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**NICKEL-GOLD ORE
OF THE MACKINAW MINE,
SNOHOMISH COUNTY, WASHINGTON**

By

CHARLES MILTON and DANIEL J. MILTON

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NICKEL-GOLD ORE OF THE MACKINAW MINE, SNOHOMISH COUNTY, WASHINGTON¹

CHARLES MILTON AND DANIEL J. MILTON

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ABSTRACT

The Mackinaw mine ore is of an unusual or unique type, consisting chiefly of niccolite, maucherite, pentlandite, chalcopyrite, cubanite, and magnetite in an altered peridotite. Valleriite, gold and sphalerite are minor primary minerals; chalcocite and violarite or bravoite are supergene minerals. Pyrrhotite and pyrite are absent. From the textural relations it is inferred that a complex copper-nickel-iron sulfide was deposited early. On cooling, the sulfide unmixed into two different complex sulfides, one of which in turn unmixed into chalcopyrite and cubanite, the other into chalcopyrite and pentlandite. The latter exsolution relationship has not been previously reported. Valleriite either exsolved from, or replaced, chalcopyrite. Late solutions altered the niccolite to maucherite, and introduced gold and magnetite. The gold is almost always with maucherite.

INTRODUCTION

The Mackinaw mine, known locally as the Weden Creek mine, is in sec. 19, T. 29 N., R. 11 E., Snohomish County, Washington, in the Monte Cristo mining district, within the Mount Baker National Forest, 40 miles east of

¹ Publication authorized by the Director, U. S. Geological Survey.

Everett. The mineralized area is in a glacial valley at an elevation of 3,000 to 5,000 feet. The prospect was located in 1900, and development work has been carried on intermittently since then, especially during World War II.

J. J. Collins and S. C. Creasey, U. S. Geological Survey (written communication, 1944), state:

The sulphide minerals occur as disseminated grains and blebs in the serpentine and may total as much as 20% of the rock in some spots. No concentration of sulphide minerals was noted on the numerous fractures in the serpentine, but the supergene oxide minerals, on the other hand, are concentrated on fault and fracture surfaces. The commonest of these minerals are probably malachite and garnierite, or annabergite, but erythrite is also much in evidence.

Further information from a Bureau of Mines report dated 1944 as follows:

The ore deposits are in a peridotite dike or intrusive that appears to be an apophysis of the large intrusive of reddish-brown peridotite that comprises the mountain that rises southeast of the ore deposits. The peridotite is interspersed with small blebs and seams of serpentine, actinolite, and tremolite. At several places in the mass, small deposits of sulphide, which contain copper and nickel minerals, were observed. The peridotite, in which the principal ore deposits occur, is a dense, dark colored fine-grained rock that has been partly serpentinized. . . . The principal ore deposits occur in the peridotite along a shear zone that . . . dips nearly vertical . . . partly on the contact between the peridotite and metamorphic rocks, but parallel seams extend into the peridotite.

Spurr (16) investigated the geology of the Monte Cristo district in 1900, but did not mention the Mackinaw prospect, if indeed it had been located at the time of his visit. He reported that the chief ores of the district consisted of pyrite, pyrrhotite, arsenopyrite, sphalerite, galena, chalcopyrite, and realgar, and that gold and silver were present. Of course, this was at a time when polished sections and modern techniques of mineral identification were not yet developed and when maucherite was unknown and cubanite poorly known. A restudy of ores from other mines in the district may show that the mineralogy of the Mackinaw mine is not unique.

A brief summary of the mineralogical features, without discussion of the inferred history of the ore, was presented by Charles Milton at the Geological Society of America meeting, El Paso, Texas, 1949 (10).

Acknowledgments.—The present study has been made on a representative suite of ore specimens collected by S. C. Creasey, U. S. Geological Survey.

We are indebted to Dr. Gunnar Kullerud, of the Geophysical Laboratory of the Carnegie Institution of Washington, who has kindly read and instructively commented on this paper, without necessarily subscribing to the ideas contained in it. Professor A. F. Hagner, University of Illinois, furnished us typical specimens of the Alistos, Mexico, ore for comparative study. The critical X-ray diffraction identifications, without which this investigation would not have been possible, were made by Joseph M. Axelrod of the U. S. Geological Survey. The photomicrography was done by J. A. Denson, of the U. S. Geological Survey.

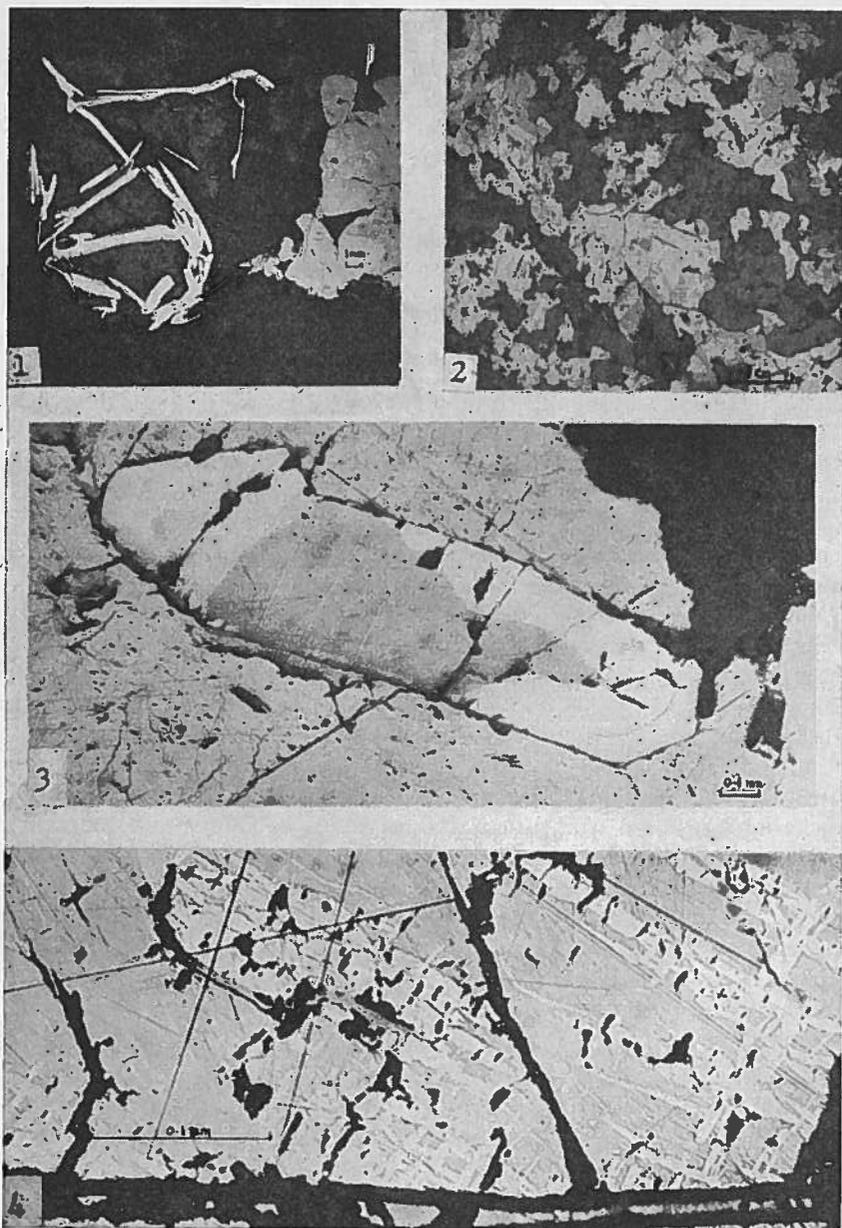


FIG. 1. At left, maucherite (light) rimmed by chalcopyrite (darker), with fine-grained chalcopyrite dispersed in gangue. At right, a massive aggregate of chalcopyrite-cubanite with pentlandite. $\times 2$.

