.2	99.3	1.41
									76.1	25.4	101.5	1.51	75.2	27.0	102.2	1.41	73.0	28.2	101.2	1.31
4	78.2	22.0	100.2	1.80	77.5	23.3	100.8	1.68	75.8	24.0	99.8	1.60	74.7	24.9	99.6	1.51	73.0	27.9	100.9	1.32
					76.6	23.2	99.8	1.67	73.3	24.7	98.0	1.50	74.5	25.6	100.1	1.47	74.9	26.9	101.8	1.40
												75.5	26.2	101.7	1.45	74.5	28.0	102.5	1.34	
5	76.7	21.0	98.3	1.80	78.6	23.8	102.4	1.67	75.1	26.2	101.3	1.45	72.0	28.0	100.0	1.32	68.0	31.4	100.0	1.10
					77.0	23.4	100.4	1.66	75.2	27.3	102.5	1.39	75.5	25.9	101.4	1.47	72.7	25.1	97.8	1.46
									72.7	27.4	100.1	1.34	72.1	25.7	97.8	1.41	73.1	28.2	101.3	1.31
6	78.6	22.2	100.8	1.80	77.7	22.3	100.0	1.76	75.0	23.6	98.6	1.60	72.5	26.4	98.9	1.39	66.8	32.7	100.5	1.03
					76.4	23.2	99.6	1.66	73.0	26.1	99.1	1.41	76.9	24.4	100.3	1.59	71.1	30.6	101.7	1.17
									73.1	27.2	100.3	1.36	70.8	27.5	98.3	1.30	69.4	29.2	98.6	1.20
									71.5	27.4	98.9	1.32	69.9	29.1	99.0	1.21	66.7	33.6	100.3	1.00
												73.2	27.2	100.4	1.36					
7	77.2	21.8	99.0	1.80	78.9	22.8	101.7	1.74	75.6	24.2	99.8	1.58	75.1	26.2	101.3	1.45	58.9	40.7	99.6	0.73
					77.1	23.3	100.4	1.67	74.1	26.8	100.9	1.40	74.2	27.6	101.8	1.35	66.4	33.2	99.6	1.01
					76.5	23.2	99.7	1.66	74.3	28.2	102.5	1.33	71.9	27.7	99.6	1.31	69.4	28.9	98.3	1.21
									71.3	27.7	99.0	1.30					69.8	31.7	100.5	1.11
10	79.3	22.3	101.6	1.79	76.2	21.9	98.1	1.75	71.0	29.2	100.2	1.23	70.5	23.6	98.6	1.60	71.3	29.2	100.5	1.23
					77.4	23.8	101.2	1.64	72.5	27.0	99.5	1.36	70.2	27.3	97.5	1.30	71.0	29.8	100.8	1.20
									72.0	30.0	102.0	1.21	70.4	28.9	99.3	1.23	61.2	41.2	102.4	0.75
									67.3	30.3	97.6	1.12	71.0	29.5	100.5	1.21	50.2	50.6	100.8	0.50
15	78.5	22.3	100.8	1.78	77.0	23.3	100.3	1.67	72.9	27.3	100.2	1.35	72.5	26.1	98.6	1.40	70.7	31.3	102.0	1.14
					77.3	23.5	100.8	1.66	71.0	27.3	98.3	1.31	67.7	33.7	101.4	1.01	65.3	33.3	99.6	0.99
					78.1	24.2	102.3	1.63	71.2	30.0	101.2	1.20	57.5	43.4	100.9	0.67	64.0	36.3	100.3	0.89
									69.0	31.7	100.7	1.10	50.5	49.8	100.3	0.51	58.1	43.8	101.9	0.67
50	78.1	22.2	100.3	1.78	75.5	23.0	98.5	1.66	66.7	33.6	100.3	1.30	72.3	27.4	99.5	1.33	68.3	34.1	102.4	1.01
					77.1	23.9	101.0	1.63	68.1	30.5	98.6	1.13	71.0	29.9	100.9	1.20	72.7	28.1	100.8	1.33
					73.1	26.4	99.5	1.40	67.2	33.9	101.1	1.00	67.8	30.7	98.5	1.11	69.4	29.5	98.9	1.19
												68.0	34.3	102.3	1.00	70.1	31.4	101.5	1.13	
100	77.3	22.3	99.6	1.75	76.5	23.7	100.2	1.62	72.3	27.4	99.7	1.33	73.6	26.4	100.0	1.41	70.5	29.3	99.8	1.21
					74.3	23.5	97.8	1.60	69.8	30.4	100.2	1.16	69.8	31.5	101.3	1.12	71.6	28.8	100.4	1.21
					74.5	24.7	99.2	1.52	68.1	34.4	102.5	1.00	65.6	32.7	98.3	1.01	67.8	31.9	99.9	1.07
300	76.5	21.9	98.4	1.76	76.4	24.1	100.5	1.60	72.8	27.8	100.6	1.32	71.4	27.3	98.7	1.32	73.2	32.2	101.0	1.08
					73.2	26.4	99.6	1.40	70.2	29.1	99.3	1.22	66.4	32.9	99.3	1.02	67.7	33.8	101.5	1.01
					69.2	29.1	98.3	1.20	66.9	31.8	98.7	1.06	66.3	34.8	101.1	0.96	69.1	30.9	100.0	1.12
					72.1	27.8	99.9	1.31	60.3	40.5	100.8	0.75	59.6	40.0	99.6	0.75	67.4	31.7	99.1	1.07
500	77.7	22.2	99.9	1.77	73.4	27.4	100.8	1.35	66.5	33.5	100.0	1.00	71.6	29.9	101.5	1.21	68.9	33.4	102.2	1.04
					74.1	25.6	99.7	1.46	70.8	29.5	100.3	1.21	68.6	30.7	99.3	1.13	68.8	30.8	99.6	1.13
					72.2	27.4	99.6	1.33	63.7	36.2	99.9	0.89	67.5	34.1	101.6	1.00	68.3	31.0	99.3	1.11
					71.7	28.6	99.3	1.31	63.1	36.2	99.3	0.88	64.4	36.4	100.3	0.89	66.8	31.7	98.5	1.06
					72.1	26.1	98.2	1.40									66.4	33.9	100.3	0.99
750	78.7	22.7	101.4	1.75	70.2	29.5	99.7	1.20	74.7	25.8	100.5	1.46	73.2	27.9	101.1	1.32	68.9	28.9	97.8	1.20
					69.8	30.6	100.4	1.15	71.6	30.1	101.7	1.20	67.9	31.9	99.8	1.07	69.5	30.8	100.3	1.14
					72.8	28.2	101.0	1.33	69.4	31.9	101.3	1.10	67.7	34.4	102.1	0.99	70.5	31.2	101.7	1.14
					67.3	31.4	98.7	1.08	66.5	34.2	101.7	0.98	62.9	36.1	98.0	0.88	67.7	33.1	100.8	1.03
1,000	77.2	22.1	99.3	1.77	70.6	29.4	100.0	1.21	72.0	27.6	99.6	1.32	71.7	29.5	101.2	1.23				
					73.1	28.2	101.3	1.31	67.9	34.0	101.9	1.31	69.1	31.5	100.6	1.11				
					65.0	36.8	101.8	0.89	57.4	43.9	101.3	1.01	67.8	31.3	99.1	1.09				
					59.6	41.2	100.8	0.73	50.2	50.6	100.8	0.66	65.6	33.1	98.7	1.00				
									71.4	27.5	98.9	0.50	66.9	33.4	100.3	1.01				
3,000	79.4	22.9	102.3	1																

