

COPPER AND COPPER-IRON SULFIDES AS THE
INITIAL PRODUCTS OF SUPERGENE OXIDATION,
COPIAPÓ MINING DISTRICT, NORTHERN CHILE

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ABSTRACT

In numerous deposits of the Copiapó mining district of northern Chile copper and copper-iron sulfides persist as early products of post-Miocene oxidation of hypogene and supergene sulfides, the latter formed during a preceding enrichment episode. The sulfides of oxidation origin have been subsequently partially altered, predominantly to malachite and goethite. In the oxidation zones of this area, hypogene chalcocopyrite has been converted to normal covellite; hypogene bornite to "anomalous bornite", idaite, chalcocopyrite, and normal covellite; supergene djurleite and hypogene chalcocite to digenite (or anilite), and to blaubleibender and normal covellite; and supergene digenite to blaubleibender and normal covellite.

Electron probe microanalysis of blaubleibender covellite revealed a wide compositional range, probably extending from stoichiometric CuS to at least $\text{Cu}_{1.4}\text{S}$, the composition of blaubleibender covellite synthesized by Frenzel (1961). Idaite is shown to have a composition closely approaching Cu_3FeS_4 , and is considered to be quite distinct from synthetic $\text{Cu}_{5.52}\text{Fe}_2\text{S}_{6.52}$. "Anomalous bornite" in these ores possesses at least 2 weight percent less copper and 2 percent more sulfur than optically-normal, hypogene bornite. These analytical data necessitate the revision of present concepts of the low temperature phase equilibria in this region of the system Cu-Fe-S.

INTRODUCTION

This paper summarizes some of the results of an investigation into the mineralogy and controls of the supergene alteration of copper deposits in the Copiapó mining district of northern Chile (Sillitoe, 1969a), in which the relations between the tectonic and geomorphic history of the region and the supergene processes have been emphasized. In the more than 50 years which have elapsed since the recognition and characterization of the phenomena of supergene oxidation and enrichment, this economically significant topic has received remarkably little attention. Despite the considerable contribution made by supergene alteration to the mineability of low-grade copper deposits, our widening knowledge of the diversity and phase relations of copper minerals stable at low temperatures has stimulated few comprehensive studies of supergene assemblages in individual mineralized areas. For this reason, we feel it worthwhile to present a description of one type of supergene sulfide assemblage of widespread occurrence, the environment of formation

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which has been adequately defined by geologic and geomorphic study.

Two distinct "massive chalcocite"¹ enrichment zones have been distinguished in the Jurassic to Eocene magmatogene copper deposits of the Copiapó region, which include veins, breccia pipes, stockworks, porphyry copper deposits, and strata-bound *mantos*. Sulfide enrichment occurred in the interval between the Lower Eocene and the Upper Miocene (Clark, Mortimer, and Sillitoe, 1968; Sillitoe, Mortimer, and Clark, 1968), beneath two erosion surfaces of regional extent, the Summit and Intermediate Surfaces. However, the youngest and most extensive major planation surface in northern Chile, the Atacama Pediplain, which developed in response to a third episode of Andean uplift, everywhere truncated pre-existing supergene alteration profiles. This phase of pediplanation has been shown to have terminated between 12.6 and 11.5 (± 0.5) m.y. B.P. (Clark *et al.*, 1967). Since the Upper Miocene, further uplift has resulted in canyon incision, and a fall in the water table, giving rise to widespread oxidation, and concomitant, quantitatively minor deposition of "sooty chalcocite" immediately below the water table.

The sulfide assemblages making up the two zones of "massive chalcocite" have been found to comprise dominant djurleite, with minor chalcocite (*sensu stricto*) and "digenite". The status of this last mineral has recently been thrown into considerable doubt by the recognition of a further, distinct phase in the system Cu-S, orthorhombic $\text{Cu}_1\text{.75S}$, named anilite by Morimoto, Koto and Shimazaki (1969). This mineral has been confirmed as a constituent of "sooty chalcocite" at one mine in the Copiapó area (Clark and Sillitoe, 1969), and probably occurs in minor amounts throughout the district. Anilite is converted to a digenite-type solid solution by even gentle grinding at room temperature and, presumably, by polishing. In the present discussion, the term "digenite" is reserved for a mineral which is isotropic and bluish in color in incident light, and which has a composition intermediate between those of djurleite and covellite. It may well be that much of the digenite formed by supergene oxidation in the southern Atacama Desert is anilite. Remnants of hypogene chalcopyrite and pyrite, and of subordinate bornite, sphalerite, galena, tennantite-tetrahedrite, and enargite persist as cores in the "massive chalcocite", and become increasingly common with depth within individual enrichment zones. "Sooty chalcocite" has a composition similar to that of the massive enrichment assemblages, with normal covellite as an additional constituent.

¹ A convenient and widely-used field term for competent aggregates of supergene copper sulfides, generally having a steely-gray appearance, and contrasting with the powdery, friable accumulations of "sooty chalcocite".

During the development of the Atacama Pediplain, the existing leached and oxidized zones were denuded, while in some areas practically all the underlying enriched ore was eroded. Pedimentation resulted in the widespread exposure at surface of "massive chalcocite" ore, and of the associated remanent hypogene sulfides. The ensuing oxidation of these sulfides, which began in the Upper Miocene, is continuing at the present time.

The sulfide assemblages generated in the initial stages of the *in situ* oxidation of earlier formed "massive chalcocite," and of hypogene chalcopyrite and bornite which have previously been partially replaced by supergene copper sulfides, are the subject of this discussion.

METHODS OF STUDY

Specimens of the sulfides and their oxidation products, mounted in cold-setting resin and polished using lead-lap techniques, were studied by standard optical methods. Quantitative measurements of the spectral dispersion of the reflectivity of several sulfides were made on the Reichert microphotometer, described by Singh (1965). X-ray powder studies of opaque and transparent minerals were carried out on a Guinier-de Wolff multiple focusing camera, using Cu K α radiation. A CAMECA Microsonde Mark I electron probe microanalyser was used to obtain both qualitative and quantitative compositional data on carbon-sputtered polished specimens. Corrections for absorption, "atomic number factor", and characteristic fluorescence were calculated according to the methods of Duncomb and Shields (1966), Duncomb and Reed (1967)¹, and Reed (1965), respectively, employing a Fortran computer program written by Mr. R. G. E. Palfree, of University College, London.

OXIDATION OF DJURLEITE AND DIGENITE

The earliest recognizable stage in the oxidation of djurleite is the formation of digenite, "blaubleibender covellite", and normal covellite, individually or in association. Both types of covellite may also have been derived from the oxidation of digenite of enrichment origin. "Massive chalcocite" has locally been altered to these copper sulfides alone, but they also form as an intermediate stage in the oxidation of djurleite or digenite to malachite or, rarely, atacamite, or to the association of malachite and goethite known locally as *almagrado*. In many specimens, however, *almagrado* formation has apparently not involved the prior deposition of copper sulfides. "Massive chalcocite", rimmed and veined by cuprite, native copper or tenorite, occurs in the Copiapó region, but covellite of oxidation origin is never present in such ores. However, a single specimen of djurleite rimmed by delafossite exhibits normal covellite as an intermediate oxidation product (Sillitoe, 1969b).

The optical properties of normal covellite are distinct from those of

¹ Duncomb, P. and S. J. B. Reed (1967) The calculation of stopping power and back-scatter effects in electron probe microanalysis. *Tube Investments Research Lab., Cambridge, Eng., Tech. Rept.*, 221, 24 p. (freely available from company or authors).

the "blue-remaining" variety, which was first fully characterized by Frenzel (1959). Blaubleibender covellite is distinguished by the absence of a purple-red (R_0) coloration in plane-polarized incident light in oil immersion; it shows bireflectance from light to dark blue in air, but this effect is only slightly intensified under oil. The anisotropism is also weaker, exhibiting orange-brown hues in the place of the distinctive fiery oranges and red-browns of normal covellite. The reflectivity and polishing hardness of the normal and blaubleibender covellites are of the same order.