FIG. 2. Chalcopyrite-cubanite with minor pentlandite (light) and magnetite (darker gray) and gangue (dark). Natural size.

MINERALOGY OF THE MACKINAW MINE ORE

The ore minerals are generally strewn sparingly through the gangue. Although different from one specimen to another specimen, the gangue is mostly serpentine, and contains minerals common to altered ultramafic rocks, such as talc, actinolite, and carbonates, and oxidized ore minerals, such as malachite, annabergite, and erythrite.

The hypogene minerals at Mackinaw are the nickel arsenides (niccolite and maucherite), the nickel iron sulfide (pentlandite), and the copper iron sulfides (chalcopyrite, cubanite, and valleriite). Minor amounts of sphalerite, magnetite, and gold are present. Supergene alteration has produced a little chalcocite and covellite from the copper-iron sulfides, and bravoite or violarite from the pentlandite.

The arsenides and sulfides form more or less separate assemblages, and the gold is almost always associated with maucherite. When the mineralogy of this deposit was first studied, a small piece of ore examined in the Geological Survey laboratory was reported as containing major pentlandite, and no arsenides or gold; another piece of ore studied in another laboratory carried no pentlandite, but much maucherite with gold. Study of more specimens showed both assemblages to be closely associated in many of them.

Niccolite and Maucherite.—Niccolite (NiAs) is distinguished from maucherite ($\text{Ni}_{11}\text{As}_8$) by its bronze color; the maucherite, though it has a pinkish cast, is much paler. Moreover, niccolite is strongly anisotropic but maucherite is almost isotropic. The two minerals occur in crystal plates, commonly coalesced into irregular masses, and generally partially replaced by the other ore minerals. Some specimens contain maucherite without niccolite, but none were found that contained niccolite without maucherite. The occurrence of maucherite, separated from niccolite by a sharp boundary and generally on the outside, indicates that maucherite has replaced niccolite (Fig. 3). Alteration of niccolite to maucherite, by loss of arsenic, is also known at Los Jarales, Malaga, Spain, and Bou Azzer, Morocco (12), where, as in the Mackinaw ores, maucherite peripherally replaces niccolite.

No rods or blebs of maucherite in niccolite, such as those found at Alistos and interpreted by Krieger and Hagner (5) as exsolved, were found in the Mackinaw ore.

The occurrence in the oxidized ore of pink erythrite (cobalt bloom) as well as green annabergite (nickel bloom) suggests the presence of cobalt in some primary mineral or minerals. X-ray fluorescence examination shows a small amount of cobalt in the maucherite, and presumably cobalt is also present in the niccolite.

FIG. 3. Maucherite (lighter gray) replacing niccolite (darker gray). The left end of the large grain is also niccolite in a less extinguished orientation. Crossed nicols. $\times 50$.

FIG. 4. Pentlandite lenses (white) in chalcopyrite, thinning at intersections. Pentlandite stops abruptly at a cubanite lamella (left, slightly darker than chalcopyrite). Magnetite in cracks (center and along bottom). $\times 260$.

Pentlandite.—Pentlandite occurs in two major forms in the Mackinaw mine ore: as massive grains (Figs. 12, 14), and as flames and lenses in chalcopyrite-cubanite (Figs. 4, 5). A minor third form consisting of irregular small grains of pentlandite in a chalcopyrite-cubanite matrix, that do not have the regularity of shape of the flames or lenses, is probably the result of extensive replacement of massive grains of pentlandite by chalcopyrite-cubanite (Figs. 5, 6).



FIG. 5. Above, bands of pentlandite flames in chalcopyrite-cubanite. Below, right, chalcopyrite-cubanite, replacing pentlandite. Left center, pentlandite-chalcopyrite-cubanite in intergrowth of uncertain origin. Center, gangue and magnetite. $\times 70$.

There was some difficulty in identifying the pentlandite. The relief indicates that it is somewhat harder than the adjacent chalcopyrite-cubanite but it is soft enough to be readily scratched by a needle (Talmage hardness of pentlandite D, chalcopyrite and cubanite C). It shows a rather vague cleavage. The mineral was confirmed as pentlandite spectroscopically and by X-ray diffraction; both examinations, including comparison with the X-ray pattern of pentlandite from Sudbury, Ontario, showed nothing anomalous.

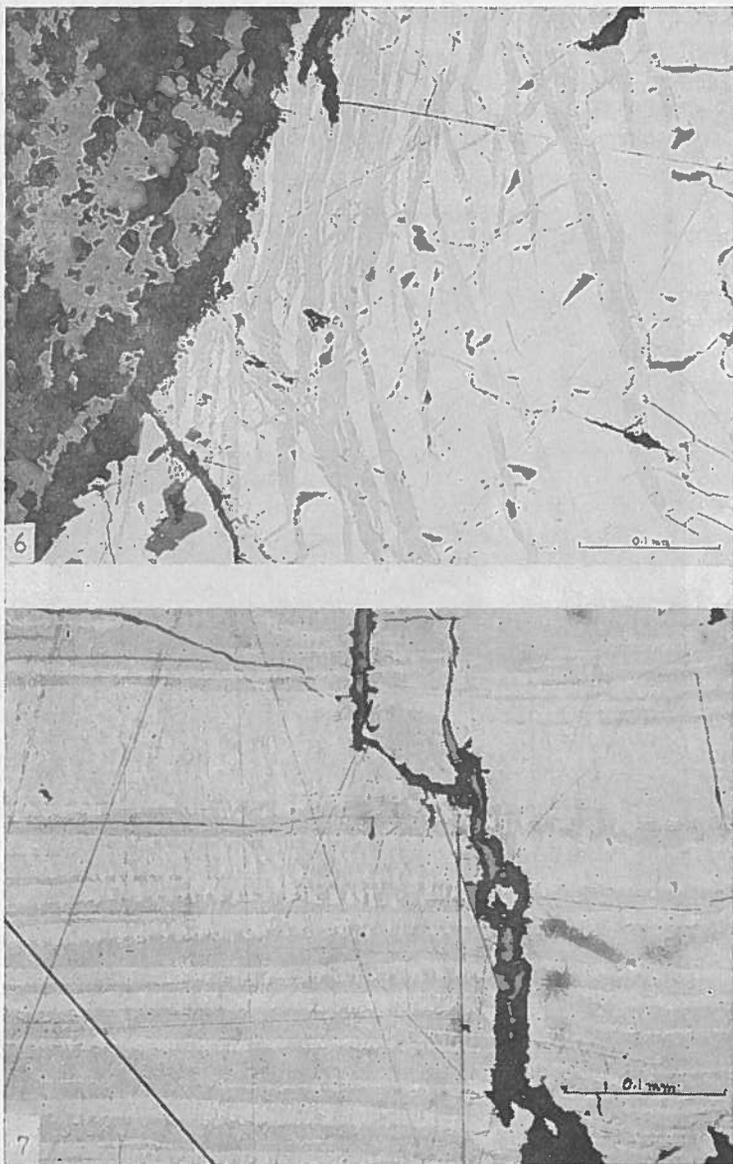


FIG. 6. Enlargement of lower right of Figure 5. Pentlandite white, chalcopyrite and cubanite gray. Magnetite in fracture above. $\times 200$.