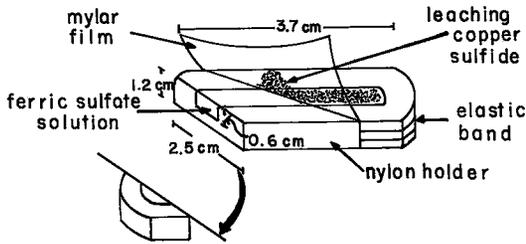


FIG. 1. Leaching apparatus used while monitoring composition of leaching grains on X-ray diffractometer. The copper sulfide grains are held to the mylar with a thin layer of cyanoacrylate glue.

grains in contact with the solution, avoiding trapped air bubbles, and sealed to the sample holder with an elastic band. The ratio of solution to mineral was large (approximately 2.25 cm^3 to 0.001 cm^3), so that all but the most dilute solutions remained essentially constant in composition throughout the experiments.

In stronger leachates, significant structural changes occur rapidly. Because of this, the above procedure needed to be very time-efficient, as monitoring with the X-ray diffractometer had to begin within twenty seconds of leach initiation. The holder was therefore kept as simple as possible.

Leaching was conducted using both synthetic chalcocite and digenite grains. All experiments were conducted over a narrow range of temperature (about $23^\circ \pm 1^\circ \text{C}$). Dutrizac *et al.* (1984) have shown that there is a considerable effect on leaching speed in bornite with temperature variation. A similar effect could be expected with chalcocite and digenite.

Monitoring structural changes

Structural changes were monitored during leaching by oscillating the X-ray diffractometer over $6^\circ 2\theta$ ($44^\circ - 50^\circ$), an interval that contains major structural peaks in each of the minerals being investigated. Filtered copper radiation was used. When a major peak change in the $6^\circ 2\theta$ interval was noted, a continuous scan ($35^\circ - 65^\circ$) was made while leaching continued. Quenching of the leach in distilled water was attempted in some instances, but in most cases this failed to completely halt structural changes. After three days of continuous monitoring, samples were removed from the diffractometer but kept in the same leachate for up to three years, subject to periodic re-investigation for additional structural changes. When a structural change was observed, a grain was plucked from the mylar, mounted on a glass fiber and further investigated using a 114.6-mm-diameter Gandolfi X-ray camera. The resulting films were compared to those of standard digenite, anilite, spionkopite, yarrowite and covellite.

In a second procedure, only peak height and position were monitored. With this technique, the goniometer was set at the top of a peak in the diffraction pattern for the structure being investigated, and changes in height of this peak were noted with time. This procedure was commonly utilized in conjunction with that previously described to detect changes in structure with time.

Stretched mylar has a very strong peak at about $29^\circ 2\theta$; the position and height vary during the leaching experiment. The other peaks from mylar and those from the glue are weak and broad, and easily subtracted from the spectrum. However, because of the peak at 29° , a section between 25° and $34^\circ 2\theta$ could not be investigated.

Monitoring compositional changes

After the structural change - time relationships had been determined, grains were leached under similar conditions, washed in distilled water and analyzed compositionally using a MAC-400 electron microprobe equipped with wavelength-dispersion spectrometers. Operating conditions were: operating voltage 12 kV, sample current 1.2 nanoamperes. The following standards were used: natural covellite (for Cu, S), bornite and chalcopyrite (for Fe). Apparent concentrations were corrected for absorption, secondary fluorescence and atomic number effects using the general ZAF program MAGIC IV (see Table 1 for analytical results).

RESULTS AND DISCUSSION

Weak leachate tests ($< 10^{-3} \text{ M}$ ferric sulfate)

No compositional or structural changes were observed when synthetic chalcocite was immersed in leachates with concentrations of less than 10^{-3} M ferric sulfate for periods of up to three years.

Weak leachates ($< 10^{-3} \text{ M}$) in contact with synthetic digenite under the conditions of this study produced cyclic variations in which the structure of the grains changed from the digenite to the anilite structure and back. In 10^{-3} M ferric sulfate solution, the digenite diffraction peak with $d = 1.967 \text{ \AA}$ (plane 10.10.0) gradually decreased in intensity over the first 100 minutes of leaching (Fig. 2). At the same time, peaks gradually appeared representing the anilite planes 040 ($d = 1.953 \text{ \AA}$), 400 ($d = 1.977 \text{ \AA}$) and 224 ($d = 1.962 \text{ \AA}$). The net result was a lessening of intensity of the original peak, with a gradual broadening of the base of the peak. A measure of the distortion from the digenite structure to the anilite structure in these grains is obtained by dividing the intensity of the peak by the base width, while maintaining an equal area within the peak. Area was determined by counting squares on the diffractometer.