Clear evidence of the existence of varieties of covellite having optical properties intermediate between those of the normal and blaubleibender modifications has been obtained from optical study of specimens from the Copiapó district, but the areas covered by these are too small to permit more detailed examination. The X-ray powder patterns of the two main types are similar to those listed by Frenzel (1959). The indistinct, diffuse lines show few appreciable differences in d-spacings, although as, pointed out by Moh (1964), blaubleibender covellite patterns lack several weak lines which characterise the normal form.

Digenite of undoubted oxidation origin was only rarely observed in the specimens examined, but, especially in ores from the Quebrada Puquios district, residual grains of djurleite (10–20 μm in diameter, and enclosed by goethite and minor malachite) are seen to have been altered to digenite, in turn oxidized to both blaubleibender and normal covellite. It was difficult in some specimens to ascertain whether digenite had formed contemporaneously with the associated djurleite during enrichment, or was a product of subsequent oxidation. The consistent occurrence in the Puquios ores of digenite only in association with djurleite which has undergone oxidation, is considered to reflect its role as the first stage in the oxidation of djurleite, preceding the appearance of covellite.

Blaubleibender and normal covellite are more widespread than digenite, and were observed in practically all the oxidized ores examined in the present study. The covellite generally takes the form of flame-shaped lamellae or minute patches, some 5 to 10 μm in diameter, in djurleite and digenite. No covellite has been distinguished in specimens of oxidized supergene chalcocite (*sensu stricto*), although hypogene chalcocite, associated with bornite in disseminated deposits in volcanics, has locally been replaced by normal covellite. The covellite flames are generally concentrated in the vicinity of cross-cutting veinlets of gangue minerals, fractures, or the boundaries of "massive chalcocite" aggregates, but are also present within apparently unfractured copper sulfides. Crystallographic control of covellite formation is evident in some samples. In specimens which exhibit remanent cores of hypogene sulfides, a zone of unaltered "massive chalcocite" may be present between each sulfide core and surrounding covellite-bearing areas.

Where both digenite and djurleite are present in a single polished section, the former has been preferentially replaced by normal and blaubleibender covellite. Blaubleibender covellite is, however, more consistently associated with digenite than is the normal variety. This relationship has been recorded by several previous workers (*e.g.* Vokes, 1957; Frenzel, 1959; Ramdohr, 1960; Grafenauer, 1963). More extensive djurleite areas, several mm in diameter, may be wholly replaced by mosaics of both covellite modifications, and exhibit irregular cracks, due to the volume-reduction which accompanies the replacement (Figure 1). The microscopic relations indicate that, where both normal- and blaubleibender covellite occur as the products of djurleite oxidation, the latter formed earlier. Thus, remanent cores of djurleite in replacive goethite and malachite are altered at their centers to flames of blaubleibender covellite, while they are replaced marginally by the normal variety. Residual grains of normal covellite are also retained in the adjacent goethite—malachite intergrowths. Normal covellite formed by the oxidation of “massive chalcocite” occurs commonly as grains in goethite, malachite, and areas of gangue, whereas the blaubleibender form has only rarely been recognized in such contexts.

Digenite and covellite, intermediate products in the transformation of “massive chalcocite” to malachite or to aggregates of malachite and goethite, are found throughout the vertical extent of oxidized zones, but are especially concentrated in their near-surface sections. “Massive chal-

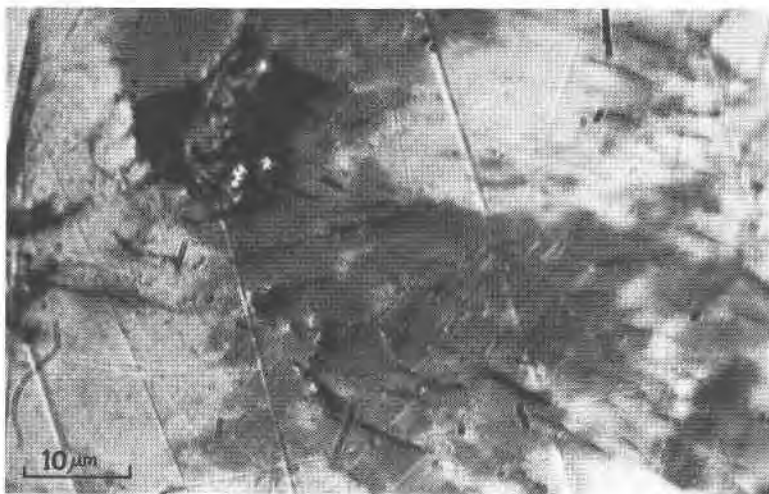


FIG. 1. Djurleite (light gray), partly altered to blaubleibender covellite (dark gray). Note the cracks due to volume reduction. 25-m level, Mina Santos, Punta del Cobre district. Plane polarized incident light; oil immersion.

cocite" altered to covellite alone occurs in many zones of preferential downward water percolation, close to the lower limit of oxidizing influences. Blaubleibender and normal covellite are consistently absent in "massive chalcocite" ore which has not undergone a subsequent phase of oxidation.

In hand specimen, it is generally impossible to distinguish covellite which has formed as an intermediate stage between "massive chalcocite" and malachite and goethite. Competent enriched ores which have been altered to covellite superficially resemble "sooty chalcocite". However, such oxidation assemblages are characterized by a gray-black color, contrasting with the black or bluish-black hue that typifies powdery sulfides formed by enrichment, and by a cavernous, sluggy texture, which reflects the volume decrease during replacement.

Much of the normal, and all of the blaubleibender covellite which occurs in the Copiapó region has been formed through *oxidation*. A minor proportion of the normal covellite is a constituent of true "sooty chalcocite", precipitated by the enrichment of chalcopyrite and pyrite. No covellite of enrichment origin has been recognized in "massive chalcocite" ores from the district. The origin of some or all normal covellite by the oxidation of "chalcocite" has been noted at Chuquicamata, Antofagasta Province, northern Chile (Bandy, 1938), at the Campbell Mine, Bisbee, Arizona (Schwartz and Park, 1932), in the Globe-Miami district of Arizona (Peterson, 1954, 1962), at Castle Dome, Arizona (Peterson *et al.*, 1951), and at Kennecott, Alaska (Bateman and McLaughlin, 1920). However, the formation of digenite in the course of supergene oxidation has apparently not been described from natural assemblages.

The composition of blaubleibender covellite

Quantitative electron microprobe analyses have been made of several specimens of blaubleibender covellite from Mina Santos, a small mine in the productive Punta del Cobre group, using optically normal covellite from Mina Flor del Llano as a standard; both covellites occur as early oxidation products of "massive chalcocite" (djurleite) rimmed by malachite. The analytical results are presented in Table 1. No analyses were made of the small areas of covellite having optical properties intermediate between those of the normal and blaubleibender varieties. Considerable difficulty was encountered in finding grains of blaubleibender covellite of sufficient purity for analysis, but it is considered that these data give a good indication of the composition of this phase.