FIG. 7. Enlargement of upper field of Figure 5. Pentlandite white, chalcopyrite light gray (in bands with pentlandite flames), cubanite dark gray (between bands). $\times 225$.

A very weak magnetism of some grains in the polished section, detected with McKinstry's magnet (7), might be due to underlying magnetite, cubanite, or perhaps valleriite, which are strongly magnetic. Minute particles, just visible to the naked eye, were tested with an alnico horseshoe magnet, and found to be definitely magnetic, probably because of intergrown cubanite.

The pentlandite is distinctly rose-colored, rather than pale yellow or cream like the usual pentlandite, as, for example, from Sudbury. This color may be merely an impression caused by the lack of contrast with pyrrhotite, against which pentlandite is usually observed. However, because the Mackinaw pentlandite is not associated with iron sulfides it may have a different composition from ordinary pentlandite, and this difference may be reflected in the color.

Violarite(?) or Bravoite(?).—The pentlandite is altered to a small extent to a gray-violet isotropic mineral of a slightly lower reflectivity than the pentlandite. This mineral is probably either violarite, Ni_2FeS_4 , or bravoite $(Ni, Fe)S_2$. It characteristically occurs in irregular patches in the pentlandite, sometimes along fractures, and is itself crossed by a network of fine irregular fractures, apparently as a result of volume decrease during formation. This alteration is probably supergene.

Chalcopyrite and Cubanite.—Chalcopyrite is found in all the ore specimens, in three forms. In one form chalcopyrite, without cubanite, occurs as aggregates of many small irregular grains separated by gangue (Fig. 1). In its other major form chalcopyrite is in all cases intimately associated with cubanite, and commonly with pentlandite and valleriite. Chalcopyrite and cubanite are generally intergrown in parallel lamellae (Figs. 5, 9), but irregular intergrowths occur and chalcopyrite commonly replaces cubanite peripherally and along fractures (Figs. 9, 11). In a third form, chalcopyrite, alone or with magnetite or gold, replaces arsenides (Fig. 8).

Cubanite and chalcopyrite are of approximately equal hardness. They are easily distinguished by their characteristic colors, as cubanite has a bronzy tint against the yellow of chalcopyrite. The chalcopyrite is less anisotropic than the cubanite, and shows its usual complex twinning, which is not observed in cubanite. The excellent cleavage of the chalcopyrite terminates abruptly against the cubanite, which has a much poorer cleavage. A further distinction is in the relation of valleriite to these two, as described below.

Valleriite.¹—Valleriite ($Cu_2{}_3Fe_4S_7?$), once considered rare but now recognized as common in high temperature (cubanite-bearing) copper ores, is beautifully developed in the Mackinaw ore. Its extraordinarily strong anisotropy and pleochroism and its characteristic feathery development in chalcopyrite make it easily recognizable (15).

The valleriite always occurs in the chalcopyrite rather than in the cubanite (Fig. 10), as is true, with minor exceptions, in all its occurrences (12). Val-

¹ Note added in proof: Preliminary results of studies in progress by C. Milton, E. C. T. Chao, and H. T. Evans, Jr., indicate that the mineral identified as valleriite in this paper is, in fact, distinct from the type valleriite from Kaveltorp, Sweden. The Mackinaw mineral is probably an undescribed iron sulfide, the Kaveltorp valleriite is perhaps a copper-iron-magnesium sulfide. Probably both these phases, if not others also, are to be found among material from other localities that has been called valleriite.

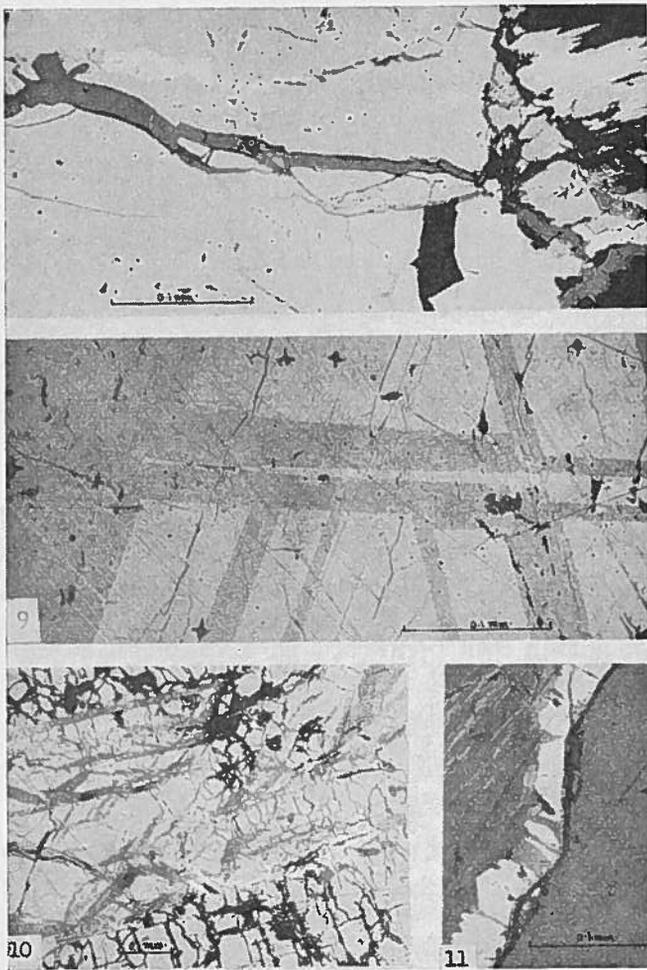


FIG. 8. Maucherite replaced by chalcopyrite-cubanite (right) and cut, above, by a vein composed of, left to right, chalcopyrite, gold and magnetite, and center and right by magnetite veins. $\times 200$.

FIG. 9. Lamellar intergrowths of cubanite (dark) and chalcopyrite (light) with sphalerite stars and irregular bodies (right, very dark). Minor chalcopyrite replaces the cubanite along fractures. $\times 205$.

FIG. 10. Cubanite (above and below) gray, and chalcopyrite (center), (slightly lighter). The chalcopyrite contains many "feathers" of valleriite. The valleriite is mostly replaced by chalcocite (dark gray), leaving only small patches unreplaced (below center, bright). The chalcopyrite and cubanite are also replaced by chalcocite and covellite (black). Crossed nicols, sensitive tint. $\times 75$.

FIG. 11. Right, pentlandite. Center, unidentified mineral (valleriite?). Left, cubanite (dark) and chalcopyrite (light). Crossed nicols. $\times 175$.

leriite also was found within a single grain of pentlandite as small ragged bodies all in parallel crystallographic orientation, perhaps aligned along a poorly developed cleavage in the pentlandite (Fig. 13).

Chalcocite and Covellite.—Minor amounts of chalcocite (or digenite) and even less covellite have formed from cubanite and chalcopyrite, along cracks.