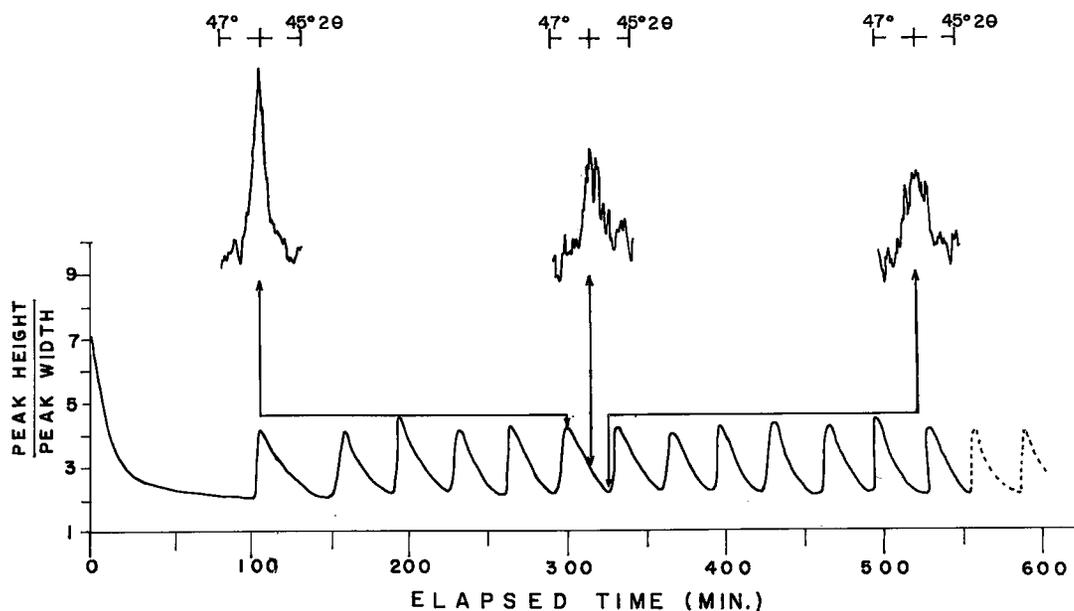


FIG. 2. Cyclic distortion of digenite plane (10.10.0) to anilite planes (040), (400) and (224) in ferric sulfate leachate of 10^{-5} M. Maximum distortion occurs at a peak height to width ratio of approximately 2.14. Representative diffraction-traces at three points in the cycle (dominantly digenite, mixed digenite/anilite and dominantly anilite) are shown above the main figure.

meter chart. This ratio is plotted as a function of time in Figure 2.

After leaching had continued for about 100 minutes, the majority of grains with the anilite structure changed rapidly back to the digenite structure. The ratio of the peak height to base doubled as the intensity of the monitored peak increased in less than one minute. All peaks representing the anilite structure were lost at this time and in each succeeding cycle. This change occurred simultaneously with the increase in height of the digenite peak, suggesting concurrent events and essentially eliminating solution reprecipitation as a possibility. Figure 2 shows the diffractometer trace at three points in this cycle. As leaching continued, this pattern of change was seen to continue in a cyclical manner. The sudden change always occurred when a certain ratio of peak height to base was reached (under the conditions of these experiments, about 2.14). After 300 minutes the variation in the periodicity of the cycles stabilized at 32 minutes 37 seconds ± 15 seconds (Fig. 2). Although these experiments were halted after ten hours, the material was left in the leachate for up to three years, and then re-examined using the above techniques; a cyclical change with a period of 32 minutes was still observed. It should be noted that the majority of the grains follow the same periodicity in cyclic change, even though they are not in contact on the mylar of the sample holder.

Intermediate leachate tests (10^{-2} to 10^{-1} M ferric sulfate)

When the concentration of the leachate is held at between 10^{-2} and 10^{-1} M, copper is leached from both synthetic chalcocite and digenite. As concentration of ferric sulfate is increased, leaching occurs at an accelerated rate (Fig. 3). When approximately 40% of the copper has been removed from the material, leaching seems to reach an equilibrium condition, as shown by the merging of the curves in Figure 3. This equilibrium is independent of leachate strength, and must therefore reflect an approach to a more stable structural state.

In intermediate leachates (10^{-2} to 5×10^{-2} M), chalcocite leaches slowly to tetragonal-phase chalcocite (Roseboom 1966) and then to digenite and anilite. From these structures it follows the same leaching pattern described below for digenite.

As digenite leaches in ferric sulfate concentrations greater than 10^{-3} M, a series of structural changes occur resulting in a group of interacting metastable structures that all seem to be based on the geerite (sphalerite-like) cubic structure, with the possible exception of type VIII. Each of these geerite-type structures has a main diffraction-peak in the investigated 2θ region, which Goble (1985) has related to the approximate radius of atoms of sulfur within the structure.

