PSEUDO-EUTECTIC INTERGROWTHS IN ARSENICAL ORES FROM SUDBURY

J. E. HAWLEY, R. L. STANTON,1 AND A. Y. SMITH
Queen's University, Kingston, Ontario, Canada

ABSTRACT

Pseudo-eutectic intergrowths involving niccolite, chalcopyrite, pyrrhotite, and maucherite in Sudbury ores have been observed to develop chiefly by replacement of gersdorffite without the latter participating essentially as a component of the two- or three-phase aggregates. As shown previously niccolite, by loss of arsenic, may likewise develop niccolite-maucherite intergrowths. New experiments confirm the reactions by which gersdorffite forms niccolite-maucherite intergrowths and the subsequent replacement of maucherite by chalcopyrite to form a niccolite-chalcopyrite aggregate. Niccolite-pyrrhotite and maucherite-pyrrhotite intergrowths may be due simply to breakdown of ferroan gersdorffite, though the former is also developed by normal replacement of pyrrhotite by niccolite. Conditions for their development require elevated temperatures and a lowering of sulphur (and arsenic) vapour pressure, but reactions do not proceed under appreciable pressures of sulphur. The intergrowths seem best explained as late-stage alterations, involving introduction of quartz and carbonates and remobilization of copper and other constituents, accompanying deep-seated fracturing.

INTRODUCTION

Numerous examples of pseudo-eutectic intergrowths involving sulphide and related minerals have been recorded. Many of these have been noted by Guild (1917) and Lindgren (1930); Anderson (1934) and Schwartz (1939) have been important contributors. Most of the mineral pairs involved have been simple cubic sulphides, though sulphosalts, native metals, and others have been noted occasionally. A full list of recorded mineral pairs is given by Edwards (1954).

The present study is an outcome of a more comprehensive general investigation, still in progress, of the mineralogy of the Sudbury nickel deposits, and its purpose is twofold:

(1) To record the occurrence of pseudo-eutectic pairs, niccolite-pyrrhotite, and maucherite-pyrrhotite.

(2) To show that most of the pseudo-eutectic intergrowths of arsenical ores at Sudbury have formed preferentially at the expense of gersdorffite, controlled by the partial pressures of arsenic and sulphur, as demonstrated by experiments.

1Present address, L. A. Cotton School of Geology, University of New England, Armidale, N.S.W.
The presence of arsenide minerals at Sudbury was first established by Barlow (1904), who described gersdorffite and niccolite from the Worthington mine. Working on material from the same locality Lausen (1930) recognized maucherite in addition, and noted that some of the niccolite and chalcopyrite are present as pseudo-eutectic intergrowths. These are confined largely to areas of niccolite surrounding grains of maucherite or gangue material, and where not visible in the section he considers they may have been present above or below. The intergrowths are attributed to replacement of niccolite by chalcopyrite rather than by unmixing of the two. Michener, in an unpublished thesis (1940), noted the pair niccolite-pyrrhotite, and Hawley & Hewitt (1948) noted niccolite-maucherite and niccolite-maucherite-chalcopyrite intergrowths in ore from the Garson mine. The latter authors also produced the niccolite-maucherite textures by heat treatment of natural niccolite, and from synthetic mixtures of NiAs-NiSb in vacuo at temperatures of 500-750°C. Zurbrigg et al. (1957), although not mentioning the intergrowths of arsenides at Frood, notes the position of the arsenides in the paragenetic sequence as between early magnetite and the common sulphides. Further details of mineral relations, as noted by Lausen, Zurbrigg, and ourselves, are discussed below.

**Occurrence of Arsenide Ore at Sudbury**

Nickel-bearing arsenides appear chiefly in the "offset" deposits but also in some of the "marginal" ore deposits along the south side of the Sudbury irruptive. Mixed arsenides—gersdorffite, maucherite and niccolite—are present in the Worthington offset, and at the Creighton, Frood, and Garson, while at Falconbridge gersdorffite occurs in places, more or less alone, where Davidson (1948) notes its tendency to favour the margins of the main sulphide zones. Lack of descriptions of such minerals in north range deposits suggests they are either absent or in negligible quantities.