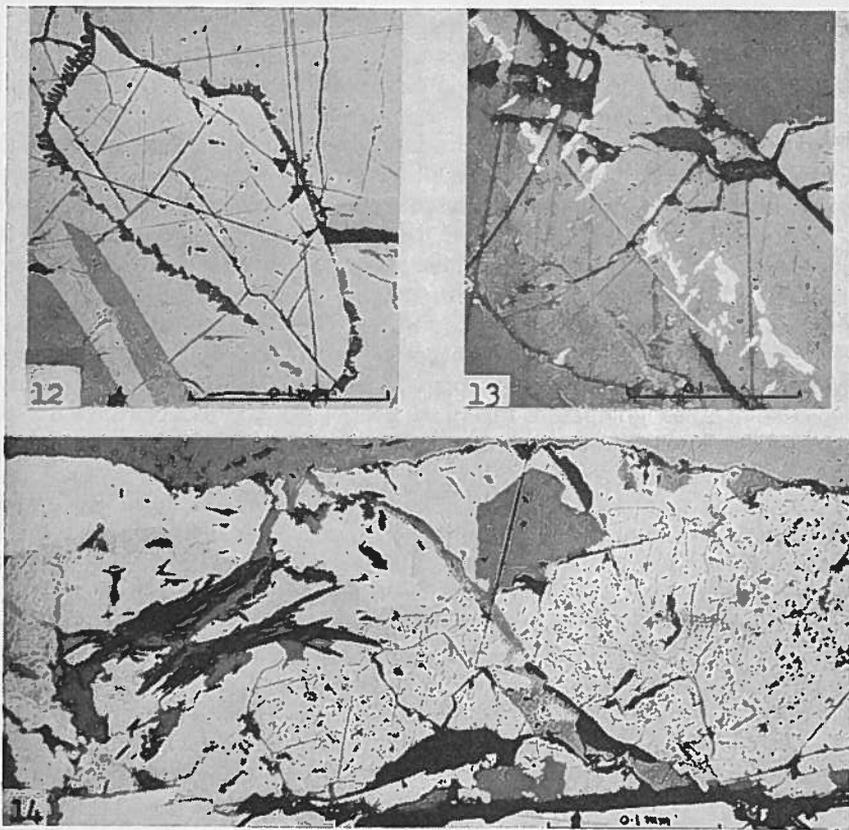


FIG. 12. Pentlandite grain mantled by sphalerite, in chalcopyrite (light)-cubanite (dark) intergrowth. $\times 260$.

FIG. 13. Valleriite (bright) in pentlandite. Cubanite at upper right. Crossed nicols. $\times 225$.

FIG. 14. Maucherite (brightest, left above and below), pentlandite (center and right, gray pitted surface), chalcopyrite (gray, smooth), sphalerite grains (dark gray, right above and below) and magnetite veinlets (dark gray). $\times 220$.

The alteration is more marked in the cubanite than in the pentlandite; these copper sulfides are considered as of supergene origin. Chalcocite and covellite also replace valleriite, rather extensively.

Sphalerite.—Sphalerite occurs in tiny skeletal crystals ("stars") in the chalcopyrite-cubanite (Fig. 9). These are randomly distributed in the chalcopyrite and cubanite and across the boundaries, indicating that they formed

before the differentiation of those two minerals. Sphalerite stars are limited to high temperature ore deposits, but are well known in such.

Sphalerite also occurs as grains in chalcopyrite-cubanite. Most of them have rather simple rounded margins but some are of more complex shape, seemingly intermediate in a continuous series extending from the skeletal stars through less delicate skeletal crystals to the irregular and rounded blebs. Such sphalerite is commonly in the chalcopyrite-cubanite along the margins of pentlandite and magnetite grains (Fig. 12). There seems to be some crystallographic control of the localization and orientation of sphalerite grains and stars in the chalcopyrite-cubanite.

Magnetite.—There are two generations of magnetite. Magnetite of the older generation occurs mostly in small grains, disseminated in the gangue, some of which contain inclusions of gangue minerals themselves. This generation is probably more closely related to the normal magmatic stage of the peridotite than to the stage of ore formation. A very few corroded grains occur within the chalcopyrite-cubanite, and are probably relics of this earlier generation.

Magnetite of the younger generation occurs in veinlets cutting, or rims surrounding, all the other major opaque minerals (Figs. 4, 8). Silicate gangue, sometimes gold, and rarely chalcopyrite, are associated with the magnetite veinlets. Similar late magnetite was found at Insizwa by Scholtz (14).

Gold.—Gold occurs in considerable quantity in cracks or openings in maucherite, rarely in niccolite and cubanite. Typically it is in irregular, more or less rounded blebs in the maucherite, but it also occurs in veinlets cutting maucherite, generally with magnetite or chalcopyrite, in some places with valleriite also (Fig. 8). Its color is variable in golden shades, probably because of varying amounts of silver; for this reason, it might be called gold-electrum, rather than gold.

Other Possible Minerals.—Our belief in the absence of pyrrhotite rests on the failure to find a rose-colored mineral with fair cleavage, sensible magnetism, and definite anisotropy after thorough scrutiny of some two dozen polished sections. Some particles at first suspected of being pyrrhotite were proven to be pentlandite by X-ray methods.

One single group of grains suspected of being pyrrhotite is too small to be positively identified. These grains occur in cubanite-chalcopyrite along the edge of a pentlandite grain (Fig. 11). The mineral is rose-gray against cubanite and chalcopyrite, is weakly but distinctly pleochroic, moderately anisotropic in gray to reddish-brown, and has a reflectivity close to that of cubanite (but perhaps slightly more or less depending on orientation) and has no apparent cleavage. This mineral may be pyrrhotite, except for a slightly higher reflectivity, but fits as well or better for valleriite in a nearly basal section. It is probably valleriite of a somewhat unusual habit.

DEPOSITS OF SIMILAR MINERALOGY

A deposit at Alistos, Sinaloa, Mexico, described by Krieger and Hagner (5) in 1943 and considered by them to be unique has some points of similarity

to Mackinaw. At Alistos, the ore occurs in an enstatite latite, but on the periphery of, and associated with, an altered peridotite intrusive. Here, too, pentlandite occurs without pyrrhotite (although with pyrite). At Alistos, moreover, two distinct types of ore were found, one containing nickel arsenides (mostly niccolite) but no nickel sulfides, the other nickel sulfides but no nickel arsenides. Gersdorffite (NiAsS) occurs in both types. Most of the gold is present in arsenide ore. The Alistos deposit, however, differs markedly from the Mackinaw deposit in the absence of copper minerals.

The ores of Insizwa, South Africa, in the basal part of a mafic intrusive, described by Scholtz (14), also have some features in common with the Mackinaw ores. At Insizwa, most of the ore contains abundant pyrrhotite, but there also occur pyrrhotite-free ores. One type, "massive chalcopyrite-cubanite ore," consists of about 50 percent chalcopyrite, 30 percent pentlandite, 18 percent cubanite, and 2 percent bornite and other unnamed minor constituents. The deposit as a whole is regarded as of magmatic origin, and the chalcopyrite-cubanite ore as representing a late copper-rich differentiate. Textures and relationships in the Insizwa ore are commonly similar to those in the Mackinaw ore. The Insizwa ores differ from the Mackinaw ores in that arsenides (niccolite) and gold are comparatively scarce, and, of course, the Mackinaw ore is entirely pyrrhotite free, whereas the chalcopyrite-cubanite ore at Insizwa is a rather aberrant type within a pyrrhotite-rich deposit.

RELATIONSHIPS OF THE SULFIDE MINERALS

The Mackinaw deposit is unusual, perhaps (excepting Alistos) almost unique, in containing pentlandite without pyrrhotite.

The cause of this absence of pyrrhotite will be discussed in detail below, but in brief, it, as well as many of the other unusual features of the ore, can be attributed to the exceptionally high Ni:Fe and Cu:Fe ratios of the Mackinaw ore. Thus, our explanation of the development of the ore, which we feel is in accord with the evidence of the polished sections, must differ in some particulars from any that has been proposed for other ore deposits.