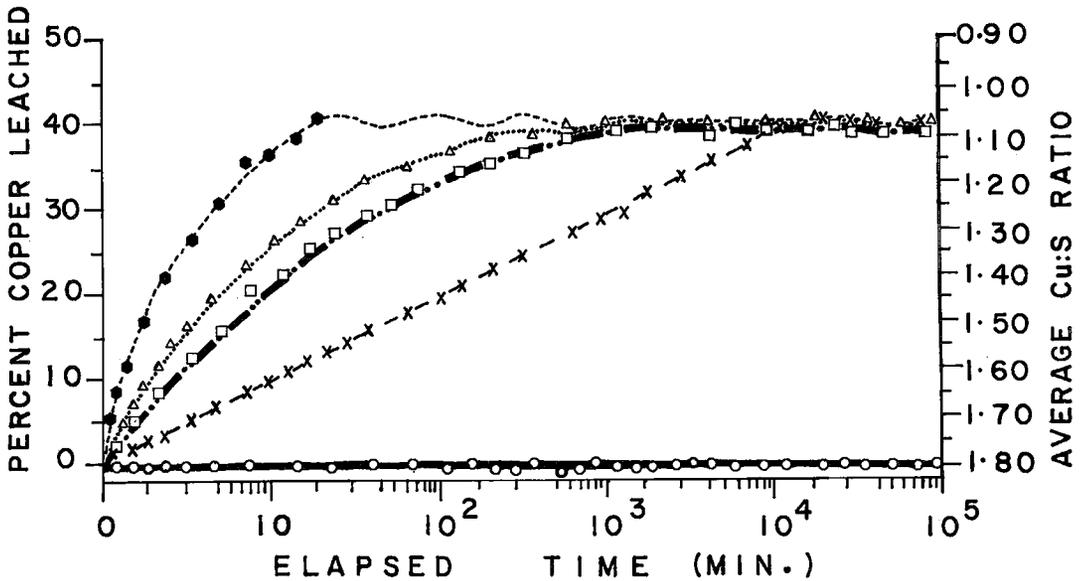


FIG. 3. The leaching of copper from digenite grains leached at 23°C in ferric sulfate media. Data are based upon microprobe analyses. A single data-point may represent multiple analyses. Ferric sulfate concentrations: open circles 10^{-3} to 10^{-2} M, crosses 10^{-2} M, open squares 10^{-1} M, open triangles 1 M, hexagons 2 M. "O" on the time axis indicates the origin of sample measurement, not zero time on this logarithmic scale.

The results presented are a compilation of thirteen experiments run under similar conditions. Erratic patterns occur in each experiment but, because the standard deviation in counts is a function of total counts, when the thirteen sets of results are added together the random variations tend to cancel each other out, leaving relatively sharp peaks whose size and position vary as leaching continues.

A compilation of the structural changes produced on leaching digenite as indicated in X-ray-diffraction data is shown in Figures 4a and 4b. Within two minutes of leach initiation, the typical grain has already changed from the digenite (d for monitored peak = 1.967 Å) to the anilite (d for monitored peak averages ~1.962 Å) structure. In the next ten minutes, anilite undergoes a series of three structural changes; d values for the peak monitored are 1.957 Å (elapsed time ~ 5 minutes, type-I structure), 1.945 Å (elapsed time ~ 7 minutes, type-II structure), 1.933 Å (elapsed time ~ 10 minutes, type-III structure). After leaching for about 20–30 minutes, a structure whose X-ray-diffraction pattern matches that of geerite (Goble & Robinson 1980) forms (d 1.918 Å, type-IV structure). After maintaining the geerite structure for about 30 minutes, the grains change to one of two closely related structures whose diffraction patterns resemble that identified in spionkopite (Goble 1980) (d 1.910, 1.907 Å, type-V structure). However, in polished section these grains do not have the parallel extinction observed in this mineral by

Goble (1981). During the next hour, another series of three discrete structural changes occur, resulting in a set of related X-ray patterns closely resembling that of the blue-remaining covellite, yarrowite (Goble 1980) (d 1.903, 1.900 and 1.898 Å, type-VI structure). Again, these grains lack the typical optical properties of yarrowite, and appear to have a cubic closest-packed structure, as Goble (1981) showed in a leaching study of single crystals of anilite.

As leaching continues, a new structure, with weak reflections, appears. This seems to be a cubic polymorph of the hexagonal covellite structure (d 1.895 Å, type-VII structure). This structure is extremely unstable, and in several hours degenerates into a series of closely related, very poorly developed structures whose diffraction patterns resemble that of the high-pressure form CuS_2 (d 1.892, 1.887, 1.883 and 1.877 Å, type-VIII structure). This form has been produced only under pressures in excess of 10 kbar (Munson 1966, Taylor & Kullerud 1972), demonstrating clearly that this is a metastable structure. With continued leaching, the last structure (type-VIII) gradually disappears over the next 15–20 hours, and structures of type VII and VI become dominant with time.

As shown in Figure 4b, several structures are present in the sample at any one time. These structures are not stable, but change back and forth into one another. When the grains are plucked, washed

and investigated with the Gandolfi camera, films do not show the discrete lines identified by careful investigation on the X-ray diffractometer chart, but show instead a broad diffuse band covering the entire region in which these lines can be found. The presence of the broad bands on the Gandolfi films suggests that cycling between the structures continues after the samples are removed from solution. This is confirmed by direct observation on the diffractometer of structural changes after removal of samples from contact with the leaching solution and by our inability to quench samples. This is to be expected if these are metastable phases that change back and forth over a short interval of time. During the several hours involved in exposing the film in a Gandolfi camera the lines from several structures tend to merge into broad bands.

Optical properties indicate that the structures of minerals based on variations of hexagonal close-packing (*i.e.*, covellite, yarrowite, spionkopite) are not present in this leaching sequence. Instead, all the major known structures in this sequence are based on cubic close-packing (*i.e.*, geerite is rhombohedral/pseudocubic, anilite is orthorhombic/pseudocubic, leached anilite forms are rhombohedral/pseudocubic, and high-pressure CuS_2 is orthorhombic/pseudocubic). Therefore, it is reasonable to assume that all the metastable structures are also based on cubic close-packing, and that no major changes occur in the packing of the sulfur atoms throughout the leaching of digenite. The structural changes are the result of loss of copper from the structure and minor changes in the layers of sulfur, resulting in compression of the structure, as evidenced by the decrease in the d value of the X-ray reflection monitored throughout the leaching (Fig. 4a). This spacing is approximately equal to the radius of the sulfur atoms in this structure (Goble 1985).

Although it is difficult to obtain good complete diffraction-patterns for each of these structures independent of others under the conditions of these experiments, it is clear from the sequence of changes produced and from optical properties that the hexagonal blue-remaining covellines, yarrowite and spionkopite are not formed during the leaching of digenite. The type-V and -VI structures are metastable polymorphs of yarrowite and spionkopite, but have cubic close-packing of the sulfur atoms rather than the combination of hexagonal close-packing and covalent bonding observed in the yarrowite and spionkopite structures by Goble (1985). In this respect, our results agree with those of Goble (1981). However, we cannot as yet reach any conclusions regarding the stability or metastability of yarrowite and spionkopite.

