SECONDARY VIOLARITE AND BRAVOITE, ENGLISH LAKE, MANITOBA

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ABSTRACT

Supergene or hypogene alteration of a pentlandite-chalcopyrite-pyrite assemblage has resulted in the formation of a number of secondary sulphides. Violarite formed first and occurs pseudomorphically after pentlandite. Alteration later intensified, resulting in the dissolution of violarite, chalcopyrite and pyrite and the concomitant deposition of bravoite, idiomorphic pyrite, anhedral pyrite, marcasite, chalcopyrite, hematite, quartz and carbonate. Bravoite, in contrast to violarite, does not occur pseudomorphically after pentlandite. This relationship is considered to be of general application. The nickel content of each sulphide was determined using an electron microprobe analyser. Relationships between idiomorphic pyrite and bravoite show that an immiscibility gap may exist between pyrite, with up to 1.5% Ni, and bravoite, with 11 to 12% Ni.

INTRODUCTION

During exploration work in southeastern Manitoba sulphide mineralization, consisting of pentlandite, chalcopyrite and pyrite lying along fractures in hornblendite was investigated. This occurrence shows intense supergene or hypogene alteration, which has resulted in the formation of both violarite and bravoite, together with a number of other secondary minerals. Violarite and bravoite are known to form by supergene processes, but the mutual relations between these two sulphides are not known in any detail from previous descriptions of natural occurrences. The parageneses described in this paper adequately outline the relationships between the minerals pentlandite, violarite and bravoite.

GEOLOGICAL SETTING OF THE PRIMARY SULPHIDES

Sulphides occur along fractures cutting rocks of Precambrian age belonging to the "English Lake Volcanic Unit" described by Russell (1949). These rocks are located in the southeastern part of Manitoba, 20 miles west-northwest of the town of Bisset. Highly metamorphosed quartz-plagioclase-amphibole gneisses and minor hornblendites are intruded by post metamorphic pyroxenites (Fig. 1). The pyroxenites are altered in varying degree and are now represented by zones of tremolitized and steatized rocks alternating with zones of unaltered material. Each

zone varies from a few feet to more than fifty feet in thickness. The mineralized fractures are exposed only where they cut the hornblendite. Their extension under drift overlying the gneisses and intrusive ultra-mafic rocks was traced by an electromagnetic survey and subsequently tested by diamond drilling as shown on Fig. 1. Nickel and copper mineralization was encountered in drill holes 1, 4 and 5, copper mineral-ization in holes 2 and 3, but no sulphides were located in holes 6 and 7. The pyroxenites, and associated altered rocks, contain no disseminated sulphides but have a nickel content of from 0.05 to 0.15%. It is tentatively assumed that this nickel substitutes for magnesium in the lattices of pyroxene, tremolite and talc. During alteration of the pyroxenites, or at some later stage, these ultramafic rocks may have been penetrated by sulphur-bearing solutions which resulted in the extraction of some nickel from the silicates. This nickel was later deposited in sulphides along fractures within the ultramafic rocks themselves and in the associated gneisses, but preferentially within the hornblendite.

The Mineralized Fractures in the Hornblendite

Sulphides subjected to intense alteration were found only in drill hole 1, which intersected the hornblendite at a depth of 200 feet. The following description is therefore restricted to these sulphides and their alteration products.

Two mineralized fractures were intersected. They vary in width from one to three feet and contain, on average, 4.5% Ni, up to 0.1% Co and trace amounts of Ag and Pd. One of the mineralized fractures contains 1.2% Cu, the other only up to 0.1% Cu. Partially replaced amphibole fragments occur enclosed in the sulphide matrix. The hornblendite adjacent to the mineralized fractures contains a few per cent of dis-seminated sulphides.