Most of the chalcopyrite, cubanite, and valleriite, and some of the pentlandite and sphalerite are interpreted as having unmixed from an originally homogeneous solid sulfide phase of complex composition, which we may call "phase I." From the relative abundance of its unmixing products, phase I is inferred to have contained copper, iron, and nickel sulfides in proportions that would very approximately give about equal parts of chalcopyrite and cubanite, and about a fourth as much pentlandite, and perhaps also small amounts of zinc sulfide.

On cooling, phase I unmixed into an intergrowth to two new phases, II and III, each of which later underwent further unmixing. Phase II, a copper-nickel-iron sulfide, formed as lamellae within, and as less regular areas along the edges of, the more abundant phase III, a copper-iron sulfide. Figure 15 shows the inferred course of exsolution for the minerals derived from phase I. An idea of the inferred composition of phase I may be obtained from Figure 16A and of phases II and III from Figure 16C. It must be understood that phases I, II, and III are only inferred, by the reasoning given below.

On further cooling phase II unmixed into mostly chalcopyrite and pentlandite, the latter characteristically in flames transverse to the phase II lamellae (Figs. 5, 7). In areas of coarser texture the flames thin at intersections (Fig. 4), generally regarded as an indication of origin by exsolution. Many bands of pentlandite flames are broader than the associated chalcopyrite lamellae, and extend into cubanite, a mineral that for the most part formed from phase III. Some bands of pentlandite flames even seem to be entirely in cubanite, although it is sometimes difficult to determine the mineral between the pentlandite grains in the finer-textured intergrowths. At each higher magnification up to the limit of resolution, the interstitial mineral in more and more bands of pentlandite flames seemingly in cubanite can be identified as

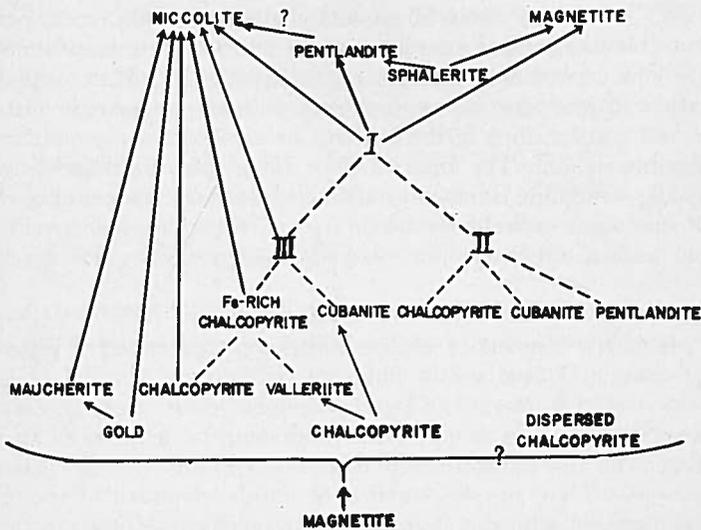


FIG. 15. Paragenetic relations of Mackinaw ore minerals. The dotted lines indicate exsolution or unmixing relationships. Solid lines indicate replacement or rimming, the arrow pointing to the older mineral.

chalcopyrite. On the other hand, some bands still seem to have very little associated chalcopyrite. However, the association of the pentlandite bands with chalcopyrite rather than cubanite is so dominant that it must be regarded as the normal occurrence. It is more likely that all the pentlandite exsolved from phase II, which contained varying amounts of excess iron that separated as cubanite, than that some of the pentlandite exsolved with cubanite from phase III. If so, the composition of phase II would correspond to a mixture of about equal parts of chalcopyrite and pentlandite and perhaps a tenth part of cubanite.

Certain patches of pentlandite that occur in either chalcopyrite or cubanite or both may be confused with the unmixed phase II. These patches consist of irregularly shaped pentlandite grains enclosed in a nearly patternless network of the copper sulfides and never arranged in bands. These patches are

probably the result of extensive veining and replacement of pentlandite grains that formed as such before the deposition of phase I, because intermediate stages seem to be present. However, similar textures may have arisen on unmixing of phase II. The origin of part of the intergrowth shown in Figures 5 and 6 is indeterminate for this reason.

No material corresponding to phase II or its exsolution product has been reported, either naturally occurring or artificially produced. The only exsolution relationship involving pentlandite and chalcopyrite mentioned by Ramdohr (12, p. 150) consists of a "*zellig-netz-formig*" (cell-net form) intergrowth of one part of chalcopyrite in ten parts of pentlandite from Igdlukunguak, Greenland. He comments that this is rare as an exsolution texture but that similar textures are produced by replacement. Elsewhere (12, p. 85), he has a photograph of an ore from the same locality containing material in which no internal structure can be seen; according to his caption this material is an almost isotropic complex mixture of pentlandite and chalcopyrite (originating from an (Fe,Cu,Ni)S mix-crystal). It is not clear whether these two references are to the same material, but in any case, neither resembles the Mackinaw intergrowths. No sulfides containing copper and nickel have been found by study of artificial mattes (8), nor are any copper-nickel-iron sulfides mentioned in the literature.

Phase III was a copper-iron sulfide with little or no nickel, that eventually unmixing into a lamellar intergrowth of about equal quantities of chalcopyrite and cubanite (Fig. 9). This chalcopyrite is quite distinct from that formed from phase II because it has no associated pentlandite. Such chalcopyrite-cubanite intergrowths are well known from many localities, although elsewhere the chalcopyrite is generally in great excess (12).

There was probably a continuity of state between phases I and III, that is, the composition of the solid solution changed continuously from that of phase I to that of phase III as a consequence of the separation of the quite distinct phase II.

After the unmixing of phase III, valleriite formed from the phase III chalcopyrite. The textures are very similar to those found by Scholtz, in which valleriite "half feathers" developed entirely or almost entirely in chalcopyrite, especially along the boundaries of cubanite lamellae (Fig. 10). The valleriite probably formed by exsolution although the textures could have been developed by replacement as well. The amount is well within the range given by Ramdohr (12) for the extent of exsolved valleriite in chalcopyrite (up to 10 percent).

Minor late chalcopyrite is present within cubanite and valleriite. As this chalcopyrite is along crosscutting cracks (or cleavage in the valleriite) it probably represents a replacement rather than an exsolution product.

The greatest part of the pentlandite occurs not as exsolved bodies, but as independent grains, at least contemporaneous with, and some earlier than, phase I. Lenses of chalcopyrite and cubanite, probably the exsolution products of an original phase III, occur within the pentlandite (Figs. 5, 6). The curved lenticular shape and the lack of relation to visible cracks might suggest exsolution from the pentlandite. However, the irregular distribution, the vary-

ing abundance, and the concentration of the lenses toward the margins of the pentlandite suggest much more strongly the replacement of pentlandite by phase III. The origin of the one example found of valleriite in pentlandite is also indeterminate although the irregular distribution suggests replacement (Fig. 13). Exsolved valleriite is common at other localities; Ramdohr reports pentlandite containing up to 25 percent of exsolved valleriite (11).

The random distribution of sphalerite "stars" within chalcopyrite and cubanite and across the boundaries between them (Fig. 9) indicates that the stars formed before the unmixing of phase III. The method of formation of sphalerite stars has never been definitely established. When Ramdohr (11) first described them, he was inclined to attribute them to mechanical inclusion of ZnS during rapid growth of the copper-iron sulfide. More recently (12) he has tended to favor an origin by exsolution. As mentioned above, there seems to be a continuous gradation from the stars to the grains of sphalerite. The latter show no indications of exsolution, but instead their irregular distribution, range of sizes, and marked preference for the margins of ore minerals that are replaced by the phase I minerals (Fig. 12), suggest that the main period of formation of sphalerite grains coincided with or preceded the beginning of deposition of formation of phase I. Whether the stars are of the same origin or are exsolved is an open question. The total amount of sphalerite is only a fraction of one percent of the amount of the phase I minerals.