It is evident that the blaubleibender modification of covellite in this region contains between 2 and 7 weight percent more copper than does

TABLE 1. ELECTRON PROBE MICROANALYSES OF BLAUBLEIBENDER COVELLITE, MINA SANTOS, PUNTA DEL COBRE, COPIAPÓ, CHILE

Sample	Wt. % Cu	Wt. % Fe	Wt. % S	Total
1	70.2	1.4	28.7	100.3
2	69.8	6.7	25.6	102.1
3	70.1	1.4	27.4	98.9
4	68.7	n.d.	28.9	97.6
5	69.5	—	—	—
6	73.3	—	—	—
CuS	66.48		33.52	100.00
Synthetic blaubleibender covellite (Moh, 1964)	67.5–68.5		31.5–32.5	
Synthetic blaubleibender covellite (Frenzel, 1961)	73.25	0.10	26.45	99.89 ^a

^a Includes 0.09 wt. % H₂O.

normal covellite, in addition to a small amount of iron. The observed iron content (determined using associated chalcopyrite as a standard) may have been contributed in part by minute inclusions of goethite, and was almost certainly due to this cause in Sample 2 (Table 1), but some at least of the blaubleibender covellite is ferroan. We have assumed in our analytical work that the normal covellite standard is stoichiometric CuS, as found by Kullerud (1965), and small errors could have been introduced by any departure from stoichiometry.

Frenzel (1959) originally considered blaubleibender covellite to be 1.5 to 2 percent richer in copper than normal covellite, but the subsequent (1961) analysis of synthetic material showed it to be as copper-rich as Cu_{1.4}S, essentially the composition of our analysed Sample 6 (Table 1) Moh (1964) delimited, by hydrothermal synthesis under oxygen-free conditions, an apparent stability field for this mineral, extending from *ca.* 67.5 to 68.5 copper at 50°C and 135°C, or one to two percent more copper-rich than CuS.

The microprobe analyses presented here demonstrate that the blaubleibender covellite from Mina Santos achieves compositions more than four percent richer in copper than that synthesized by Moh (1964). It is evident that, under natural conditions, blaubleibender covellite may have an extremely variable composition, probably ranging from stoichiometric CuS to at least Cu_{1.4}S; if the optical properties of this phase are

directly influenced by its Cu:S ratio, such wide compositional variations appear to be represented in very restricted areas. The status of blue-remaining covellite as a phase in the system Cu-S remains unclear, but it is considered that the field of stability put forward by Moh does not adequately reflect the compositional relations of the natural mineral. The blaubleibender phase ($\text{Cu}_{1.4}\text{S}$) synthesized by Frenzel (1961) may, on the other hand, indicate the limit of tolerance for copper of the covellite structure at low temperatures. Whereas Moh (1964) has concluded that, in view of its higher symmetry relative to that of normal covellite and its apparently distinct composition, the term "blaubleibender covellite" is misleading, we feel that this convenient description should be retained until the crystal structure and stability field of this phase are clarified.

OXIDATION OF CHALCOPYRITE

Residual grains of chalcopyrite, generally marginally replaced by djurleite, have been oxidized *in situ* in many ores to aggregates of malachite and goethite, which in hand-specimen have a deep-brown color and a speckled appearance, owing to the presence of areas of a blackish pitch-like goethite. In polished section, small spikes and patches of normal covellite may be observed as intermediate products of this oxidation, rimming the chalcopyrite, and penetrating inwards along (111) cleavage directions. The chalcopyrite residua are eventually pseudomorphosed by goethite, which may retain lamellae of normal covellite. Covellite occurring in the surrounding goethite may have been derived from the oxidation of either the chalcopyrite or djurleite. This normal covellite of oxidation origin is readily distinguished from that formed (as "sooty chalcocite") in the enrichment of chalcopyrite, which is unaccompanied by other contemporaneous minerals, and criss-crosses chalcopyrite grains in a network of cleavage-controlled laths and veinlets.

OXIDATION OF BORNITE

The ultimate products of the oxidation of bornite, malachite and goethite, are similar to those resulting from the oxidation of djurleite and chalcopyrite. However, the intermediate stages in the alteration of bornite involve the formation of a chalcopyrite-like phase, idaite, and a bornite-like phase, here referred to as "anomalous bornite", in addition to covellite.

Idaite was first named and comprehensively described by Frenzel (1958, 1959, and 1960), although an apparently similar phase in the system Cu-Fe-S had earlier been synthesized by Merwin and Lombard (1937) and by Roseboom and Kullerud (1958). Frenzel described idaite

as a supergene sulfide which is formed, characteristically, by the alteration of bornite. This mineral has since been recognized, in association with bornite, at Yauricocha, Peru (Kobe, 1961), in various deposits in Argentina (Brodtkorb, 1961), from deposits in Japan (Takeuchi and Nambu, 1961), at Litija, Yugoslavia (Grafenauer, 1963), at Sommerkahl, Germany (von Gehlen, 1964), at Konnerud, Norway (Krause, 1965), and at Trattenbach, Austria (Tufar, 1967). The optical properties of idaite from the Copiapó region are distinctive, and closely comparable to those described by Frenzel (1958 and 1959). The bireflectance in air is strong, from reddish-orange to gray-yellow; oil immersion enhances these colors. The anisotropism of idaite is enormous, ranging from pale green to yellow-green in air, while the reflectivity at 589 nm is approximately 23 to 32 percent.

The anomalous bornite distinguished in the present study has a more yellowish-brown coloration than the normal bornite in these and other deposits, and some grains are distinctly anisotropic in air, from red-brown to gray-brown. The white-light reflectivity appears to be slightly higher than that of the normal variety, an impression confirmed by quantitative reflectivity measurements. The reflectivity dispersion curves of normal and anomalous bornite (Fig. 2) differ significantly, the anom-

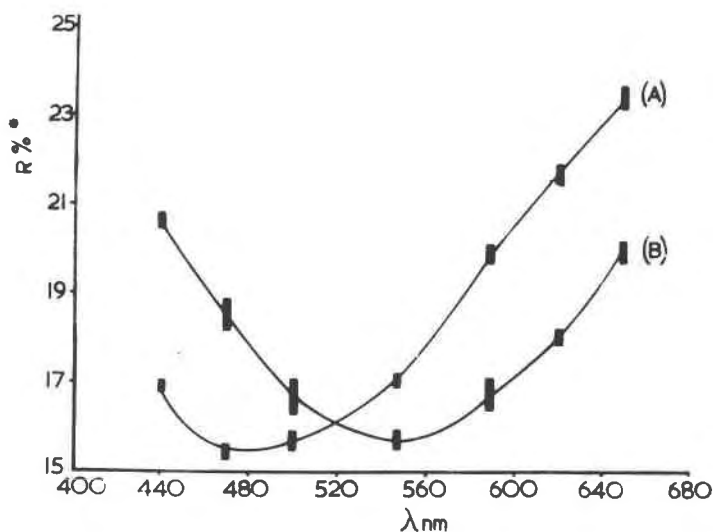


FIG. 2. Reflectivity dispersion profiles for anomalous (A) and normal (B) bornites from Mina Esmeralda, Cerro Blanco district. Each curve represents the mean of four sets of values. (*Reflectivity relative to Royal School of Mines carborundum standard (N.P.L. calibrated—see Singh, 1965).)

alous phase having a reflectivity lower at short wavelengths and higher at long wavelengths than that of optically normal bornite. Apparently similar, optically unusual varieties of bornite have been observed to occur in close association with idaite by Frenzel (1959), Brodtkorb (1961), Tufar (1967), and von Gehlen (1964), who alone, before the present study, investigated its composition.

The oxidation of hypogene bornite, earlier rimmed and veined by supergene djurleite, to yield, successively, anomalous bornite, the chalcopyrite-like phase, idaite, and covellite, has been studied in detail in polished sections of ores from the Jardinera, Abundancia de Puquios, Manto Esperanza, and Esmeralda mines in the Copiapó area. This sequence of mineralogical transformations is represented wherever bornite has been exposed to oxidation, but is absent from assemblages which have been affected by sulfide enrichment alone. The generalized alteration process has been diagrammatically represented in Figure 3 (A-I).