The primary sulphides

Pentlandite, now completely violaritized, is the dominant primary sulphide, and encloses idiomorphic crystals of pyrite. Pyrite is also present along pentlandite grain boundaries associated with chalcopyrite (Fig. 2). Rarely, chalcopyrite occurs as the dominant sulphide, and then contains sparse idiomorphic crystals of violaritized pentlandite (Fig. 3). In the latter mineral, lamellae of chalcopyrite occur in three crystallo-graphic directions, reflecting the replacement of pentlandite along its octahedral cleavages. Monomineralic chalcopyrite stringers up to a few millimetres in thickness penetrate gangue minerals adjacent to the major fracture zones.
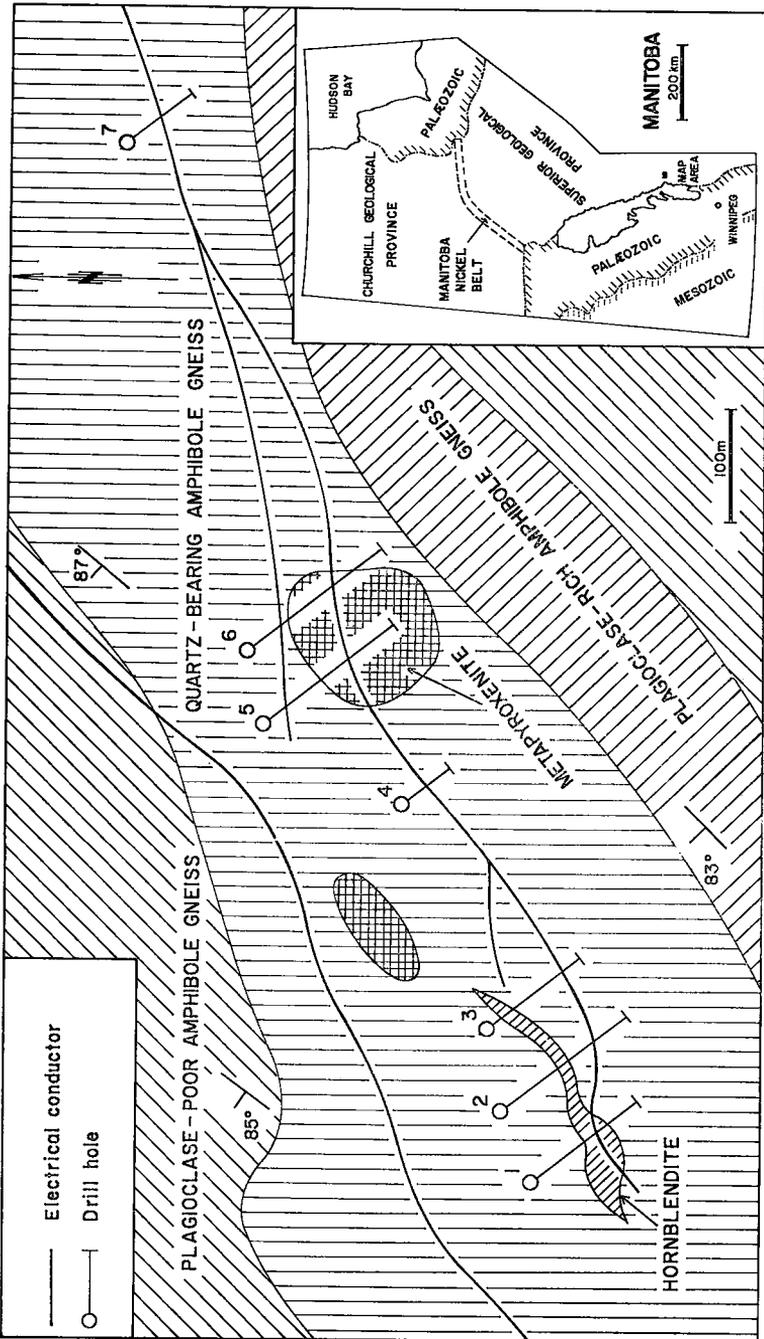
FIG. 1. Geological plan of the area at English Lake tested by diamond drilling.
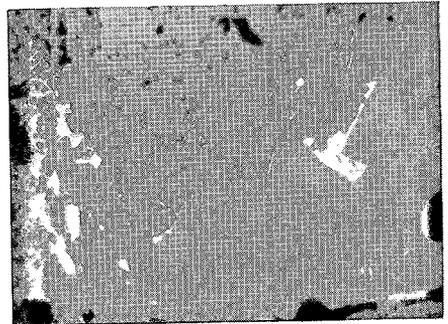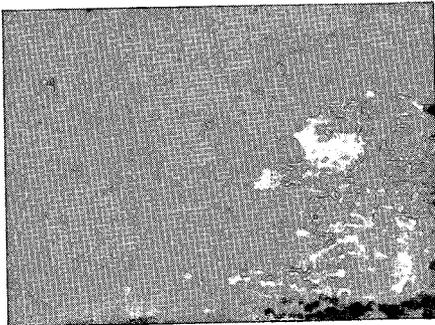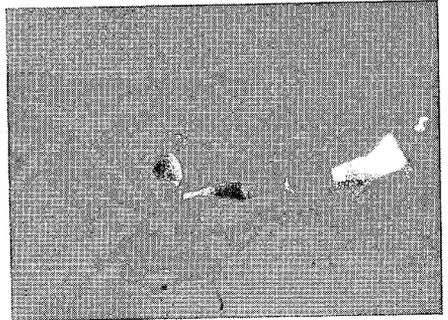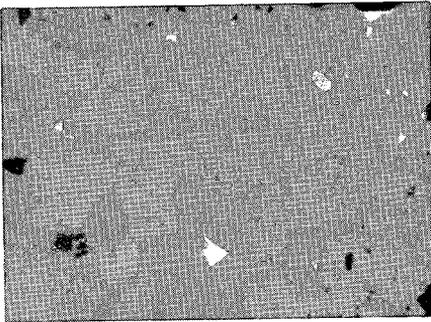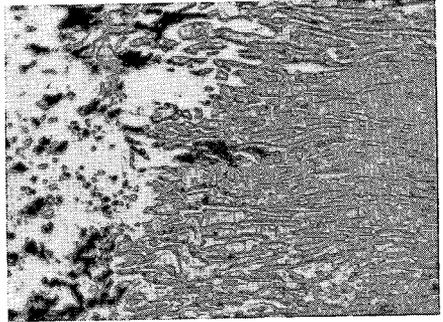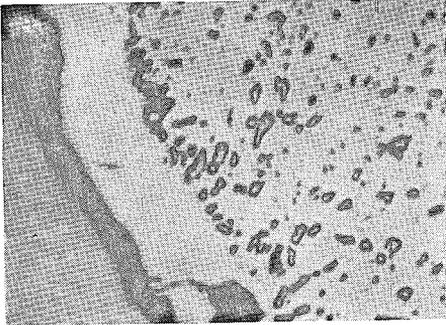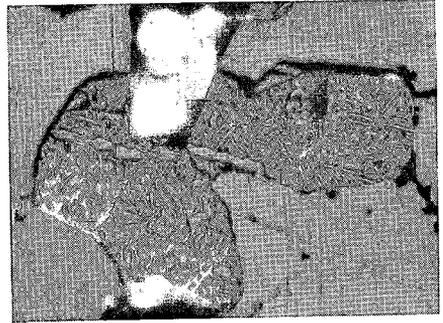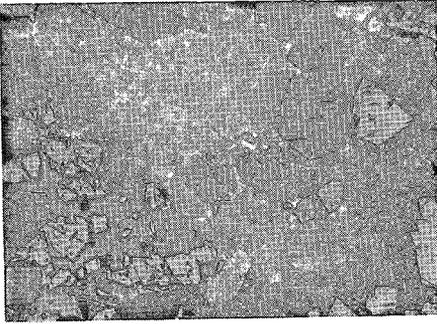
The secondary sulphides