As the history of the Mackinaw ore is quite different from that of any other known deposit, comparative studies are of little help in understanding the paragenesis. There has been no experimental work on the quaternary system Cu-Ni-Fe-S although some data are available on the ternary systems Cu-Fe-S (9, 2) and Fe-Ni-S (4, 6). Therefore, there is little except the observed relations and some rather incidentally applicable experimental work to aid in the interpretation of the paragenesis, in particular the nature and history of the phase I complex.

At about 540° C, the copper and iron atoms in chalcopyrite disorder, and the disordered phase has a sphalerite-type crystal structure (3). The tolerance for a high ratio of iron to copper and the tolerance for other metals—tin, zinc, and presumably nickel—increase. Phase III is very likely such an iron-rich disordered chalcopyrite, and probably phase I is a nickelian variety of the same. However, until this suggestion is confirmed by experimental work, it seems best not to use mineral names for these hypothetical phases.

Phase II is more difficult to explain. The relative amounts of pentlandite and chalcopyrite in its unmixed derivatives suggest a compound with a Cu:Ni:Fe:S ratio of about 1:1:2:4. That no such material has been found naturally, as either a mineral or its unmixed equivalent, is understandable on the basis of the different overall composition of Mackinaw ore from that of other investigated deposits. However, if such a substance exists, it might be expected to occur in artificial mattes, but it has never been reported. It is possible that phase II, as well as phase III, is a chalcopyrite-type mineral. Even its stable coexistence with phase III does not preclude the possibility that there is a continuity of state between them, even at the same temperature

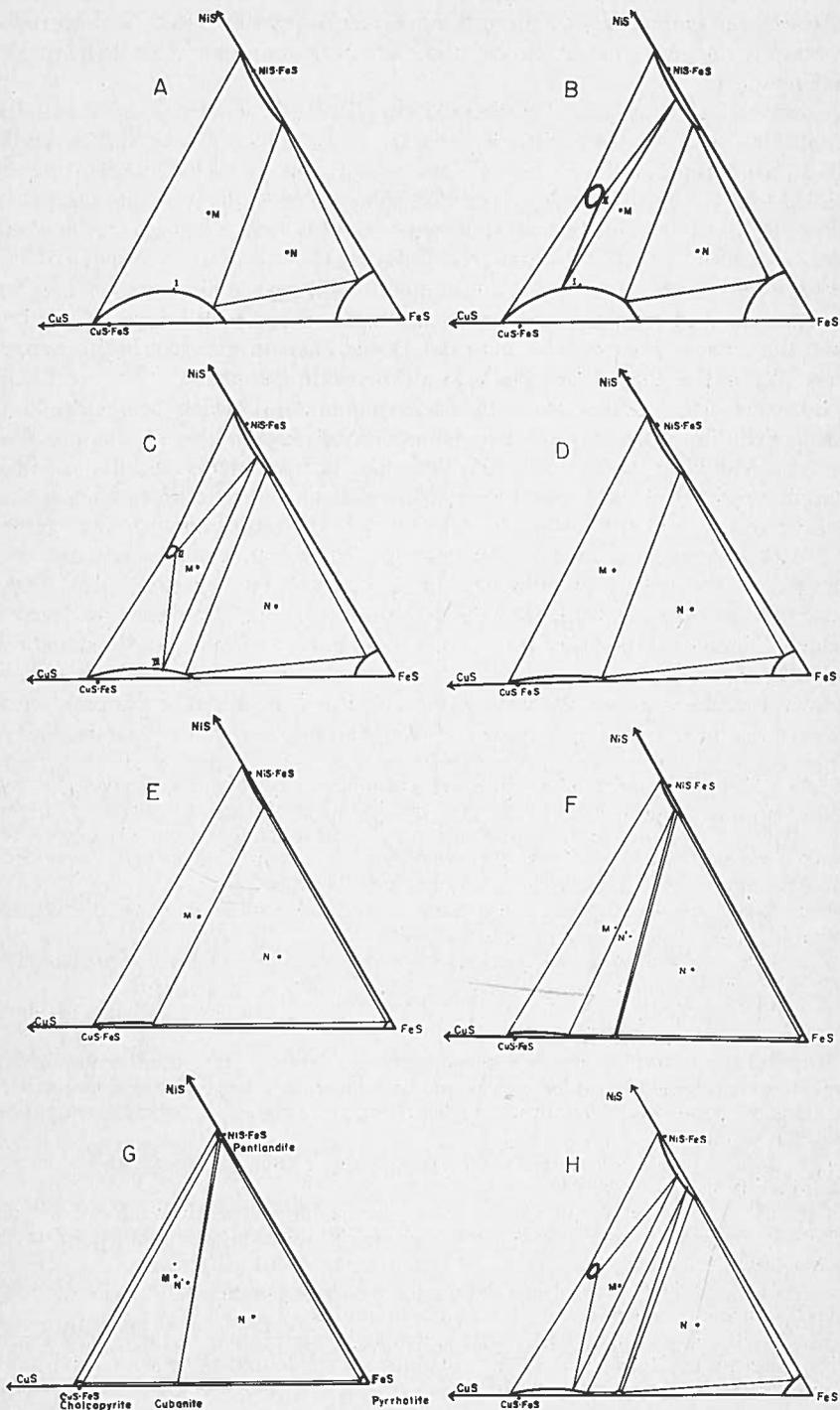


FIG. 16.

and pressure. However, as there is no evidence on this point, in Figure 16 we merely indicate the inferred composition of the phase present in the Mackinaw ore.

Borchert (2) studied unmixing in the Cu-Fe-S system experimentally. His findings are summarized in Figure 17. The solid solution that is stable only at temperatures above 255° C, but preservable to room temperature by rapid chilling, he called chalcopyrrhotite. The range in composition of chalcopyrrhotite shortens with decreasing temperature until a composition about midway between cubanite and pyrrhotite is reached at the eutectoid, 255° C. Below this temperature, only chalcopyrite and pyrrhotite are stable but cubanite and valleriite become stable in that order on still further cooling. Thus, the cooling history of a material in the chalcopyrite-pyrrhotite system (especially in the copper-rich end) would be quite complex.

Borchert also found a naturally occurring mineral which he identified as chalcopyrrhotite. The fullest discussion of chalcopyrrhotite as a mineral is given by Ramdohr (12), who has identified it from many localities. It is isotropic, or very weakly anisotropic, brownish like pyrrhotite but somewhat more yellowish, and has a similar reflectivity. It occurs alone or intergrown with chalcopyrite or cubanite. Nickel may enter into chalcopyrrhotite and, Ramdohr believes, may increase its stability at low temperature. No X-ray investigations of chalcopyrrhotite have been made, but Ramdohr believes it probable that chalcopyrrhotite has the disordered chalcopyrite structure. Such a structure, however, seems rather unlikely for a substance that has, at the lowest temperature of stability, as high an Fe:Cu ratio as chalcopyrrhotite. If the shoulder on the chalcopyrite-chalcopyrrhotite solvus at about 325° C

FIG. 16A to H. Inferred equilibrium assemblages during development of copper-nickel-iron sulfide ores. These are pseudo-ternary diagrams, as the minerals may not be stoichiometric and so would not lie on a plane. Point M shows the overall composition of the Mackinaw ore; Point N that of the normal (Sudbury) type ore, point N' (on 16 F and G) another possible type.