The initial stages of alteration of the bornite and associated djurleite (Fig. 3A) involve the marginal conversion of djurleite to goethite and malachite, and the formation of patches and flames of blaubleibender or normal covellite in the djurleite where it abuts against the replacive goethite and malachite (Fig. 3B and 3C). Minor normal covellite may develop in the malachite and goethite close to the boundary with the djurleite at this stage (Fig. 3C and Fig. 4). The bornite at first remains unaltered, but the oxidizing solutions then gain access via microscopic cracks in the narrower djurleite rims, or on the total replacement of the surrounding djurleite by the oxidate assemblages.

Where the bornite has not been partially replaced by djurleite in a preceding enrichment episode, its oxidation commences immediately. Where a narrow ($<5 \mu\text{m}$) djurleite rim is preserved, small tufts and patches of the chalcopyrite-like phase, sometimes bordered by normal or blaubleibender covellite, may form along its contact with the bornite (Fig. 3D). The chalcopyrite, which differs in no way from hypogene chalcopyrite in its general optical properties, locally penetrates inwards along the cleavage planes of the bornite. In some specimens, the breakdown of bornite and djurleite to chalcopyrite and covellite has led to the formation of a distinct halo of these two sulfides at the margin of bornite grains, enclosed in remanent "massive chalcocite" (Fig. 3E). Very occasionally, sparse lamellae of idaite accompany this chalcopyrite.

The succeeding stage in the alteration of the bornite involves the gradual accession of the optical characteristics of anomalous bornite, and the marginal development of bundles of idaite and chalcopyrite lamellae along cleavage planes in the bornite (Fig. 3F, and Fig. 4 and 5). In some

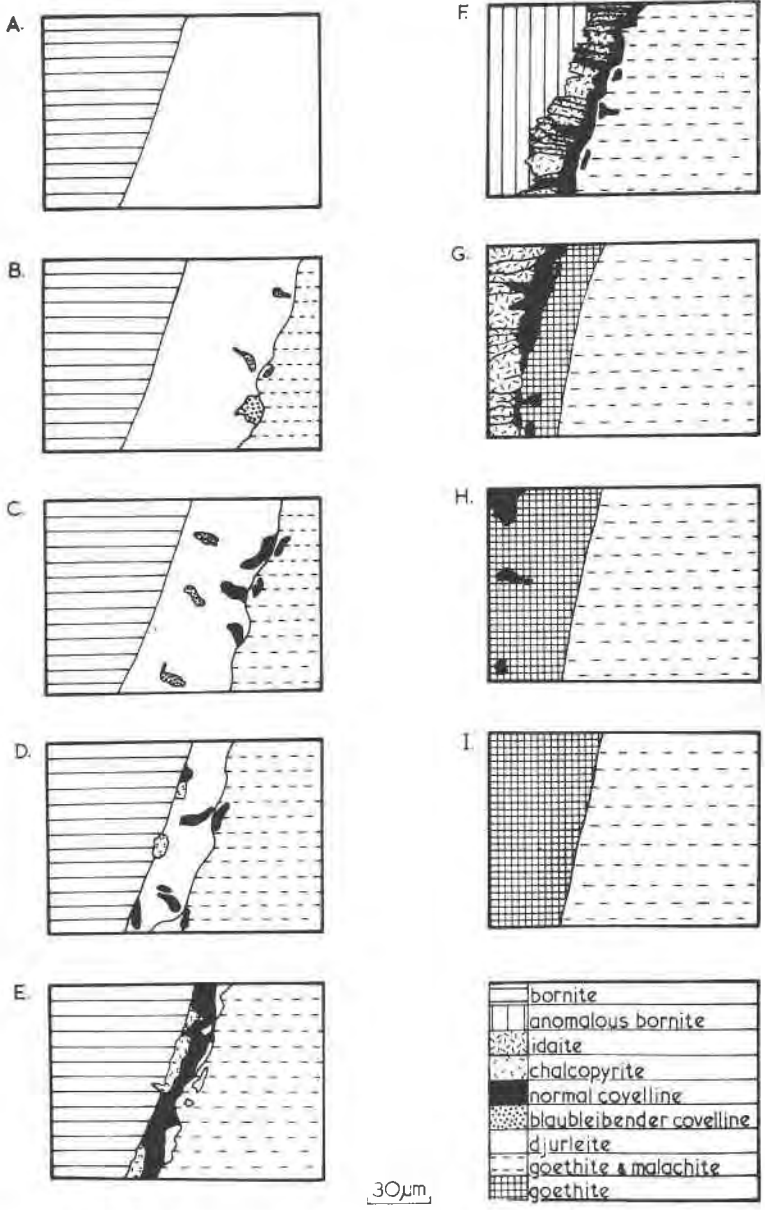


FIG. 3. An idealized oxidation sequence for bornite previously partially replaced by djurleite.

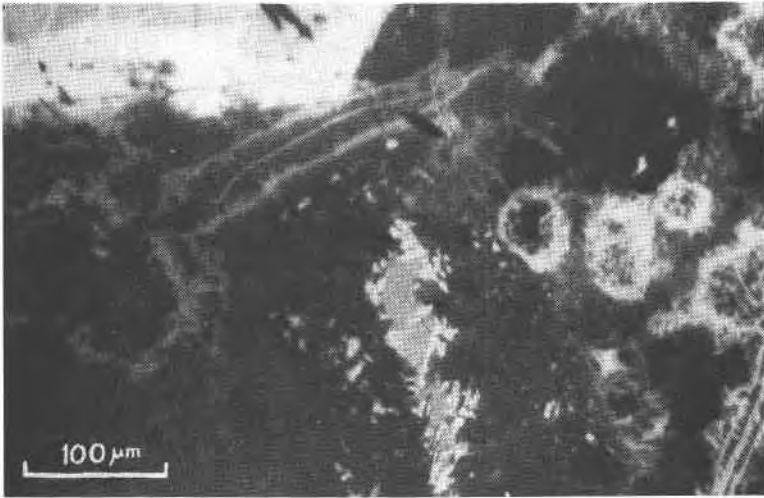


FIG. 4. Bornite (medium-gray) enriched by djurleite (white-top left) and oxidized to goethite (light gray) and malachite (black). A grain of normal bornite (lower middle of field) has suffered oxidation to anomalous bornite (medium-gray), rimmed by lamellar idaite (whitish) and normal covellite (dark gray). Scattered grains of djurleite and normal covellite occur in the surrounding malachite. 6-m level, Mina Jardinera. Plane polarized incident light; oil immersion.

specimens, idaite alone is present at this stage (Fig. 5), but in others chalcopyrite is well represented. The chalcopyrite has a tendency to occur, generally as isolated lamellae, close to the centers of grains of anomalous bornite, while the idaite is concentrated at their margins. The idaite lamellae average 23 to 45 μm in length, and, with continued oxidation, advance inwards at the expense of the anomalous bornite until the aggregate consists predominantly of idaite (Fig. 3G), with or without chalcopyrite. The chalcopyrite and idaite are often interleaved with goethite or normal covellite (Fig. 5), and, rarely, with blaubleibender covellite, giving a striped appearance in polished section. A rim of normal covellite, with minor goethite, may separate the zone of chalcopyrite and idaite from the surrounding goethite and malachite (Fig. 3F and 3G; Fig. 5). Veinlets of normal covellite occasionally cross-cut the idaite and chalcopyrite lamellae and the outermost parts of anomalous bornite grains.

The idaite and chalcopyrite are subsequently transformed to goethite (Fig. 3I), which is at first intergrown with minor normal covellite (Fig. 3H). In the course of the sequence of mineral replacements described above, the volume occupied by sulfides gradually decreases in favor of goethite and malachite.