Strong leachate tests ($> 10^{-1} M$ ferric sulfate)

With higher concentrations of ferric sulfate, the

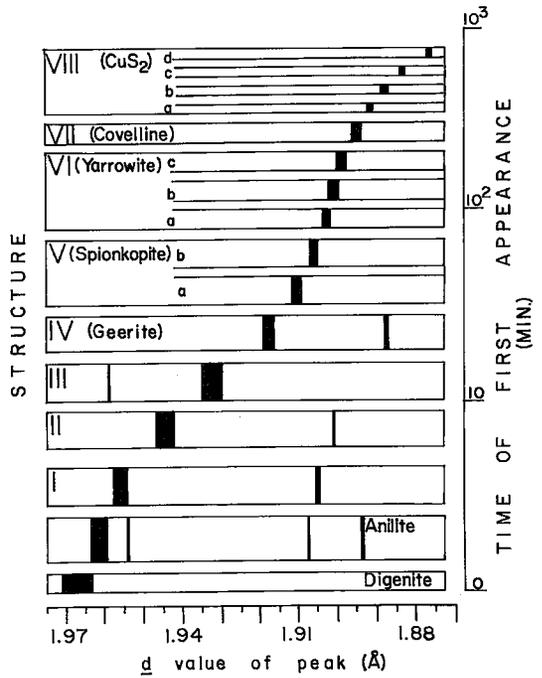


FIG. 4A. Position of X-ray-diffractometer peaks ($44-50^\circ 2\theta$) for various leaching-produced structures as a function of time of first appearance. Line width represents relative intensity of peak.

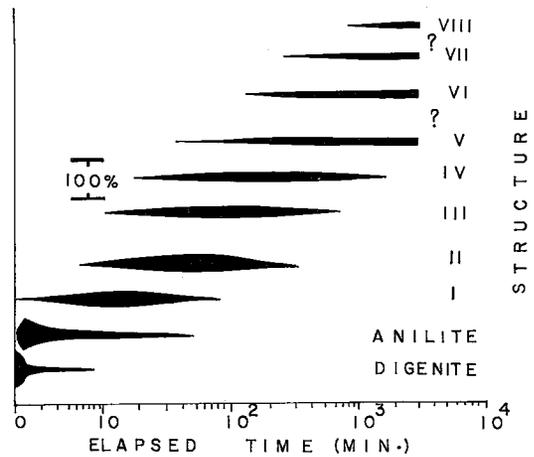


FIG. 4B. Relative proportion of each of the observed structural types present with time, based on relative intensity of X-ray-diffraction peaks ($10^{-2} M$ ferric sulfate). "O" on the time axis indicates the origin of samples measurements, not zero time on this logarithmic scale.

leaching of digenite produces no structural changes other than those observed in weaker solutions (see above). The speed with which these structural

changes occur is, however, greatly accelerated, as shown in Figure 3. For example, at a concentration of 2 M, the type-VIII structure is reached in about ten minutes.

Higher concentrations of solution combined with a chalcocite starting material, however, gives dramatically different results. When concentrations of ferric sulfate greater than 10^{-1} M are used, instead of leaching from chalcocite to tetragonal chalcocite, chalcocite transforms first to a form whose diffraction pattern is identical with that of djurleite, which has hexagonal close-packing of sulfur layers. As leaching continues, instead of digenite a discrete, poorly developed metastable state is observed with a d value of ~ 1.92 Å for the reflection monitored. This transformation occurs within 20 minutes of leach initiation. As leaching continues, two apparently stable quenchable forms are produced; X-ray-diffraction patterns strongly resemble those of natural spionkopite and yarrowite (Goble 1980). These forms also show the typical optical properties of these blue-remaining covellines, although as shown by Goble (1981), these properties are not by themselves proof that they have the same structures. When leached for three years in this same leachate concentration, the structure does not change further. However, in stronger concentrations (*i.e.*, ~ 2 M) a further change to the covelline structure appears to occur after three days. This structure then persists.

Structurally, the existence of this second type of leaching in copper sulfides is not surprising. Takeda *et al.* (1967) showed that low chalcocite and djurleite

were based on the same hexagonal subcell, and Evans (1979) showed that the dominant co-ordination of sulfur about copper is triangular, based on hexagonal close-packing, and similar in low chalcocite Cu_2S and djurleite $\text{Cu}_{1.94}\text{S}$. Portions of the covelline CuS structure are similar. With this in mind the existence of two pathways for the structural changes in the leaching process, one built around cubic close-packing and one around hexagonal close-packing, is a natural consequence. The existence of this second pathway is further substantiated by the optical observation of Dutrizac *et al.* (1984) of < 1 -micrometre masses of blue-remaining covelline in bornite leached in 0.2 M ferric sulfate. Their suggestion that this might have originated from leaching of chalcocite impurities seems to confirm our observations.

Since there are two pathways in the leaching, there is a further ambiguity in the observations of Potter (1977) and Goble (1980) relative to the stability or metastability of yarrowite and spionkopite in the system copper-sulfur. Whereas our results and those of Goble (1981, 1985) clearly demonstrate that phases produced by leaching digenite or anilite in ferric sulfate solutions do not have the hexagonal structures of yarrowite and spionkopite, it remains to be shown that the phases produced by leaching chalcocite in the same solutions, even though apparently based upon hexagonal close-packing of the sulfur atoms, have these structures. The starting products and conditions of leaching are clearly important factors that must be considered in any studies of stability.