The secondary sulphide minerals are violarite, marcasite, bravoite and two textural varieties of pyrite. One form of pyrite is anhedral, while the other is distinctly idiomorphic and is always associated with bravoite. Minor secondary chalcopyrite and hematite are also present. The formation of the supergene sulphides was accompanied by the deposition of gangue minerals, principally quartz and carbonate. The nickel content of the various phases was determined by means of the electron microprobe analyser using pure Ni as standard.

Violarite

Violarite formed by the pseudomorphic replacement of pentlandite (Fig. 2 and Fig. 3). No remnant pentlandite is present in the sulphides intersected by drill hole 1. Hypogene chalcopyrite and pyrite were not affected by the formation of violarite. No additional secondary minerals, either sulphides or gangue, were formed in immediate association with the violarite, indicating that circulation of aqueous solutions played a minor role in the violaritization of pentlandite. This contrasts with the conditions under which the formation of the remaining secondary sulphides tookplace. These sulphides developed during replacement and dissolution of violarite, chalcopyrite and pyrite, and their formation was

FIG. 2. (top left) Violarite pseudomorphic after pentlandite, which enclosed hypogene pyrite crystals and interstitial areas of chalcopyrite also containing pyrite. (110×, 1 nicol, oil imm.).

FIG. 3. (top right) Violaritized pentlandite crystals in chalcopyrite. Chalcopyrite lamellae replace the pentlandite along cleavages. (195×, 1 nicol, oil imm.).

FIG. 4. (second from top, left) Anhedral pyrite in contact with chalcopyrite. Well-defined areas within the pyrite contain irregular remnant grains of unreplaced chalcopyrite. (550×, 1 nicol, oil imm.).

FIG. 5. (second from top, right) Violarite in the process of replacement by anhedral pyrite. (525×, 1 nicol, oil imm.).

FIG. 6. (third from top, left) Slightly zoned, idiomorphic pyrite in a matrix of bravoite. (500×, 1 nicol, oil imm.).

FIG. 7. (third from top, right) Irregular veinlet in pyrite composed of alternating layers of bravoite and secondary pyrite. The higher reflectivity of the secondary pyrite indicates a lower nickel content compared with that of the primary pyrite. (615×, 1 nicol, oil imm.).

FIG. 8. (bottom left) Zoned idiomorphic pyrite and bravoite which formed through the breakdown of violarite. (470×, 1 nicol, oil imm.).

FIG. 9. (bottom right) Zoned crystals of idiomorphic pyrite and bravoite formed through the breakdown of pyrite and violarite. (470×, 1 nicol, oil imm.).

accompanied by that of abundant secondary quartz and carbonate. Circulating aqueous solutions therefore played a significant role in their formation.