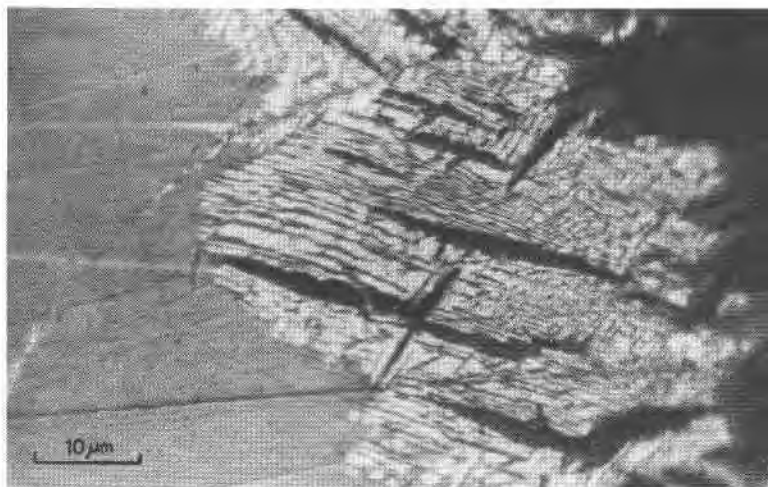


FIG. 5. Anomalous bornite (medium-gray) rimmed by lamellar idaite (whitish) and interleaved normal covellite (dark gray) and malachite (black). The idaite is rimmed by normal covellite (dark gray) and malachite (black). 6-m level, Mina Jardinera. Plane polarized incident light; oil immersion.

Frenzel (1959) originally described idaite as a product of supergene oxidation, but, although later workers have recognized its supergene origin, the general textural relations have led to the erroneous conclusion that this sulfide has formed during enrichment (*e.g.* Takeuchi and Nambu, 1961; Grafenauer, 1963; Krause, 1965). In the assemblages described by these authors, bornite is rimmed by various associations of idaite, chalcopyrite, and covellite, and in some cases, by an outer zone of "chalcocite" or "digenite". This sequence (*cf.* Fig. 3E) has given rise to the assumption that the chalcopyrite-idaite-covellite association is an intermediate stage in the formation of the enriched ores. It is, however, clear that these phases are formed during oxidation. Such an assemblage is widespread near surface in the Copiapó region, but is invariably absent in enriched ores which have not undergone subsequent oxidation.

Compositions of anomalous bornite and idaite

Electron probe microanalyses have been made of associated normal, hypogene bornite, anomalous bornite, and idaite in three specimens from the Abundancia de Puquios and Esmeralda (Cerro Blanco) mines. The analytical data are presented in Tables 2 and 3, and in Figure 6. Three analyses of normal bornite yield compositions in the immediate environs of stoichiometric Cu_5FeS_4 (Table 2), in agreement with the conclusions of most earlier workers (*e.g.* Zeis and Merwin, 1955; Brett and Yund,

TABLE 2. ELECTRON PROBE MICROANALYSES OF NORMAL AND ANOMALOUS BORNITE, COPIAPÓ DISTRICT

Sample	Wt. % Cu	Wt. % Fe	Wt. % S	Total	Locality
Hypogene bornite	63.06	11.84	25.79	99.69	Mina Abundancia de Puquios
Hypogene bornite	63.40	11.62	25.87	100.89	Mina Esmeralda (surface)
Hypogene bornite	63.79	11.84	26.55	102.18	Mina Esmeralda (10 m level)
Cu_5FeS_4	63.33	11.12	25.55	100.00	
Anomalous bornite	61.13	12.06	27.80	100.99	Mina Esmeralda (surface)
Anomalous bornite	61.20	12.63	27.49	101.32	Mina Esmeralda (10 m level)
Anomalous bornite	60.8	11.4	26.2	98.4 ^a	Mina Esmeralda (10 m level)
Anomalous bornite	61.1	11.5	29.0	101.6 ^a	Mina Esmeralda (10 m level)
Anomalous bornite (von Gehlen, 1964)	61.5	11.5	26.5	99.5	Sommerkahl (Spessart)

^a Average of two discrete areas.

TABLE 3. ELECTRON PROBE MICROANALYSES OF IDAITE, COPIAPÓ DISTRICT

Sample	Wt. % Cu	Wt. % Fe	Wt. % S	Total	Locality
Idaite	53.78	15.28	33.26	102.32	Mina Abundancia de Puquios
Idaite	51.71	15.11	33.80	100.62	Mina Esmeralda (surface)
Idaite	52.87	16.52	33.78	103.17	Mina Esmeralda (10 m level)
Cu_3FeS_4	50.87	14.90	34.23	100.00	
Cu_3FeS_6	56.14	9.87	33.99	100.00	
$Cu_{3.5}FeS_{6.3}$	56.94	9.11	33.95	100.00	
"Idaite" (Frenzel and Ottemann, 1967)	56.3	9.8	33.7	99.8	Nukundamu, Fiji

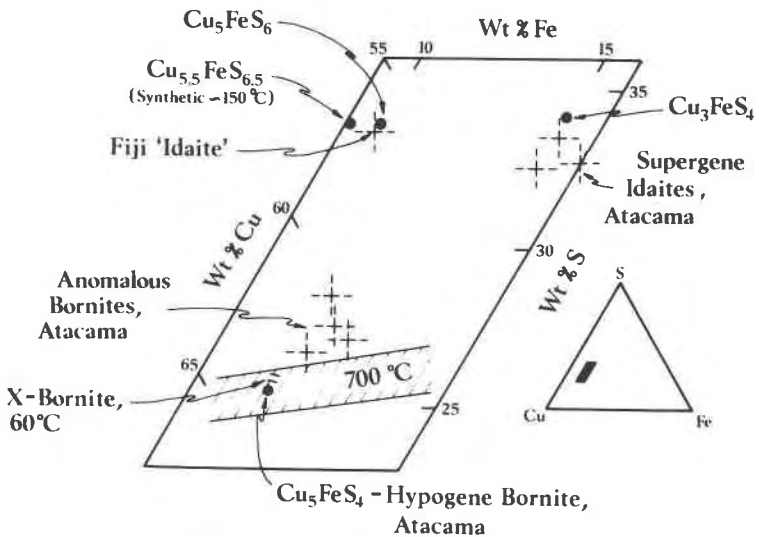


FIG. 6. Compositional relations in part of the system Cu-Fe-S, illustrating the lack of correspondence of the anomalous bornite and idaite from the Copiapó region with known synthetic phases. The boundaries of the bornite-digenite solid solution at 700°C (Yund and Kullerud, 1966) and the composition of the idaite-like mineral described by Frenzel and Ottemann (1967) are included for comparison.

1964). Cell edge determinations were carried out on four specimens of optically normal, hypogene bornite from the Copiapó area, by measurement of the angular position of the (440) reflection, using a Norelco diffractometer, Cu K α radiation, silicon internal standard, and an oscillation technique. The measured values of 10.950, 10.950, 10.952, and 10.952 Å (± 0.001 Å) are essentially identical to that of stoichiometric Cu₅FeS₄, and are evidence of the compositional homogeneity of normal bornite in these deposits.

The differences in the optical properties of normal and anomalous bornites were considered by Brodtkorb (1961) to be due to the presence in the latter of submicroscopic inclusions of chalcopyrite. However, microprobe line scans across several areas of anomalous bornite have shown that, at least in the Copiapó ores, this phase is homogeneous with respect to copper, iron, and sulfur at a beam resolution of ca. 1.5 μ m. Four microanalyses of the anomalous bornite (Table 2, and Fig. 6) indicate that this phase contains up to three weight percent more sulfur, and is consistently richer in iron and poorer in copper than the optically normal bornite. Analyses standardized against metallic iron and copper, and pyrite, and against the associated normal bornite yielded essentially identical results. The four analyses outline a compositional field lying

beyond the boundaries of the bornite—digenite solid solution field at 700°C (Figure 6). It is clear, moreover, that, with increasing sulfur content, the anomalous phase takes on a more yellowish coloration in plane polarized light, and progressively becomes more distinctly anisotropic.