The occurrences in the Worthington offset, described by Lausen at the Worthington mine, and by Barlow (1904) at the old Gersdorffite mine, have associated with them quartz and "flesh-coloured" carbonates. At the former Lausen was lead to believe the quartz and arsenides formed veins cutting the normal type of sulphide ore and enclosing fragments and residuals of such sulphides, presumably broken from adjacent walls. Mineralization there was considered to have occurred in three stages, (1) magnetite and the sulphides, pyrrhotite, pentlandite, chalcopyrite;
(2) gersdorffite, maucherite, niccolite, and chalcopyrite (the latter two in intergrowths); (3) pyrite, sphalerite, and galena.

Similar mineralization of quartz, carbonates, and arsenides has been noted by Lausen at Creighton and Frood, but in the latter Zurbrigg et al. indicate the presence of arsenides with abnormal precious metal content in the massive cubanite-rich zone and the siliceous mineral zone below, and note their pre-sulphide age. There also, Michener (1940) states that the arsenides occur marginal to the sulphide bodies, their greatest concentrations being along certain hanging wall contacts. Some zoning is present, "where niccolite, maucherite and chalcopyrite are seen together along a contact they are arranged in the order named with niccolite next to the contact rock." In addition, he noted arsenides occurring as small veins and stringers penetrating the contact rocks for several feet.

Thus from published descriptions, some arsenides appear earlier than the normal sulphides and some later. This will be considered further. The three arsenides themselves occur in massive granular aggregates as well as participating in one way or another in pseudo-eutectic intergrowths with each other or with chalcopyrite or pyrrhotite. Gersdorffite is everywhere clearly the earliest of the three. At the Worthington, Lausen notes its deposition with quartz, followed by maucherite, then niccolite, and still later by chalcopyrite. In Frood ores, Zurbrigg also places (massive) maucherite as earlier than niccolite though recent examination of some ores (by us), believed from this deposit, as noted below, suggests the reverse age relations of this pair. Where maucherite is present in fine pseudo-eutectic intergrowths in niccolite, however, it may be contemporaneous with or slightly later than the niccolite.

The composition of the arsenides is of interest in the present study. Analyses of gersdorffite (Barlow) indicate a nickel content of 26.3 per cent; iron, 7.9 per cent; and cobalt, 2.01 per cent. Partial analyses in our laboratory of Falconbridge gersdorffite, uncontaminated with other arsenides, show a content of 23.9 per cent nickel, 6 per cent iron, and about 5 per cent cobalt. Michener also found gersdorffite from the Frood and Garson mines to contain 4.96 to 6.68 per cent iron and 7.2 to 12.0 per cent cobalt. It is clearly ferroan and cobaltoan in character.

Niccotine has not been found in sufficiently pure form to allow analysis of the single mineral, but T. L. Walker's analysis of a mixture of it with gersdorffite (Barlow, p. 102) shows 2.43 per cent iron and 0.64 per cent cobalt. In view of the iron and cobalt contents of gersdorffite it is likely the niccolite alone is much lower in these constituents than gersdorffite.

Maucherite, similarly, even when present in its more massive form is usually associated with some niccolite and some sulphides. A partial
Fig. 1. Gersdorffite crystals (white) with interstitial chalcopyrite (right) and pyrrhotite (grey, left), showing no replacement. Refl. light in air, X 22 (Ni 38).

Fig. 2. Fractured gersdorffite crystal bordered and partly replaced by pyrrhotite (grey) with some very fine secondary pyrite (white, upper left), chalcopyrite (lower centre and right), and white niccolite (just below and right of centre). To left of centre
analysis of the purest material available shows a negligible iron content and 0.42 per cent cobalt. It is clearly much lower in iron and cobalt than gersdorffite, but may not differ much in this respect from niccolite.

**Microscopical Features of the Arsenides and their Intergrowths**

The three principal arsenide minerals are, in approximate order of abundance, gersdorffite, niccolite, and maucherite. Sperrylite is a minor, though of course economically important, member. Their relations to one another and to the sulphides, pyrrhotite, pentlandite, and chalcopyrite with which they are commonly associated, are of interest in arriving at an explanation for their peculiar pseudo-eutectic intergrowths.