Anhedral pyrite

Anhedral pyrite occurs in relatively large and homogeneous areas up to a few millimetres across, and developed during the replacement of both primary sulphides and violarite. In general it formed before marcasite and bravoite, as described later.

This pyrite is bordered in some places by an irregular and narrow zone of secondary chalcopyrite. Rare myrmekitic intergrowths between the two sulphides occur along their mutual contact, where pyrite penetrates chalcopyrite. Well-defined areas within the pyrite contain abundant, extremely fine chalcopyrite inclusions. These probably originated as particles of chalcopyrite entrapped by the advancing pyrite in areas of incomplete replacement. Both chalcopyrite varieties are shown in Fig. 4.

Rarely, a very fine network of pyrite penetrates violarite in front of the massive pyrite (Fig. 5), and represents an intermediate stage of replacement. Remnants of these network areas of incompletely replaced violarite are preserved within the secondary pyrite. Morphologically these areas bear a close resemblance to those in which pyrite contains abundant chalcopyrite inclusions. Ahead of the network areas irregular, fine fractures filled with pyrite occur in the violarite, and are only rarely controlled by the cleavage of this mineral. Occasionally pyrite has diffused out into the violarite from the fractures, resulting in the formation of an intergrowth of the two sulphides similar to that described above. Minor hypogene chalcopyrite originally present in the violarite has been simultaneously penetrated by the pyrite network.

Bravoite and idiomorphic pyrite

Bravoite is generally associated with idiomorphic pyrite and occurs as a matrix for this material (Fig. 6). Rarely bravoite is associated with marcasite, in which case it occurs as extremely thin flakes parallel to marcasite lamellae. The association bravoite-idiomorphic pyrite developed during breakdown of violarite, primary pyrite and even secondary anhedral pyrite. Figure 8 illustrates the formation of the bravoite-idiomorphic pyrite association after violarite, and Fig. 9 shows the formation of the same two sulphides after violarite and earlier pyrite. The pyrite grain shown in Fig. 7 is cut by an irregular vein composed of alternating layers of bravoite and secondary pyrite. It appears that the formation of this vein took place along a fracture in the pyrite grain.

Nickeliferous solutions penetrated this fracture, dissolved the pyrite and deposited the two secondary sulphides. The differing reflectivities of the host and vein pyrite indicate a lower nickel content of the latter variety.

Marcasite

Marcasite occurs in both dendritic and granular aggregates (Fig. 12). Marcasite dendrites are composed of a sheet from which lamellae grow in opposite directions. Each such lamella is composed of numerous, extremely fine-grained marcasite crystals or twin individuals, all of which extinguish in the same position.

Marcasite has replaced violarite, and both primary and anhedral secondary pyrite. Growth of the composite dendrite crystals was controlled by a crystallographic direction in the mineral it replaces. The marcasite lamellae are always parallel to the direction along which they replace the violarite. In partially replaced violarite grains, marcasite lamellae occur parallel to remnant wisps of violarite (Fig. 16). The growth of marcasite dendrites in pyrite (Figs. 10 and 11) is also controlled by crystallographic directions. This is apparent where several partly replaced pyrite grains occur together.

Granular marcasite may replace pyrite, but is less common than the dendritic variety. Gangue minerals, mostly quartz and carbonate, are generally associated with marcasite.

Areas showing no trace of original sulphides are characterized by marcasite dendrites with intervening areas occupied by granular marcasite (Fig. 12), by the association bravoite-idiomorphic pyrite (Fig. 6), or by a mixture of these three minerals.

In general, the formation of anhedral pyrite began before that of the other secondary sulphides, since it is commonly replaced by them, in particular by marcasite. However, in some cases the reverse relationship is observed, anhedral pyrite replacing marcasite and bravoite. Figure 16 shows violarite at an early stage of replacement by lamellar, dendritic marcasite. Unreplaced lamellar fragments of violarite occur parallel to the marcasite lamellae. Extremely fine flakes of bravoite are also present and are aligned parallel to the marcasite lamination. At a later stage, marcasite is replaced by anhedral pyrite. A marginal zone in this pyrite, adjacent to the marcasite, contains bravoite flakes, which possibly represent remnant flakes originally occurring within and parallel to the lamellar marcasite before its replacement by pyrite. At a still later stage pyrite was partly replaced by marcasite. This late marcasite is associated with the growth of the gangue minerals, and occurs as relatively large, equidimensional grains.