These observations clearly invite comparison of the anomalous bornite with the sulfur-rich natural bornites discussed at length by Brett and Yund (1964) and by Yund and Kullerud (1966), and with the “X-bornite” phase synthesized by the latter authors. In their work on the system Cu-Fe-S, Yund and Kullerud describe the ready formation of “X-bornite” at temperatures below ca. 140°C. This phase contains approximately 0.4 atomic percent more sulfur than stoichiometric Cu_5FeS_4 , and a portion of its apparent stability field at 60°C is indicated in Figure 6 for comparison with the present data. Although stating that “X-bornite” is optically very similar to normal, tetragonal bornite, Yund and Kullerud give no details of its properties; this sulfur-rich phase does, however, yield a distinct X-ray powder pattern. Unfortunately, no comparative X-ray data could be obtained for the anomalous bornites from the Copiapó region because of the small size of the available specimens.

The natural and synthetic sulfur-rich bornites investigated by Brett and Yund (1964) were found to exsolve chalcopyrite, and sometimes digenite, when heated to temperatures of 75°C and over. *In vacuo* heating of a sample of anomalous bornite from Mina Esmeralda similarly yielded a small number of chalcopyrite lamellae after seven days at 115°C, suggesting that this mineral is stable only at lower temperatures. Yund and Kullerud (1966) X-rayed a natural “anomalous bornite”, and found it to consist of a “mixture” of their “X-bornite” and normal tetragonal Cu_5FeS_4 . The anomalous bornite which has been recognized at several localities in the Copiapó mining district might, therefore, be equated with such a mixture, if it were not for the marked compositional disparity between the Copiapó phase and “X-bornite” and normal bornite. The mineral under consideration appears to be significantly richer in both sulfur and iron than any of the sulfur-rich bornites observed by earlier workers, with the exception of that briefly described by von Gehlen (1964) from the Sommerkahl deposit, Spessart. Von Gehlen obtained, by microprobe analysis, a composition almost identical to that of one of the Copiapó specimens (Table 2). He found that annealing at (apparently) 75°C caused the development of small bodies of a chalcopyrite-like phase, which, however, had an approximate composition of $\text{Cu}_5\text{Fe}_2\text{S}_7$.

Correlation of the Copiapó and Sommerkahl anomalous bornites with the known low temperature phase equilibria in this region of the system Cu-Fe-S encounters serious difficulties. Although they established the presence of the sulfur-rich “X-bornite”, Yund and Kullerud (1966)

determined its stability limits only along the Cu_5FeS_4 - Cu_5FeS_6 "join", and the effects of varying the copper:iron atomic ratio were not investigated. The coincidence of the present analyses with that of von Gehlen lead us to propose that these data outline part of a true field of stability for the anomalous bornite phase at approximately 25°C. This phase may or may not be identical to, or continuous with, "X-bornite", and further low temperature synthetic work is required to delimit their relations. At the present time, however, Yund and Kullerud's assertion (1966, p. 484) that "all anomalous bornites contain the X-bornite phase" surely remains unfounded.

From the three microanalyses of lamellar idaite grains (Table 3 and Fig. 6), it is evident that this mineral contains, on average, some 3.5 weight percent less copper, and six percent more iron than are represented by the formula, Cu_5FeS_6 , given for idaite by Frenzel (1959). The Copiapó sulfide is even more divergent in its composition from the general formula, $\text{Cu}_{5.52}\text{Fe}_2\text{S}_{6.52}$, proposed by Yund (1963). A mean (Cu+Fe):S atomic ratio of 1.06 is yielded by the three new analyses (recalculated to 100 percent), in close agreement with that of the idaite-like phase synthesized by Yund and Kullerud (1966), but the analyses give a mean Cu:Fe ratio of 2.97, radically different from that of the synthetic phase. The compositions of the three analysed idaites may be represented by the formulae: $\text{Cu}_{3.1}\text{FeS}_{3.8}$; $\text{Cu}_{3.0}\text{FeS}_{3.9}$; and $\text{Cu}_{2.8}\text{FeS}_{3.6}$. This mineral, therefore, has a composition closely approaching stoichiometric Cu_3FeS_4 , albeit showing a slight, and perhaps significant, sulfur-deficiency. Minute inclusions of covellite and goethite may have contributed minor errors to the analyses, but the coincidence of the compositions determined for the optically normal, hypogene bornites (Table 2) with stoichiometric Cu_3FeS_4 , encourages confidence in the accuracy of the new data. It is concluded that the mineral occurring in these oxidized assemblages is compositionally quite distinct from the phase synthesized in the system Cu-Fe-S.

These observations are in excellent agreement with those recently presented by Lévy (1967), who concluded, on the basis of five microprobe analyses of reasonably pure specimens from two localities, that idaite, occurring in association with bornite and presumably of supergene origin, has a composition of Cu_3FeS_4 . Lévy demonstrated that natural idaite yields spectral reflectivity dispersion curves differing markedly from that of the original " Cu_5FeS_6 " synthesized by Merwin and Lombard (1937). We have confirmed Lévy's observations on the reflectivity of idaite through measurements on specimens from the Manto Esperanza mine (Figure 7). Two areas of polygranular idaite aggregates yielded dispersion curves essentially parallel to those found for pure idaite from

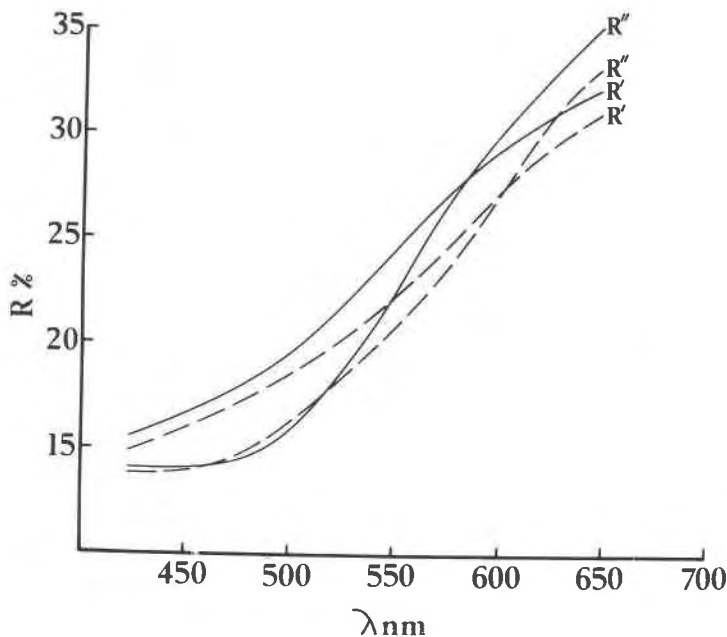


FIG. 7. Reflectivity dispersion profiles (dashed lines) for idaite from Mina Manto Esperanza, Copiapó district, with that for idaite from Bancairoun, France (Lévy, 1967), for comparison.

Bancairoun, France (Lévy, 1967), but lying at slightly lower values. We have been unable to obtain reliable X-ray powder data for idaite from the Copiapó ores, but Lévy, who encountered similar difficulties, has pointed out that the powder data given by Frenzel (1959) in fact bear close comparison with the tetragonal pattern of mawsonite, an intermediate member of the idaite (Cu_3FeS_4)—stannite ($\text{Cu}_2\text{SnFeS}_4$) series.