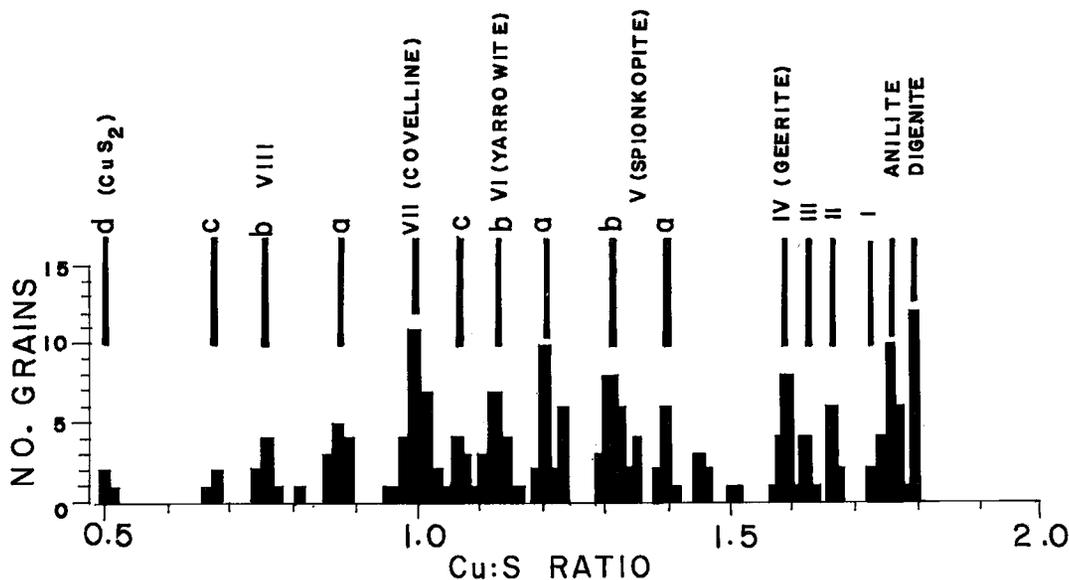


FIG. 5. Histogram of observed compositions of leached grains. All analyzed grains are from the digenite leaching experiments (chalcocite experiments are not included). Mineral names indicate compositions of known minerals but do not imply that these minerals are actually present (*i.e.*, we are probably looking at polymorphs). Cu:S ratios are to the nearest 0.01. Total number of grains analyzed is 282 (three separate experiments on similar samples).

COMPOSITIONAL DETERMINATIONS

Once the structural variations with time and leachate concentration had been determined, compositional analysis of grains with each structure was performed using a MAC 400 electron microprobe.

Synthesized starting material was leached under conditions approximating those previously determined for the production of each of the eight structural types. The only difference was that the grains were not mounted on mylar, but leached unmounted in a sealed container. At time intervals determined by the previous experiments, several grains were removed from the solution, mounted in cold-setting epoxy, polished and analyzed for copper, sulfur and iron. The data are summarized in Table 1 and Figure 5. Iron was determined in all grains but never exceeded background values. As can be seen, compositions determined for individual grains are occasionally not in keeping with the gross conclusions of this study. This is probably due to variations in factors such as grain size, orientation and degree of fracturing. Such factors have been shown by Dutrizac *et al.* (1984) to influence the leaching speed of individual grains of bornite (and presumably digenite) to a considerable extent. It is also uncertain that conditions in the experiments done without the mylar film are completely equivalent to those previously determined (*i.e.*, the questions of how much influence the cyclic variation has on the structures and whether the cyclic variation is mylar-dependent are still not completely answered). However, as a group, grains leached without the presence of mylar or glue seem to behave in a similar fashion to those leached on mylar in the nylon holder while being subjected to X radiation.

TABLE 2. PERCENTAGE OF SULFIDE GRAINS IN EACH STRUCTURAL TYPE AS A FUNCTION OF TIME. THE PERCENTAGE OF THE ORIGINAL COPPER LEACHED FROM THE GRAINS IS ALSO SHOWN

Leaching Time (min)	Structural Type								% Cu Leached		
	DIG	AN	I	II	III	IV	V	VI		VII	VIII
0	100	-	-	-	-	-	-	-	-	-	0
1	25	75	-	-	-	-	-	-	-	-	2.2
2	10	90	-	-	-	-	-	-	-	-	3.3
3	0	90	10	-	-	-	-	-	-	-	3.6
3.5	-	35	50	15	-	-	-	-	-	-	4.0
4	-	35	35	30	-	-	-	-	-	-	4.5
5	-	25	40	35	-	-	-	-	-	-	4.8
6	-	25	35	40	-	-	-	-	-	-	4.9
7	-	20	30	50	-	-	-	-	-	-	5.2
10	-	15	35	50	-	-	-	-	-	-	5.4
15	-	15	30	45	10	-	-	-	-	-	6.4
50	-	-	10	50	20	10	10	-	-	-	9.1
100	-	-	-	30	30	20	10	10	-	-	12.2
300	-	-	-	10	10	20	20	20	20	-	16.0
500	-	-	-	5	10	20	40	10	15	-	20.7
750	-	-	-	-	5	25	30	15	23	2	22.0
1,000	-	-	-	-	-	15	30	25	20	15	23.1
3,000	-	-	-	-	-	-	40	30	25	5	33.0
10,000	-	-	-	-	-	-	20	40	40	-	38.0

Starting material was digenite; leachate concentration 10^{-2} M ferric sulfate. All percentage values for structural types are approximately $\pm 5\%$, and are based upon a comparison of composition values from Table 1 with peak intensities for each structure as observed on the X-ray diffractometer. DIG indicates the digenite and AN the amelite structure, respectively. The values for percent copper leached are atomic percentages based upon changes in Cu:S ratio.

Compositions for the leached grains tend to cluster about known values in the system copper-sulfur (Fig. 5), but the grains are probably polymorphs of known minerals, as discussed above. A number of other compositional peaks also occur; the relationship between these compositions and the structures determined by X-ray-diffraction means are indicated on Figure 5. In addition to compositions that match each of the identified structures, several anomalous Cu:S values were found (*i.e.*, 1.51, 1.45, 1.35, 1.23 and 0.80). These may represent mixtures of two or more phases found in the X-ray studies.

In this study a number of grains were analyzed that have Cu:S values of less than 1. Grains of this composition are unknown in the natural system. Several additional leaching and analytical experiments were carried out to test the accuracy of these findings, with similar results. Therefore, we believe that these compositions are real.