The lamellar marcasite dendrites described here show some resemblance
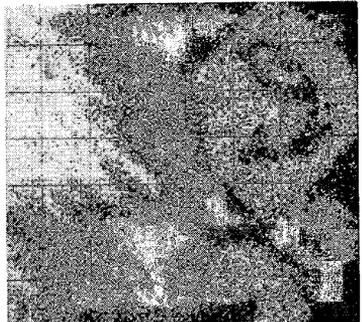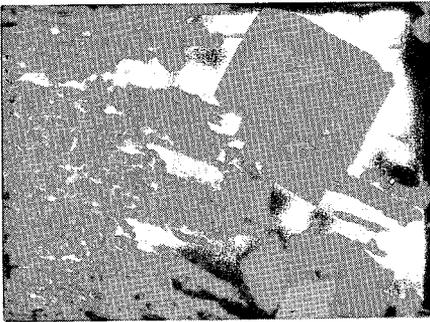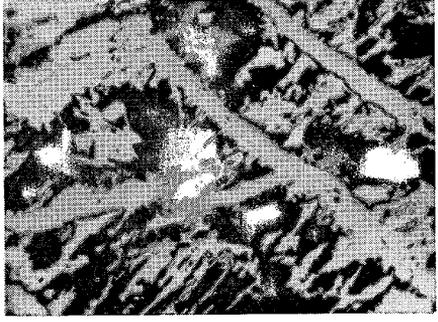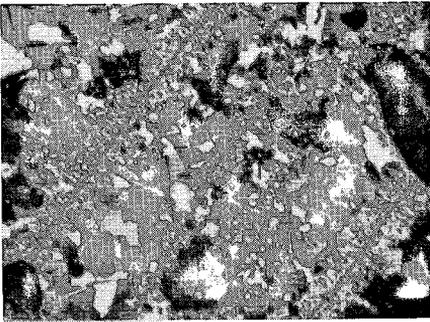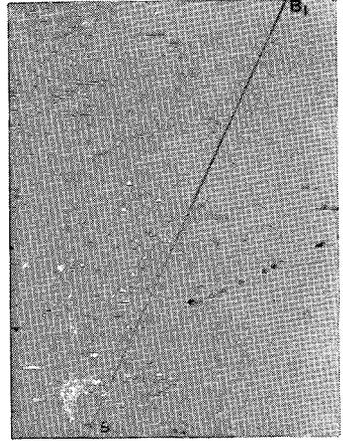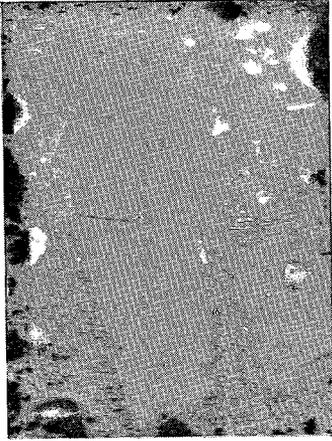
to the lamellar marcasite described by Edwards (1953) and by Oelsner & Starke (1964), which is considered to represent the replacement of pyrrhotite by marcasite. They also resemble the marcasite described by Oen Ing Soen & Pauly (1967), which crystallized by replacement of siderite. However, in the present case, marcasite has formed from both violarite and pyrite.

Chalcopyrite

The relationship between the chalcopyrite and anhedral pyrite has been described above. When complete replacement of the primary minerals has resulted in the development of the association marcasite plus bravoite and idiomorphic pyrite, the fate of the hypogene chalcopyrite cannot be determined. However, in some instances secondary chalcopyrite has crystallized as irregular lamellae with interstitial marcasite and gangue minerals (Fig. 13).

Hematite

Hematite occurs rarely as small crystals disseminated in areas of marcasite and the bravoite-idiomorphic pyrite association.

Gangue minerals

The major gangue minerals are carbonate and quartz. These are preferentially associated with the formation of marcasite and bravoite-idiomorphic pyrite. A massive vein of quartz three feet in thickness follows the hanging wall of one of the mineralized fractures. It contains no disseminated sulphides.

FIG. 10. (upper left) Lamellar marcasite replacing pyrite. A bravoite rim has developed between the two minerals. The mottled surface of the pyrite indicates a variable nickel content. Traverses with the electron microprobe analyser were taken along profiles A-A$_1$ and B-B$_1$. (155X, 1 nicol, oil imm.).

FIG. 11. (upper right) Enlarged area of Fig. 10 showing lamellar marcasite, mottled pyrite and a bravoite rim between them. The dark grey grain at the bottom left is hematite. Line B-B$_1$ indicates traverse location with the electron microprobe analyser. (550X, 1 nicol, oil imm.).

FIG. 12. (centre left) Marcasite dendrites with intervening areas of granular marcasite. (170X, X nicols, oil imm.).

FIG. 13 (centre right) Supergene chalcopyrite lamellae with intervening areas occupied by marcasite and gangue. A cluster of idiomorphic marcasite crystals in gangue at bottom centre. (240X, 1 nicol, oil imm.).