In contradistinction to the evidence obtained from the microprobe analysis of natural, supergene idaite, Frenzel and Ottemann (1967) have recently demonstrated that a *hypogene*, idaite-like phase occurring in the Nukundamu deposit, Fiji, has a composition (Table 3; Fig. 6) closely approaching stoichiometric Cu_5FeS_6 , or that of the synthetic phase in the Cu-Fe-S system. This coarsely-crystalline mineral has an apparently hexagonal unit cell with c_0 markedly shorter than that calculated for natural idaite by Frenzel (1959), and Frenzel and Ottemann therefore suggest that two distinct polytypes of this mineral exist. We consider, however, that the clearly hexagonal synthetic phase, $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$, and the probably tetragonal natural Cu_3FeS_4 are unrelated, and that the copper-iron sulfide described by Frenzel and Ottemann is a new mineral,

perhaps corresponding to the synthetic compound. The name, idaite, was originally applied by Frenzel (1959) to a supergene mineral formed through the oxidation of bornite, and closely comparable in all respects to the phase investigated by Lévy (1967) and by the present authors, and should therefore be retained for the tin-free end-member of the $\text{Cu}_{2+x}\text{Sn}_{1-x}\text{FeS}_4$ solid solution series.

To date we have paid only cursory attention to the chalcopyrite-like mineral which is formed together with idaite in the oxidation of bornite. As mentioned above, however, it differs to no significant degree in its general optical properties from the hypogene chalcopyrite in these ores, although accurate measurement of its reflectivity is prevented by its small grain-size and intimate association with idaite. Of the previous authors who have described assemblages of this type, only von Gehlen (1964) examined the composition of this phase. He concluded, on the basis of electron probe microanalysis, that the chalcopyrite-like mineral is not stoichiometric CuFeS_2 , but perhaps contains minor oxygen, so that it approaches $\text{Cu}_5\text{Fe}_4\text{S}_{10}\text{O}_4$ in composition. No details were given of the evidence which led von Gehlen to propose that oxygen may be present, but we tentatively assume that his microprobe analysis may have totalled to significantly less than 100 percent.

In view of these interesting results, we have carried out preliminary microprobe analyses of lamellae of the chalcopyrite-like mineral in specimens from the near-surface zone of the Manto Esperanza mine, using associated remanent hypogene chalcopyrite and bornite as standards. Despite the very small dimensions of the yellow sulfide grains (maximum $5 \times 15 \mu\text{m}$), the determined values for copper, iron, and sulfur total to more than 99.0 percent in the two analysed areas, and no oxygen could be detected. On the assumption that the hypogene chalcopyrite and bornite have the compositions, $\text{CuFeS}_{1.99}$ (Yund and Kullerud, 1966) and CuFeS_4 (Table 2), a composition of $\text{Cu}_{1.06}\text{FeS}_{2.01}$ is deduced for the chalcopyrite-like mineral. This is approximately one percent richer in copper than stoichiometric CuFeS_2 , but it should be stressed that our analytical precision was certainly insufficient to rigorously confirm the small compositional difference between the hypogene and supergene chalcoprite phases. At present, the reasons for the divergence in our results from those of von Gehlen is unexplained, and clearly further work should be done on this mineral.

CONDITIONS OF FORMATION

Mineralogical reactions closely comparable to those described above have been simulated in uncomplicated low-temperature hydrothermal experiments by several workers. The formation of covellite by reaction

of aqueous solutions of CuSO_4 with copper-iron sulfides was accomplished by Zeis and Allen (1916), and, by the action of ferric sulfate and, more slowly, sulfuric acid solutions on "chalcocite", by Sullivan (1930). Both blaubleibender and normal covellite were formed chalcocite and digenite by Frenzel (1959), using hydrochloric and nitric acids, while Moh (1964) demonstrated that blaubleibender covellite may be formed at 25° and 50°C as an intermediate step in the formation of covellite in experiments modelled on those of Zeis and Allen. We have similarly converted djurleite to intergrowths of the two covellite varieties by reaction with sulfuric acid solutions at 20–25°C. Blaubleibender covellite was initially produced, and was subsequently transformed to the normal modification. In a recent study of the low temperature oxidation of chalcocite and digenite by ferric sulfate solutions, Thomas, Ingraham and Macdonald (1967) have concluded that the reaction rate in such systems is controlled by diffusional processes; both digenite and blaubleibender covellite were observed as intermediate products of the oxidation of "chalcocite", supporting our identification of these sulfides as early oxidation products of "massive chalcocite" ores in the Copiapó region.

The action on bornite of inorganic acids has been found to yield idaite and chalcopyrite (Frenzel, 1959), while Schouten (1934) earlier obtained a yellowish-brown variety of bornite, perhaps comparable to our anomalous bornite, by the reaction of normal bornite with ferric and ferrous sulfate solutions at 85°C.

It is considered that the action of ferric sulfate-bearing solutions in the oxidized zone, above the water table, has given rise to the assemblages described in this paper, ultimately producing the widespread goethite-malachite association. The solutions containing trivalent iron and sulfate ions have certainly been derived from the immediate oxidation of pyrite and chalcopyrite which had survived previous sulfide enrichment. Chalcopyrite may be altered to goethite and malachite solely by the action of oxygenated water in the absence of sulfate. The alteration of "massive chalcocite" to porous aggregates of covellite may be attributed to sulfate-bearing solutions with a low ferric iron activity. The formation of blaubleibender and normal covellite as intermediate products of the oxidation of djurleite to malachite could be attributed to the action of sulfate or, possibly, bicarbonate ions in the oxidizing solutions. The former mechanism is favored, however, since low sulfate ion activities have been confirmed experimentally for malachite-precipitating solutions by Garrels and Dreyer (1952).

The present extremely arid climate of northern Chile has probably prevailed at least since the end of the Miocene, and the rate of supergene oxidation has, therefore, been slow for over ten million years (Clark *et al.*,

1967). For instance, grains of normal, hypogene bornite now exposed at surface in the Mina Esmeralda vein, which outcrops on the Atacama Pediplain, have been only partially transformed to anomalous bornite, idaite and covellite over this very extended period. Frenzel (1959) considered that an arid climate is necessary for the formation of blaubleibender covellite and idaite, and it is indeed possible that such an environment favors the crystallization and preservation of these sulfides. However, Frenzel's suggestion that chloride-rich ground waters are required for the formation of these minerals has not been supported by the present study, which has shown that the basic copper chlorides (indicative of a high chloride ion activity) have a rather restricted distribution in the southern Atacama Desert (Sillitoe, 1969a).

Garrels and Christ (1965) demonstrated that comparatively low Eh conditions are a prerequisite for the precipitation of sulfides, such as covellite and chalcopyrite, in the supergene environment. The alteration of "massive chalcocite" to covellite alone is best shown by ores from the base of the oxidized zone, immediately above the water table, particularly in zones of preferential downward percolation of water, where low oxidation potentials would be expected. However, the formation of sulfides as the initial stage in the development of goethite-malachite assemblages is favored in the near-surface zone. It might, therefore, be postulated that the micro-environment immediately surrounding an oxidizing copper or copper-iron sulfide grain possesses a low oxidation potential, owing to the exclusion of oxygen by the enclosing malachite and goethite.

DISCUSSION

The broad compositional changes which have occurred during the *early* stages in the oxidation of djurleite, digenite, chalcopyrite, and bornite in the copiapó region are diagrammatically illustrated in Figure 8 (*cf.* Runnells, 1969, Fig. 14), to the extent that they can be represented wholly in terms of the system Cu-Fe-S.

Oxidation of the binary copper sulfides clearly results in a loss of copper, and an effective gain in sulfur, whereas chalcopyrite initially exhibits an enrichment in copper where covellite is formed, the iron thereby released being reprecipitated as goethite. The effect of oxidation on bornite is a significant increase in sulfur, and a comparable concentration of iron, leading to the essentially contemporaneous formation of anomalous bornite, idaite, and chalcopyrite. Iron is then lost, presaging the complete replacement of the sulfide aggregate by goethite.