**The Arsenides**

Where gersdorffite occurs as the only arsenical mineral, as it does in places at Falconbridge, it forms a selvage, 6 inches wide, clearly replacing adjacent chlorite schist. Inward it passes into typical pyrrhotite-pentlandite-chalcopyrite ore, the gersdorffite presenting sharp crystal boundaries against the sulphides with only minor indications of replacement by them. Here and there within the massive crystalline gersdorffite the sulphides lie in isolated aggregates in the interstices. A few grains of gersdorffite contain rounded blebs of pyrrhotite or chalcopyrite, some of which have smooth boundaries as if introduced along concealed ducts, but others are more ragged and could be interpreted as replacement remnants. In general however, crystallization of gersdorffite here appears to have been followed by the normal sulphides. In this particular occurrence no pseudo-eutectic intergrowths were apparent.

In mixed arsenide specimens from Garson, gersdorffite occurs in complex intergrowths with appreciable massive niccolite and variable amounts of pyrrhotite-pentlandite and chalcopyrite. The gersdorffite occurs either as sharply euhedral to variably corroded crystals, or as heavily frayed,
often spongy, irregular areas and particles. It shows a strong tendency
to idiomorphism, and where isolated in either niccolite, pyrrhotite, or
chalcopyrite may be completely bounded by sharp crystal faces (Fig. 1). Embayment and fracture and replacement veining by these minerals
is common (Fig. 2). As indicated later, there is a notable coincidence of
“spongy” gersdorffite (Figs. 3, 4) with pseudo-eutectic intergrowths of
either niccolite-chalcopyrite, niccolite-pyrrhotite, or more rarely niccolite-
maucherite.

Both niccolite and maucherite in specimens from Frood and Garson
occur in two distinct forms, though usually separately—massive, or as
constituents of the pseudo-eutectic intergrowths with which we are
presently concerned. Both may form massive particles 2.0–3.0 mm.
diameter, and maucherite has been noted in concentrations up to 3 cm.
across. Where each of these contains gersdorffite, some pseudo-eutectic
intergrowths are present, but where gersdorffite is absent, normal re-
placement borders and textures between either chalcopyrite, cubanite,
or pyrrhotite and the arsenides prevail.

Niccolite, free from other arsenides but associated with chalcopyrite,
has been noted chiefly within quartz veins as irregular seams or stringers. In one such specimen in the adjacent, mineralized wall rock, niccolite is
associated with gersdorffite, pyrrhotite, pentlandite, and chalcopy-
rite. It clearly replaces gersdorffite, appears to replace the pyrrhotite,
which here has much included pyrite and marcasite (Fig. 8), rarely re-
places pentlandite, and is in turn replaced by chalcopyrite. Both chal-
copyrite-niccolite and pyrrhotite-niccolite pseudo-eutectic intergrowths
are present and are discussed later.

In specimens consisting chiefly of massive maucherite, rare remnants
of gersdorffite crystals are enclosed by maucherite (Fig. 6) and appear
in various stages of replacement by a pseudo-eutectic intergrowth of
fine maucherite and pyrrhotite, an occurrence reported here for the
first time. Minor quantities of niccolite, pyrrhotite-pentlandite and
chalcopyrite are also present. Pyrrhotite, with intergrown flames of
pentlandite, and chalcopyrite characteristically follow and exploit the
grain boundaries of maucherite and gersdorffite and appear younger than
both arsenic minerals. Apparent rounded embayments of maucherite
into pyrrhotite are interpreted as original rounded grains of maucherite
along which pyrrhotite or chalcopyrite have been introduced. In such
ores the age relations of niccolite and maucherite are not clear when
viewed in ordinary light, the niccolite occupying in part intergranular
spaces between grains of maucherite. Under crossed nicols, however,
maucherite clearly replaces niccolite and encloses odd “islands” in
optical continuity with larger areas of niccolite. This relation would
seem to agree best with observed zoning at the Frood where maucherite follows niccolite away from wallrock contacts. Maucherite also clearly replaces the gersdorffite crystals and in turn is replaced by both pyrrhotite and chalcopyrite. Where pyrrhotite adjoins gersdorffite-free maucherite no pseudo-eutectic intergrowths are apparent.