FIG. 16A. An early stage, in which the Mackinaw assemblage consists of pentlandite and phase I. Phase II is unstable at this temperature.

FIG. 16B. Phase II is assumed to be stable, but M lies outside its stability field. This may be an alternative or a successive stage to that of 16A.

FIG. 16C. A later stage, in which the Mackinaw assemblage consists of phase III, phase II and pentlandite.

FIG. 16D. A stage after the disappearance of phase II. Pentlandite and a compound near chalcopyrite form from the breakdown of phase II. Although there is a complete solid solution between chalcopyrite and phase III, both phases persist in disequilibrium.

FIG. 16E. A later stage before the appearance of cubanite, in which the extent of solid solution has decreased.

FIG. 16F. A stage after cubanite becomes a stable phase, although not for ore of the composition of the Mackinaw ore. N and N' indicate two possible cubanite-bearing ores.

FIG. 16G. A late stage in the history of the Mackinaw ore, with an assemblage of nearly pure chalcopyrite, cubanite and pentlandite.

FIG. 16H. A possible equilibrium assemblage, alternative to those of the preceding diagrams. Here phase II and cubanite are stable under the same conditions, but not for the same overall compositions.

reported by Borchert (Fig. 17) has any existence, it may indicate a phase change, perhaps from a chalcopyrite structure to some unknown chalcopyrrhotite structure.

The relationship of our phases I, II, and III to chalcopyrrhotite is not clear. At high temperatures there may be complete solution between the compositions of all these materials. Borchert's diagram indicates that chalcopyrrhotite must form during the cooling of a CuS-FeS mixture with any significant excess of FeS over that necessary to form CuFeS_2 , and that chalcopyrrhotite in turn must unmix to pyrrhotite and either chalcopyrite or cubanite or both. Neither chalcopyrrhotite nor pyrrhotite was found in the Mackinaw ore. One might possibly regard phase II as a nickelian chalcopyrrhotite that unmixes to chalcopyrite and pentlandite rather than to chalcopyrite and pyrrhotite. However, until the nature of chalcopyrrhotite and other phases in this system are better understood it seems best not to extend Borchert's and Ramdohr's usage but to use noncommittal terms for other solid solutions. Borchert's diagram shows chalcopyrite and cubanite to be stable together only between 225° and 235° C. To account for the lamellar intergrowth of these two minerals, from his diagram, it is necessary to assume that the Mackinaw ores, as well as almost all other chalcopyrite-cubanite bearing ores, were completely reconstituted between these temperatures, and that all the pyrrhotite and/or chalcopyrrhotite (which must have been present according to Borchert's diagram) completely reacted with chalcopyrite to form cubanite. Below 225° C cubanite and chalcopyrite would be unstable together, and should react to form vallerite. However, this reaction proceeded to a very slight extent. This history is improbable to the point of impossibility. The common occurrence of chalcopyrite-cubanite intergrowths strongly suggests a solvus (represented by the unmixing of our phase III) with ends at the chalcopyrite and cubanite compositions rather than at the chalcopyrite and chalcopyrrhotite compositions. Just what chalcopyrrhotite is, is an extremely interesting problem, but there is no reason to believe a phase fitting Borchert's conception of chalcopyrrhotite was at any time present in the Mackinaw ore.

PARAGENESIS

A diagrammatic representation of the paragenetic relations is given in Figure 15. The scheme of the diagram is somewhat similar to, although simpler than, that of Robertson and Vandever (13). Solid lines indicate a replacement or a rimming relationship, and the arrow points to the older mineral. Dotted lines indicate exsolution relationships. If both solid and dotted lines extend upward from a mineral, it means that the mineral formed by exsolution and, at about the same time, was deposited directly, replacing or rimming other minerals as shown. Generally, the downward direction indicates decreasing age, but no attempt has been made to indicate the extent of the period of formation of each mineral, as is done on the usual paragenetic line diagram. For the sake of clarity, some of the less critical observed relations have been omitted.

Successive stages in the development of the sulfides in the ore, are shown on eight triangular diagrams in Figure 16. Similar diagrams have been

widely used in understanding igneous and particularly metamorphic rocks in light of the phase rule restrictions on mineral associations. However, they have been little used for ore deposits, perhaps because of a feeling that these are not equilibrium assemblages and so are not subject to the phase rule. Recently, opinion has been changing toward the viewpoint that ore deposits, cautiously interpreted, can be regarded as near enough to equilibrium assemblages to allow the use of phase rule diagrams, which, indeed, help to point out disequilibrium when it is present. Betekhtin (1), in particular, has developed such diagrams and presented a series showing the more common assemblages in hydrothermal deposits. He plotted the commonly occurring assemblages of the Cu-Fe-Ni-S system (none like the Mackinaw association, of course) on the projection of a tetrahedron.

A triangle, rather than a tetrahedron, can be used if the compositions of all phases involved lie on a plane within the tetrahedron. Cubanite has a nearly stoichiometric 1:1 metal-to-sulfur ratio, pyrrhotite generally has a sulfur excess, pentlandite and perhaps chalcopyrite are sulfur deficient. Therefore, a plane can be passed through the Cu-Fe-Ni-S tetrahedron that will pass near the points representing these phases. The vertices of the triangle are close to, but not exactly, CuS, FeS, and NiS, although Figure 16 has been so labelled for convenience. The deviation of the composition of the minerals from the plane is assumed to be so small that it has no effect in determining the equilibrium assemblages, that is, only three phases can coexist stably in the system at an arbitrary temperature and pressure. Valerite, however, probably has a sufficiently different metal-to-sulfur ratio that, like pyrite, it cannot be plotted on the plane diagram, but must be considered separately.

There are three types of regions in triangular diagrams: one-phase fields that denote the extent of solid solutions; two-phase fields, in which the equilibrium assemblage consists of a solid solution lying at one end of the field and either a solid solution or a compound of fixed composition at the other; and finally, three-phase fields, in which the equilibrium assemblage consists of the phases (compounds or fixed members of a solid solution) lying at the vertices of the triangular field.

Each triangular diagram indicates the equilibrium assemblages only at specific conditions of temperature and pressure. In the system under consideration, pressure is probably of secondary importance. The metal-to-sulfur ratios of the phases are so nearly the same that reactions between them may be considered as taking place at a constant partial pressure of sulfur. Therefore, the sequence of diagrams of Figure 16 may be considered as representing our idea of the change of equilibrium assemblages with changing temperature. It must be emphasized that these diagrams are entirely inferred, drawn so as to present a reasonable interpretation of the mineral relations of the Mackinaw ore.

Niccolite, pentlandite, and the rare early magnetite are the oldest ore minerals. Relations such as those in Figure 14 suggest that pentlandite is later than niccolite, but this age relation cannot be proven. Phase I and sphalerite are later than the pentlandite; sphalerite tends to be the earlier of

the two as it is usually immediately in contact with the pentlandite (Fig. 12). Of course, there may be considerable overlap in the paragenetic sequence. This stage, characterized by the deposition of the greater part of the ore minerals, as contrasted to the alteration of pre-existing ore minerals, may be considered the early stage. Two slightly different alternative diagrams (Fig. 16, A and B) show the assemblage during the early stage. Point M represents the approximate overall composition of the Mackinaw ore, and point N that of the more common nickel-copper ores, such as that of Sudbury. The ore (in addition to the minerals such as niccolite, which cannot be plotted on our diagram) is composed of pentlandite and phase I, which, if it is structurally a disordered chalcopyrite, would lie on the edge of a solid-solution field extending at least to the chalcopyrite composition. Either phase II is not stable at these temperatures (Fig. 16A) or it is stable but the composition of the ore is not within its stability field (Fig. 16B).