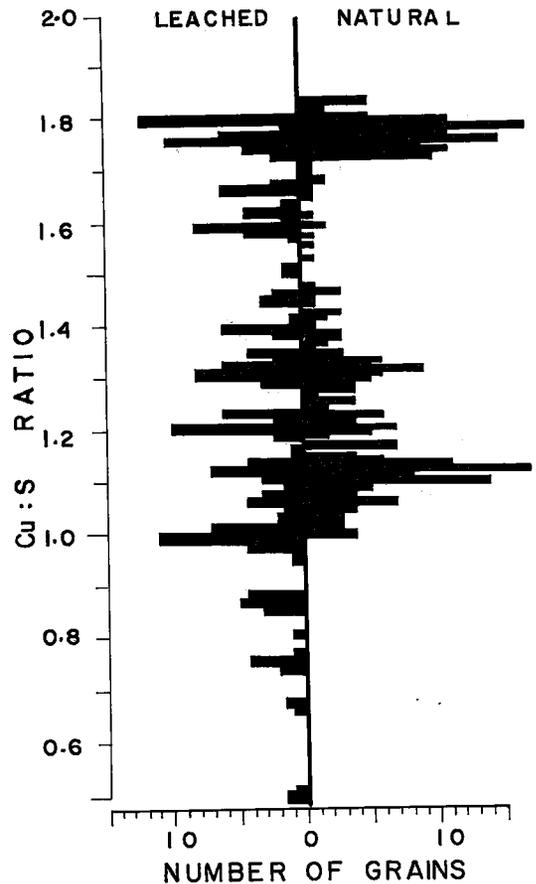


FIG. 6. Comparison of composition of grains leached in ferric sulfate in this study and naturally occurring copper sulfide grains analyzed by Goble & Smith (1973).

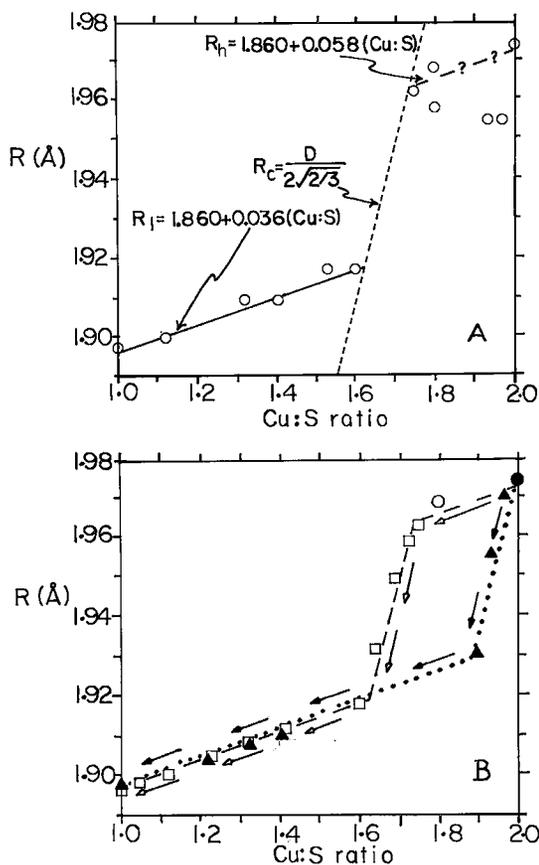


FIG. 7A. The relationship between radius R of sulfur atoms within sulfur layers and composition for copper sulfides (after Goble 1985). Data points at $\text{Cu}_{1.32}\text{S}$ and $\text{Cu}_{1.53}\text{S}$ indicate Goble's analyzed compositions for spionkopite and geerite; two data points at $\text{Cu}_{1.8}\text{S}$ indicate two possible R values for digenite; data points at $\text{Cu}_{1.93}\text{S}$ and $\text{Cu}_{1.97}\text{S}$ indicate two possible compositions for djurleite. B. Changes in composition and d value produced during dissolution of grains of digenite and chalcocite. Circles indicate starting materials; squares indicate leached phases having structures based upon cubic close-packing; triangles indicate leached phases having structures based upon hexagonal close-packing.

Cu:S values of less than 1 were not found in any of the long-term leaching experiments (Table 2). This suggests that had the grains been left to reach equilibrium with the solution, they would have returned to a Cu:S value of 1.06 in less than one day. This appears to be the composition that the grains approach with longer leach-times as well (Goble 1981). This compositional change is in agreement with the X-ray observation that the structure of CuS_2 (type-VIII structure, Fig. 4a) is produced as a poorly developed metastable phase during the leach-

ing and then changes back to a type-VI or -VII structure with further leaching. This gives further evidence for the continued existence of the cubic close-packing of sulfur atoms throughout the digenite leach, because Goble (1981) showed that material leached for seven to ten days retains cubic close-packing of sulfur atoms.

When the determined compositions are compared with natural copper sulfide compositions, such as those reported by Goble & Smith (1973), a close match is found in the Cu:S range 1.00 to 1.35, and in the anilite - digenite region ($\text{Cu}_{1.75}\text{S}$ - $\text{Cu}_{1.80}\text{S}$), but agreement is poorer in the intermediate range and below CuS (Fig. 6). In the range $\text{Cu}_{1.0}\text{S}$ - $\text{Cu}_{1.35}\text{S}$ we are apparently looking at polymorphs of the natural phases. The lack of natural analogues in the ranges $\text{Cu}_{1.35}\text{S}$ - $\text{Cu}_{1.60}\text{S}$ and $\text{Cu}_{0.5}\text{S}$ - $\text{Cu}_{1.0}\text{S}$ is not unexpected, since the phases in these compositional ranges have only short-term stability in the leachate and occur only under very specialized conditions. It should be noted, however, that some anomalous values in the study of Goble & Smith (1973) appear to match compositions found in this study and that we do find a significant compositional peak corresponding to geerite ($\text{Cu}_{1.6}\text{S}$). With the exception of the starting material and anilite, this is probably the only case in which the structure we are seeing corresponds to that of a natural phase.

STRUCTURE - COMPOSITION RELATIONSHIPS

In a series of papers, Goble (1980, 1981, 1985) proposed a relationship between structure, as represented by sulfur radius and spacing between sulfur layers, and composition for the copper sulfides. Because of lack of data and anomalous data for djurleite, only a tentative relationship between sulfur radius and composition was given for the interval $\text{Cu}_{1.75}\text{S}$ - $\text{Cu}_{2.0}\text{S}$ (Fig. 7a). In addition, there were no data points between digenite and geerite.