FIG. 14. (bottom left) Violarite (bottom) replaced by marcasite. Idiomorphic bravoite with a core of pyrite is enclosed in secondary gangue minerals. (535X, 1 nicol, oil imm.).

FIG. 15. (bottom right) Electron scanning micro-photograph of the area outlined in Fig. 14, showing distribution of nickel in the various sulphide phases.
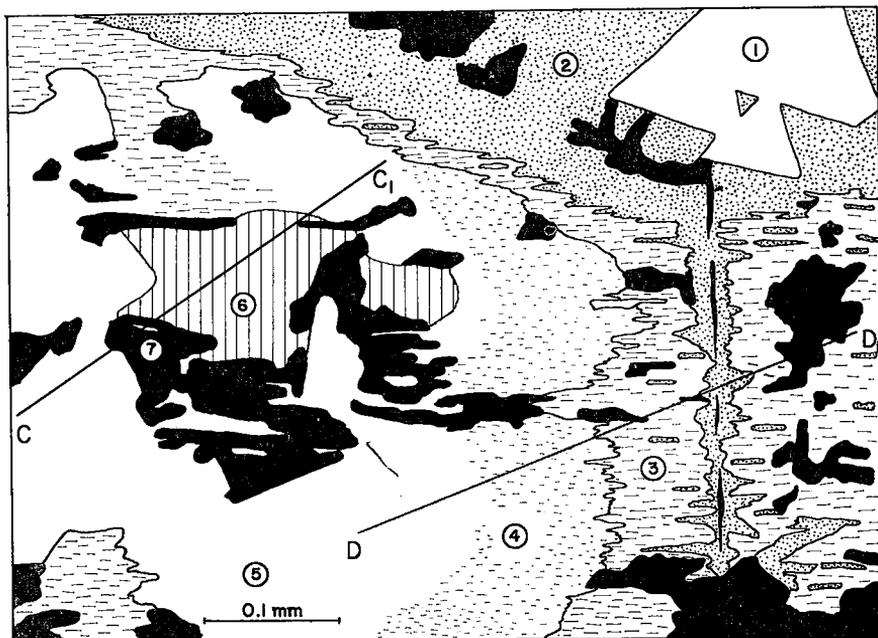
FIG. 16. Tracing from a photomicrograph. Violarite (2) with primary pyrite (1) replaced by lamellar marcasite (3) containing very fine bravoite flakes. Later marcasite has been replaced by anhedral pyrite (5). A border zone (4) in the pyrite adjacent to marcasite contains remnant bravoite flakes. Still later the anhedral pyrite has been replaced by granular marcasite (6). This area is entirely occupied by only two marcasite grains. Both marcasite generations are associated with secondary gangue minerals, mostly carbonate (7). Two scanning nickel profiles C-C_1 and D-D_1 gave results as shown on Fig. 17c and Fig. 17d.

DISTRIBUTION OF NICKEL IN THE SECONDARY SULPHIDES

The distribution of nickel in the various sulphide phases has been determined using the electron microprobe analyser. Three areas were investigated where anhedral pyrite and violarite have been partially replaced by marcasite.

1. In general, the anhedral pyrite has a low nickel content. However, in some cases a mottled surface of the mineral indicates a variable content of this metal. During replacement of such pyrite by lamellar marcasite, a zone of bravoite has often developed along their mutual contact (Figs. 10 and 11). Distribution of nickel across this contact was investigated by two line scans, A-A_1 and B-B_1 in Fig. 10 and Fig. 11. The emission profiles for nickel are illustrated graphically in Fig. 17a and Fig. 17b respectively. Profile B-B_1 crosses the anhedral pyrite where the

mottled surface is most evident. The nickel content of the pyrite ranges between 0.5 and 7 weight per cent. Between 5 and 8% Ni is contained in the lamellar marcasite replacing pyrite. The bravoite rim around the pyrite contains 11 to 12% Ni and shows that a relative concentration of Ni has taken place along the contact zone between the two minerals.

2. It was found that some of the nickel released during the replacement of violarite by marcasite entered the lattice of the latter mineral, but the major part has reprecipitated elsewhere as bravoite intergrown with pyrite (Fig. 14). The electron scanning photograph (Fig. 15) shows the Ni distribution of the sulphides in the area covered by Fig. 14. The average nickel content determined for these minerals are: violarite, 26%; marcasite, 5 to 8%; bravoite, 11%; and pyrite, 1.5%.

3. The distribution of nickel in the various phases represented in Fig. 16 is evident from the two scanning profiles C-C_1 and D-D_1. The results of these are illustrated in Fig. 17c and Fig. 17d respectively. The following values were obtained: violarite, 26%; lamellar marcasite, 3 to 6% (the presence of minor bravoite flakes intergrown with the marcasite does not affect these values significantly); pyrite with remnants of bravoite flakes, 2 to 4%; homogeneous anhedral pyrite, 0.5 to 2%; and granular marcasite, 0.5 to 2%. A spot analysis of the primary idiomorphic pyrite crystal enclosed in violarite (Fig. 16) gave a nickel content of only 0.25%.