The separation of phase I into phases II and III was the first event of the intermediate stage (unless some sphalerite exsolved from phase I). Figure 16C shows the assemblage after this event. As a consequence of the retraction of the chalcopyrite solid-solution phase field back toward the nickel-free side of the triangle and as consequence of either the appearance of phase II as a stable phase or of the extension of its stability field toward the right, the ore composition point M finds itself in the three phase field, II-III-pentlandite. Chalcopyrite-cubanite intergrowths replace the arsenides and pentlandite, and it is reasonable to suppose that the actual replacement occurred when these minerals formed a solid solution (phase III), and the unmixing took place later. The overall composition of the ore probably was continually changing by reaction with a fluid phase, but these changes were probably small enough not to prevent plotting point M in the same place on each diagram.

Subsequently phases II and III each separated into their unmixing products. One of the simpler of the alternative possible sequences of events is given by Figure 16C, D, E, F, and G. In this sequence, first phase II became unstable, unmixing into pentlandite and chalcopyrite, the latter with a slight excess of iron that eventually appeared as cubanite, as discussed in the preceding section. Figure 16D shows the situation after the disappearance of phase II. Both before and after this stage, the maximum possible content of iron in the chalcopyrite-phase III solid solution was constantly decreasing, as is illustrated by the change from Figure 16D to 16E. Note that for one of the composition shown at point N, iron is released and appears as pyrrhotite but M is still within the two phase field. Finally, cubanite appears as a stable phase. Figure 16E shows the situation before and Figure 16F soon after its appearance. As cooling continues toward the final stage of Figure 16G, the excess iron is almost entirely expelled from the chalcopyrite and appears as cubanite.

Three ore assemblages are possible in the system. From point M we get an equilibrium assemblage of pentlandite-cubanite-chalcopyrite, as we find at the Mackinaw mine. From point N we get an equilibrium assemblage of pentlandite-cubanite-pyrrhotite with chalcopyrite as a disequilibrium mineral

relict from stage 16E. This assemblage is probably the most common in ore deposits throughout the world. Finally, from point N' we get an equilibrium assemblage of pentlandite-cubanite-chalcopyrite, with pyrrhotite as a disequilibrium relict mineral. This assemblage probably also occurs, but less commonly than the preceding.

Figure 16H is a variant that illustrates one of the numerous possible alternative sequences of events that are in accord with the textural evidence. Here, phase II remains stable until after the appearance of cubanite. Experimental work is necessary to decide between such alternatives.

Not only the major changes in the system, such as the appearance or disappearance of phases, but the details of equilibrium diagrams, such as the

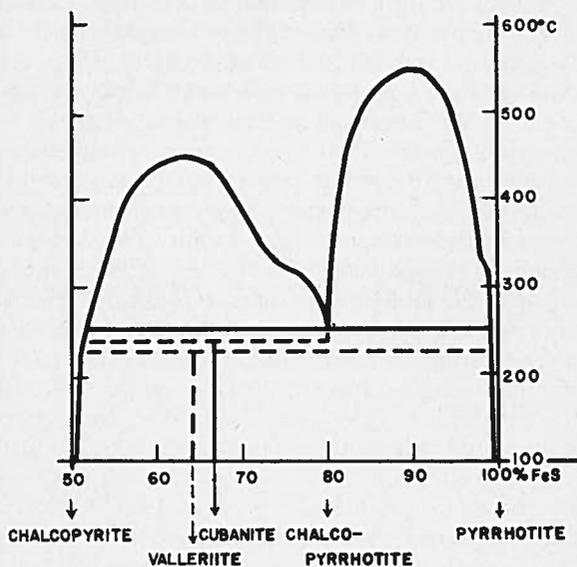


FIG. 17. Cu-Fe-S system, between CuFeS_2 and FeS (after Borchert).

exact composition of solid solutions in equilibrium with other phases—for instance the exact composition of phase III in equilibrium with phase II and pentlandite—are each associated with a definite temperature (if pressure and other variables are considered unimportant). Therefore, such ores as that of Mackinaw mine contain a record of the temperatures at which each feature developed. Experimental work is necessary to enable us to determine what these are.

Some time in the later stages of this process, valleriite exsolved from (or perhaps replaced) chalcopyrite. Probably the critical factor controlling the appearance of valleriite is the sulfur pressure. If so, it is very misleading to ignore the deviation from the 1:1 metal-to-sulfur ratio and to project valleriite onto a diagram between chalcopyrite and pyrrhotite, as Borchert did. It is possible, however, that sulfur pressure is not important but that valleriite is a late phase occurring in a disequilibrium assemblage in the CuS-FeS-NiS

system, as we have suggested for cubanite at Sudbury. Simply knowing the correct composition of valleriite would go a long way toward answering these questions.

Still later, chalcopyrite replaced (or perhaps exsolved from) cubanite and valleriite. Replacement, if it occurred, was probably caused by later solutions, richer in copper.

The arsenides are replaced not only by chalcopyrite-cubanite (phase III) but by a few composite grains of chalcopyrite and valleriite and commonly by chalcopyrite alone (Fig. 15). These relations indicate that the replacement occurred not only during the period of stability of phase III, but during the period of stability of chalcopyrite with dissolved excess iron (later exsolved as valleriite), and during the period of stability of chalcopyrite and valleriite as separate phases.

Almost all the gold is within maucherite. Not only is gold very rare in niccolite but it is much more abundant in maucherite that has completely replaced niccolite than in maucherite that only rims niccolite. This distribution suggests that the same solutions that extracted arsenic from the niccolite deposited the gold. There is no indication of exsolution of gold from maucherite. The gold in the maucherite is commonly associated with chalcopyrite, in places together with valleriite, but apparently never with cubanite. This association indicates that deposition of gold commenced after the breakdown of phase III but extended from the period of stability of the chalcopyrite-valleriite solid solution into the period when only pure chalcopyrite was stable. Magnetite veins and rims almost all the other ore minerals. From its common occurrence in fracture openings, it seems to belong to a definitely later stage than the other opaque minerals. However, association of a small part of the gold and a very little chalcopyrite with magnetite in veinlets indicates the persistence of the formation of these minerals into the late stage. The magnetite is commonly separated by a thin screen of gangue from the arsenide or sulfide that it rims, which indicates that there has been slight replacement of the arsenide or sulfide by gangue after the magnetite deposition, with the magnetite undisturbed by the replacing solutions.

The fine-grained chalcopyrite disseminated in the gangue shows no textural relationships to other ore minerals that would indicate its place in the sequence. However, if it were contemporaneous with the earlier copper sulfides, it would be expected to have contained excess iron, as they did, which would eventually have exsolved as cubanite or valleriite. Because cubanite and valleriite never occur with the disseminated chalcopyrite, it seems most reasonable to attribute formation of the last to a time when chalcopyrite in the rest of the ore contained no excess iron. If the disseminated chalcopyrite formed as late as the magnetite, when excess iron would be deposited as the oxide rather than as a sulfide, the absence of directly precipitated, as well as exsolved, cubanite and valleriite is easier to explain.

Finally, bravoite(?) or violarite(?) replaces pentlandite and chalcocite and covellite replace the copper sulfides. These are late, probably supergene, minerals.

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