The cavernous textures which result from the replacement of "massive chalcocite" by covellite (Figure 1), and from the formation of idaite,

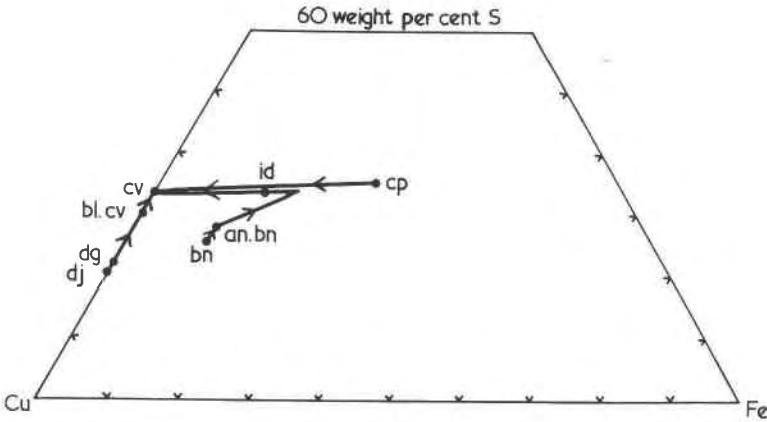


FIG. 8. Compositional changes which have occurred during the initial stages of the oxidation of djurleite, digenite, bornite, and chalcopyrite in the Copiapó district (dj = djurleite; dg = digenite; cv = normal covellite; bl cv = blaubleibender covellite; bn = bornite; an bn = anomalous bornite; id = idaite; cp = chalcopyrite).

and covellite after bornite, clearly indicate a volume reduction; part of the copper passes into solution, and nothing is precipitated in its place. The "volume-for-volume" law is not, therefore, always followed in the oxidized zone. However, the later stages of the replacement of sulfides by goethite and malachite do not appear to have involved appreciable volume reduction; indeed, voids formed during the crystallization of the sulfides were infilled in the course of the subsequent formation of the oxidate phases.

Intrepretation of the supergene sulfide assemblages described in this paper in terms of the equilibrium phase relations in the systems Cu-S (Roseboom, 1966) and Cu-Fe-S (Yund and Kullerud, 1966) is inherently hazardous. Supergene oxidation of this type involves radical changes in bulk composition, and there is no reason to expect that the eventual products of the oxidation will bear equilibrium relations with the minerals undergoing alteration under any conditions (*cf.* Yund and Kullerud, 1966, p. 486). Obviously, tie-lines must be drawn with extreme caution between "coexisting" minerals in such assemblages. Ideally, however, the stable phase relations in the Cu-Fe-S system should constitute a precise restraint on the nature of the oxidation products throughout the alteration process, so long as no additional elements (*e.g.* O) enter into solid solution in the reacting phases. While the system remains strictly binary or ternary, alteration should proceed in a "step-wise" manner via compositionally contiguous, stably-coexisting phases. Thus, djurleite would be converted to digenite (or anilite) as an intermediate stage in the

formation of covellite, according to the stable phase equilibria at 25°C in the system Cu-S (Roseboom, 1966). If, as seems probable (N Morimoto, pers. comm., 1969), digenite, *sensu stricto*, is invariably an iron-bearing mineral, anilite should presumably form initially in the replacement of djurleite by covellite, and would then appear in polished section as a digenite-like phase. As we have noted above, digenite is indeed occasionally observed as an early product of the oxidation of djurleite, but its rarity in such environments demonstrates that evidence of such local "equilibration" is not generally preserved, if in fact it was ever attained.

Alongside such omission of stable intermediate minerals, the demonstrated occurrence of a number of clearly metastable, intermediate solid solutions in *enriched* assemblages introduces further uncertainties to interpretation. In the north of Chile, the supergene replacement of pyrite and chalcopyrite by djurleite and chalcocite has led to the formation and preservation of compositionally extensive "chalcopyrite-bornite" and "bornite-digenite" solid solutions, ranging across ternary space from the immediate chalcopyrite region to the Cu-S join (Clark, Clark, and Sillitoe, 1968; and in preparation). Similarly, Cu-As-S solid solutions intermediate in composition between enargite and djurleite have been confirmed from ores in which the former sulfide has undergone enrichment (Clark and Moraga, 1969). In both instances, the intermediate solid solutions may be regarded as metastable diffusion fronts, wholly unrelated to the low temperature phase relations in the respective ternary systems, and, in the latter case, bearing no relation to phase equilibria at any temperature below the liquidus (B. J. Skinner, pers. comm., 1969).

The wide compositional range confirmed for blaubleibender covellite of supergene oxidation origin might similarly be interpreted as an indication of a metastable origin, *in this instance*, as a transitional stage in the formation of covellite from more copper-rich sulfides. Moh (1964, and personal communication, 1969), however, considers that this phase does have a definite stability field in the system Cu-S. If that author attained equilibrium in his hydrothermal experiments at 50°C and 135°C, the possibility remains that the stability field of blaubleibender covellite broadens markedly between 50°C and 25°C, the approximate temperature of formation of this mineral in the Copiapó ores. We feel, however, that blaubleibender covellite is either inherently unstable relative to the association covellite + anilite, or more probably, has a field of stability considerably more extensive, in terms of Cu:S ratio, at all temperatures below $157 \pm 3^\circ\text{C}$ (Moh, 1964), than that indicated by Moh's study.

We consider that the ternary sulfides formed in the earliest stages of the oxidation of bornite, on the other hand, have compositions which were controlled by phase relations in the system Cu-Fe-S at $\sim 25^\circ\text{C}$.

The apparently arbitrary, but consistent, path of sulfur- and iron enrichment revealed by the alteration assemblages, and the absence of ternary solid solutions colinear with the hypogene bornite and covellite, the final sulfide formed before the advent of exclusively oxidate associations, suggest to us that the development of the anomalous bornite-idaite-chalcopyrite assemblage took place in response to phase equilibria. Tie-lines might, therefore, be drawn between these phases, as well as from normal- to anomalous bornite, outlining a univariant field, and invalidating the tie-line connecting digenite (or digenite solid solution) and pyrite, proposed by Yund and Kullerud (1966) and Barton and Skinner (1967). Clearly, the much debated chalcocite-pyrite tie-line (Yund and Kullerud, 1966) cannot, in this case, exist at temperatures below the upper stability limit of idaite, even if, as seems unlikely, those connecting djurleite and digenite with bornite are unrepresented at very low temperatures.

The available analytical evidence, as detailed in this paper, strongly implies that the supergene mineral idaite is represented by the essentially stoichiometric formula, Cu_3FeS_4 , and that this phase is distinct from the $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$ solid solution synthesized by Yund and Kullerud (1966) and earlier workers. Idaite apparently becomes unstable at temperatures as low as 100°C , since the association $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x} + \text{pyrite}$, originally synthesized at 150°C , failed to yield the more iron-rich ternary sulfide when heated at that temperature for as long as 67 days (Yund and Kullerud, 1966). Similarly, the non-formation of the $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$ phase in the course of the conversion of the idaite-chalcopyrite association to covellite (see above) is interpreted as indicating that it is unstable at 25°C , in view of its approximate compositional colinearity with idaite and covellite. The idaite-like hypogene mineral described by Frenzel and Ottemann (1967) would then be considered to have been preserved metastably on cooling.

While we favor the hypothesis that the microprobe analyses of the anomalous bornite in the Copiapó deposits approximately delimit part of the $\sim 25^\circ\text{C}$ stability field of a low temperature ($< 75^\circ\text{C}$), bornite-like, sulfur-rich phase, the possibility that this mineral is in fact a metastable, albeit homogeneous, reaction product between hypogene bornite and idaite would be supported by its intermediate composition, and cannot be discounted without further observational and experimental study.

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