The results of the analyses support the explanation of the replacement pattern given on page 635. During the replacement of violarite by marcasite some nickel was accepted into the marcasite lattice, but the major part was removed from the immediate area. During replacement of marcasite by anhedral pyrite some nickel was taken up by the pyrite and some remained within remnant bravoite flakes, but again the major part was removed. The pyrite zone with bravoite flakes has a nickel content which lies approximately halfway between that of the lamellar marcasite and that of the homogeneous anhedral pyrite. This indicates that such zones represent areas where incomplete replacement of marcasite by pyrite has taken place. The similar average nickel contents of the granular marcasite and the homogeneous anhedral pyrite, which is considerably lower than that of the lamellar marcasite, supports the supposition that the granular marcasite is derived from the anhedral pyrite. The variable nickel content across these two sulphides, which is evident from the scanning profile C-C_1, is surprising, because both minerals are optically homogeneous. The marcasite area tested is in fact composed of a single marcasite grain.

SOLID SOLUTION POSSIBILITIES BETWEEN PYRITE AND BRAVOITE

The possibility of a solid solution series existing between pyrite and bravoite has been discussed by various authors with conflicting views,
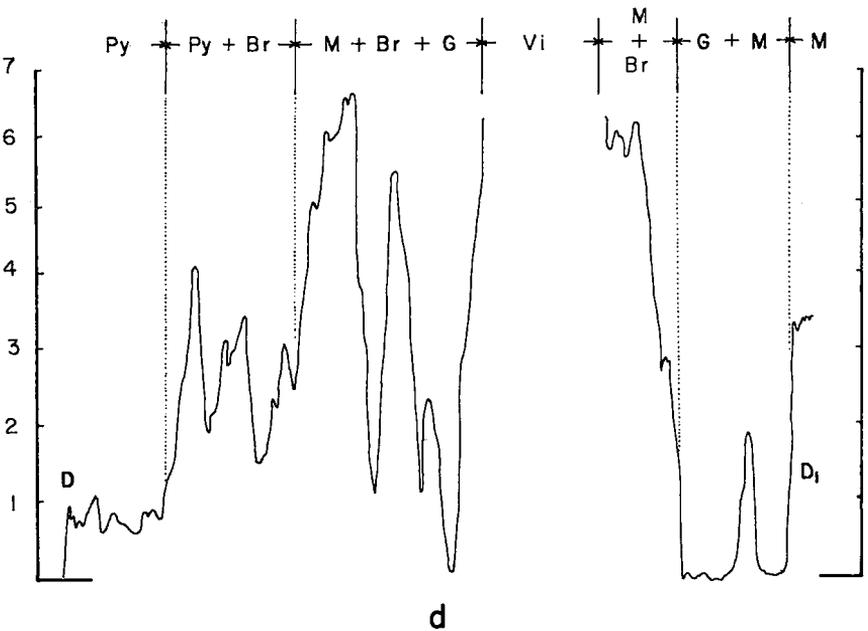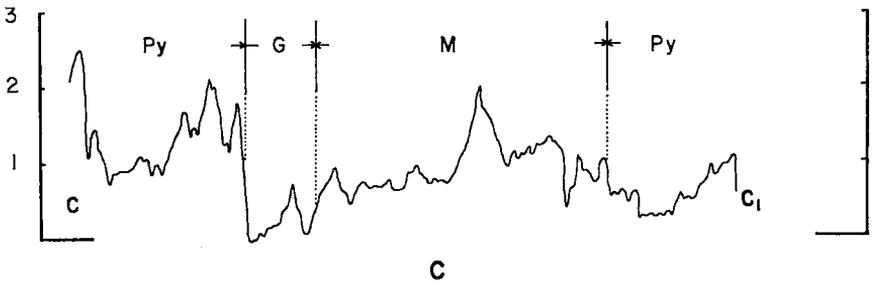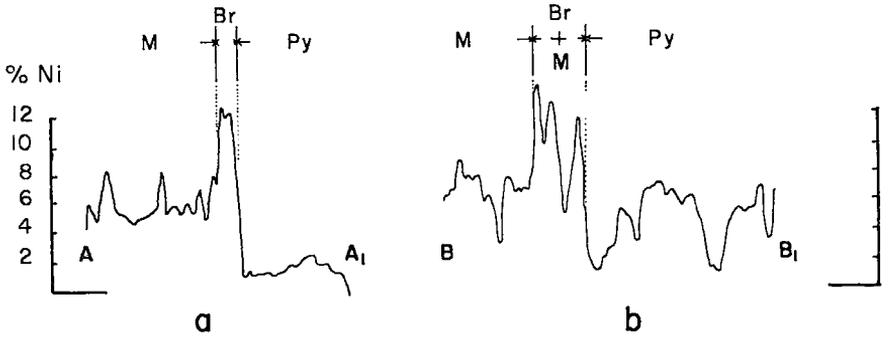
Hegeman (1941), Bannister (1940), Gritsaenco, *et al.* (1953), Clark & Kullerud (1963) and Springer *et al.* (1964).