When the new metastable structures identified here are added to Goble's (1985) plot of sulfur radius versus composition (Fig. 7b), it is seen that the original relationship from digenite to covellite appears to be approximately correct. Triangles represent the new data-points (Fig. 7b). The relationship shown can now be used to indicate a pathway of structural transformation produced upon leaching digenite, as indicated by the arrows in Figure 7b. Chalcocite, upon leaching in dilute ferric sulfate solutions, follows the $\text{Cu}_{1.75}\text{S}$ - $\text{Cu}_{2.0}\text{S}$ relationship originally suggested by Goble (1985). In addition, a new leaching pathway for hexagonal closest-packed sulfur atoms can now be added, in which chalcocite leached in more concentrated ferric sulfate solutions is transformed to djurleite to spionkopite to yarrowite to covellite as shown in Figure 7b. It is particularly interesting to note the path through djurleite and

near $\text{Cu}_{1.9}\text{S}$, since this clears up the djurleite anomaly in the earlier data of Goble (1985).

SUMMARY AND CONCLUSIONS

In this series of experiments, we have found that chalcocite and digenite leach differently as concentrations of ferric sulfate leachate are varied. Chalcocite can take at least two paths as copper is leached from the structure. If leaching is done slowly, tetragonal-phase chalcocite forms and leaches through a series of structures that are all based on cubic close-packing of the sulfur atoms, but that have no apparent natural analogues. With rapid leaching of chalcocite, cubic close-packing is never produced, and all leached forms seem to be based upon hexagonal close-packing of the sulfur atoms, or a variation of this, as in covelline. We suspect from the optical properties of these forms that they are true blue-remaining covellines, possibly yarrowite and spionkopite, which eventually transform to covelline upon further leaching or dissolution. However, as noted by Goble (1981), we cannot be certain of this since we did not do single-crystal studies.

Under the conditions of these experiments digenite does not appear to transform to structures found in nature, with the exception of anilite and geerite. Geerite, found in nature as an epitactic replacement of sphalerite (Goble & Robinson 1980), appears in this leaching system as only one of a series of metastable structures, which all appear to be based on cubic close-packing of sulfur atoms.

The appearance of phases with Cu:S values of less than 1.0 and the similarity of X-ray patterns of these structures to that of CuS_2 , which is known to have covalent bonding of sulfur atoms, suggest that given sufficient time in the leachate, covalent bonding of S_2 atoms will begin to form in the cubic close-packed structures. However, the instability of the phases encountered and the observed cyclicity in their stability suggest that these covalently bonded sulfur atoms are not oriented in layers as in the covelline, yarrowite and spionkopite structures. Instead they are probably arranged in several different orientations as in the structure of high-pressure CuS_2 . The many different type-VIII structures that we observe (Fig. 4a) and their transformation with time to a phase with the approximate composition of $\text{Cu}_{1.06}\text{S}$ may reflect an ordering of these covalent bonds toward the more stable configurations of covelline, yarrowite and spionkopite.

An unusual aspect of the leaching behavior of digenite is observed where very low concentrations of ferric sulfate are used. In this case, a cyclic transformation from digenite to anilite and back again is set up, with a set periodicity established for each cycle. Calculations indicate that with even the very minor change in composition involved the very dilute

solutions used (10^{-5} to 10^{-3} M) will probably be depleted in ferric ion. However, even if equilibrium between the solution and the sample is reached, this fails to explain the cyclical change from digenite to anilite and back again.

Since the change from the digenite to the anilite occurs with great ease (simple physical grinding can cause this transformation), the cause of this cyclic pattern need not involve large exchange of energy. In this experiment, the grains are not in physical contact, so any simultaneous change in the individual grains must involve one of the two media that are in physical contact with all the grains, *i.e.*, the glue or the mylar. Any hypothesis must also explain why this change occurs after a certain number of grains change to the anilite structure, and why this occurs in a constant interval of time.

It is possible that as the digenite distorts to the anilite structure the energy lost from the digenite accumulates on the mylar as an electric charge, and that at the end of the cycle the charge reaches a sufficiently high level to discharge back into the structure, transforming the anilite back to digenite. In less controlled experiments other glues and petroleum jelly were tried as replacements for the "Krazy Glue", with only minor variations on the original results. There are many other variations on this experiment that could further elucidate this process, including using a variety of mounting media and repeating the process with other minerals whose structures do not transform as readily. At the very least, it can be said that the readily observable transformation from the digenite to the anilite structure is reversible and does not require a compositional change.

This process, with different time-sequences, is also observed as structural transformations occur between the other phases identified in this paper, and is a clear signal that a transformation is actually occurring. As a check, a blank consisting of quartz on mylar and glue was monitored. No cyclic variation was noted, eliminating the possibility that we were actually seeing a cyclic variation in our instrumentation or experimental setup.

The cyclic variation of digenite to anilite and its reverse in weak solutions has some very interesting aspects for investigation of other easily transformable structures in other systems. Much work still remains to be done to establish the conditions governing the transformation.

Although the preponderance of evidence from this study clearly suggests that both Goble (1981, 1985) and Potter (1977) were correct in their observations regarding the stability or metastability of the blue-remaining covellines (*i.e.*, under the conditions of Potter's work he would have seen metastable forms resembling the natural stable (?) minerals identified by Goble (1980) as yarrowite and spionkopite), we

cannot as yet reach any conclusion with regard to the stability or metastability of yarrowite and spionkopite. However, it is now obvious that further work needs to be conducted on the leaching of chalcocite and its end products. This seems to be the most likely way in which synthetic specimens of yarrowite and spionkopite can be produced. Such experiments must of course be conducted in conjunction with single-crystal studies.

Further single-crystal X-ray work on all phases produced will be needed to fully demonstrate their true nature. It is also necessary to test the second technique used for synthesizing blue-remaining covellite (sulfurization of anilite in organic solvents) using the methods of Moh (1971), to see if similar structural changes are produced. It would be useful to vary temperature at each concentration since Dutrizac *et al.* (1984) have shown that this is a factor of some importance. Finally, electrochemical studies and differential thermal analysis (DTA) of the materials prepared using the two types of synthesis should be employed to determine stabilities and similarities in behavior.

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