The relation of maucherite to chalcopyrite-cubanite is well shown by specimens from the Frood in which a 2-inch grey quartz vein is bordered by massive maucherite. Away from the vein the maucherite is gradually replaced by an intimate intergrowth of cubanite-chalcopyrite over a distance of 3 inches, the maucherite occurring as irregularly rounded particles 1 to 3 or more mm. in diameter in a gradually increasing cubanite-chalcopyrite matrix. The maucherite grains show radiating cracks around their periphery, and locally are veined by the sulphides. In some cases fine blades of pentlandite develop at the border, projecting into cubanite, but no pseudo-eutectic intergrowths are apparent. Again gersdorffite is notably absent from this assemblage.

In summary, our observations indicate that of the arsenides gersdorffite is always the earliest deposited, and this is followed by niccolite and maucherite. Where gersdorffite occurs alone it is clearly earlier in age than the common sulphides, pyrrhotite, pentlandite, and chalcopyrite-cubanite. Massive occurrences of maucherite likewise seem earlier than pyrrhotite, pentlandite, and chalcopyrite of some ores, and also than chalcopyrite-cubanite of the Frood. Niccolite being earlier in places than maucherite would also seem necessarily earlier than the common sulphides as noted at Frood by Zurbrigg et al. There are indications, however, in some ores with abundant quartz that niccolite of a different generation has replaced pyrrhotite and is in places either almost contemporaneous with chalcopyrite or slightly earlier, as both niccolite and chalcopyrite fill the fractures and seams in the quartz and form segmented veinlets along cleavage planes in gersdorffite.

The Intergrowths

Mineral groups involved in the intergrowths are (1) niccolite-chalcopyrite; (2) niccolite-pyrrhotite; (3) niccolite-maucherite; and (4) maucherite-pyrrhotite. Three-phase intergrowths consist of (5) niccolite-pyrrhotite-chalcopyrite; and (6) rarer niccolite-maucherite-chalcopyrite. Spongy replaced remnants of gersdorffite are found with each of these typical assemblages, but may be missing in some specimens owing perhaps to complete replacement.

The most common intergrowths are of niccolite and chalcopyrite and/or pyrrhotite. Niccolite-maucherite intergrowths with minor chalcopyrite are not as common, but have already been described (Hawley &
Fig. 5. Pseudo-eutectic intergrowth of niccolite (white), chalcopryrite (medium grey), and pyrrhotite (darker grey); black is a silicate. Pol. light in oil, X 79 (Ni 41).

Fig. 6. Crystals of gersdorffite (centre) enclosed in maucherite, but now largely replaced by maucherite-pyrrhotite intergrowth. Replacement veinlets and rounded bodies of pyrrhotite (dark grey), containing flames of pentlandite, also occur in the main mass of maucherite (lower right and left). Refl. light in air, X 49 (Ni 184b).

Fig. 7. Niccolite-pyrrhotite pseudo-eutectic intergrowth replacing massive gers-
Hewitt, 1948). Maucherite-pyrrhotite intergrowths are also rather rare. For the most part the intergrowths appear as fine, sponge-like aggregates of rounded blebs and interconnected club- or hook-shaped masses, essentially as described by Lausen (Figs. 4, 5).

In the niccolite intergrowths niccolite is generally the dominant member but the other phases may, in places, almost equal it in volume. In spite of the fineness of the texture, the niccolite when viewed between crossed nicols, is seen to be in the form of quite coarse grains (up to 1.5 mm. across); the actual size of the structurally continuous niccolite is thus of the order of ten to twenty times coarser than the "grain size" of the intergrown phase with which it is involved. Actually however, the apparently discontinuous phase may be optically continuous and have a grain size close to that of niccolite, as is evident in highly anisotropic pyrrhotite. In the majority of cases niccolite of the intergrowths is not optically continuous with adjacent "growth-free" grains, the border being marked by original boundaries of gersdorffite, fine residuals of which may remain. Exception to this is noted especially in gersdorffite-free areas where niccolite adjoins coarse grains of pyrrhotite (Fig. 8).

Where two of the normally subordinate phases—chalcopyrite, pyrrhotite, or maucherite—are present in niccolite, their positions are always analogous and, as is evident in Fig. 5, chalcopyrite and pyrrhotite, for example, give way to each other in a continuous fashion within the limits of their own network. Under crossed nicols some grains of niccolite contain only blebs of chalcopyrite, others only pyrrhotite, but both may be found in a single grain or following niccolite grain boundaries and projecting into grains on either side. Here and there too, discontinuous, gash-like veinlets lie within the intergrowth, transect niccolite, and are filled with both pyrrhotite and chalcopyrite.