Clark & Kullerud (1963) synthesized bravoite from aqueous solutions at temperatures below 137°C. They found their bravoites always had a Fe:Ni ratio very close to 1:1. Either synthetic pyrite or synthetic vaesite coexist with bravoite at temperatures below 137°C. Above this temperature bravoite does not form and pyrite and vaesite are stable together. They contain very little Ni and Fe respectively. Bravoite was heated to temperatures above 137°C and decomposed to pyrite and vaesite, a reaction found to be reversible. Natural bravoite and nickel-iferous pyrite both with highly variable metal ratios are known to exist. Analyses of a number of these have been compiled by Springer *et al.* (1964). These authors have also synthesized a number of bravoites however with variable metal ratios. Both Clark & Kullerud, and Springer *et al.* conclude that most of the natural bravoites and nickeliferous pyrites represent metastable phases.

On the basis of the work summarized above, it appears that the bravoite and the nickeliferous pyrite described in the present paper represent metastable phases. The observed mineral relationships indicate changes in conditions during the formation of the secondary sulphides. Rosenthal (1956) states, on the basis of experimental data, that pyrite forms in solutions with pH values greater than 7, and marcasite in solutions with less than 7. It is therefore apparent that variations in the pH value of the secondary solutions could control the deposition of either pyrite or marcasite. Fluctuating pH values in the vicinity of 7 may have been responsible for the repetitive replacement patterns observed, particularly those illustrated in Fig. 16.

The mineral association bravoite-idiomorphic pyrite (Fig. 6), which formed contemporaneously with marcasite, suggests that an immiscibility gap exists on the pyrite-vaesite join between pyrite with less than 1.5% Ni, and bravoite with 11 to 12% Ni. In Fig. 8 it may be observed that some pyrite has a lower reflectivity than normal and therefore presumably a higher nickel content, and that some bravoite has a higher reflectivity than normal and consequently may have a lower nickel content. These changes in the limits of the immiscibility gap could be affected by the changes in pH of the mineralizing solutions.

FIG. 17. Electron scanning profiles for nickel across selected sulphide areas. Profile A-A$_1$ and B-B$_1$ (Fig. 17a and Fig. 17b) are located on Fig. 10, profile B-B$_1$ also on Fig. 11. Profile C-C$_1$ and D-D$_1$ (Fig. 17c and Fig. 17d) are located on Fig. 16.

CONCLUSION

"Mineral X" described by Buddington (1924) as a supergene alteration product of pentlandite was found to be violarite by Short & Shannon (1930). Violarite was later recognized as a common supergene alteration product of pentlandite (Sandfur (1942), Dennen (1943), Michener & Yates (1945) and others). Ramdohr (1960) considers, however, that bravoite is the most common alteration product of pentlandite. Bravoite also occurs as a hypogene hydrothermal mineral.

Unfortunately only one drill hole intersected the mineralized hornblendite. It is therefore not possible to assign a supergene or hypogene origin to the secondary minerals described in this paper. However, the observed parageneses adequately explain the replacement relationships between violarite, bravoite and pentlandite. Violarite first developed pseudomorphically after pentlandite. No other secondary minerals developed simultaneously with the violarite, and the conditions leading to its formation did not cause the alteration of pyrite or chalcopyrite. Later, these sulphides, in addition to violarite, were partly dissolved, possibly due to an access of new aqueous solutions, and a number of secondary minerals including bravoite were precipitated. Bravoite, in contrast to violarite, does not occur pseudomorphically after other minerals but resembles, in its mode of formation, hypogene bravoite deposited from hydrothermal solutions.

This relationship between the three nickel sulphides has been observed in numerous deposits by A. R. Graham (personal communication 1968). A large number of samples from various localities in Canada containing pentlandite affected by supergene, and in some cases hypogene, alteration have been investigated by Graham and his co-workers. Violarite (identified by its x-ray powder pattern in a large number of the samples investigated) occurs as the only pseudomorphic alteration product after pentlandite. Bravoite has rarely been identified in samples with altered pentlandite. The general conclusion, therefore, must be that violarite is the common alteration product of pentlandite, and is the only one of the two secondary sulphides which develops pseudomorphs after pentlandite.

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