Niccolite-pyrrhotite intergrowths were reported first by Michener (1940) from the Frood, and have been observed by us both in Garson ores and recently in a quartz-bearing specimen containing rather abundant niccolite intergrown with gersdorffite and the common sulphides, described briefly above (p. 561). The textural relations of the minerals in this ore are very complicated and remind one of a metamorphic rock, such as granophyre. Gersdorffite is present as scattered crystals, some showing sharp boundaries against pyrrhotite or even pentlandite, but is more often in various stages of replacement by both niccolite and chal-

dorffite (top and right). Darker phase of intergrowth is pyrrhotite. Fine light residuals (high relief) in intergrowth are of gersdorffite. Pol. light in oil, X 158 (Ni 501–1).

Fig. 8. Niccolite-pyrrhotite intergrowth in niccolite (top) along contact with pyrrhotite (lower left) containing fine cube pyrite and shreds of marcasite. Pol. light in oil, X 158 (Ni 501–1).
copyrite, both of which are also found closely associated within quartz vein material and both of which appear also to replace pyrrhotite. The pyrrhotite of this ore everywhere contains abundant secondary cube pyrite and marcasite-like shreds, paralleling the parting, a type of alteration, described by Michener & Yates (1944), associated with millerite and violarite, and ascribed to supergene solutions working downward along deep fault zones. Cube pyrite is always accompanied by minor gangue-quartz or carbonate. Niccolite replacing and deeply embaying such pyrrhotite is in sharp contrast to it and shows nothing which could be interpreted as supergene alteration. In this ore the niccolite-pyrrhotite pseudo-eutectic intergrowths have two distinct modes of occurrence. One is a clear-cut replacement of gersdorffite crystals, both as distinct rims or partial rims along the borders of the crystals and as deep embayments within (Fig. 7). Spongy strings of gersdorffite remain here and there within the intergrowth. Clear, pyrrhotite-free niccolite grains surround such altered crystals. Grain size of the niccolite of the intergrowth is fairly coarse but somewhat less than that of niccolite outside the intergrowth. Curving, club-shaped and fan-shaped inclusions of pyrrhotite tend to have one orientation within one grain of niccolite. Peculiarly both niccolite and chalcopyrite follow cleavages in other grains of gersdorffite as fine veinlets and also as irregular replacements without the development of such pseudo-eutectic intergrowths, although locally niccolite-chalcopyrite intergrowths form either alone or in close association with niccolite-pyrrhotite intergrowths.

The second type of niccolite-pyrrhotite intergrowth occurs in niccolite along its contact with pyrrhotite (Fig. 8). Here rounded and curving, hook-shaped blebs of pyrrhotite lie as islands off the adjacent pyrrhotite and are optically continuous with it. (No pyrite or marcasite is associated with the pyrrhotite of the intergrowth.) Interpreting the niccolite as younger than pyrrhotite, the pseudo-eutectic intergrowth in essence would be a relict texture due entirely to replacement and is similar to tennantite-stromeyerite intergrowths described by Lindgren. Further discussion of these intergrowths is given after consideration of experimental evidence.

Maucherite-pyrrhotite intergrowths have only been found in coarse or massive maucherite ore. These are precisely similar texturally to the more common niccolite intergrowths, but have been found only as small areas pseudomorphous after euhedral and subhedral gersdorffite enclosed by massive maucherite (Fig. 6). As noted earlier, pyrrhotite replaces maucherite grains, but only within the associated gersdorffite are the pseudo-eutectic intergrowths found.

In view of some general statements on pseudo-eutectic intergrowths...
there are two features of the Sudbury occurrences that merit particular comment:

(1) Examples of each of the different types of intergrowths have been found developing in the presence and at the expense of gersdorffite. In those cases where no gersdorffite is now visible it may have been present above or below the section examined, or have been entirely replaced by the intergrowth. Gersdorffite, therefore, must have played an important part, either directly or indirectly, in the development of the textures.

(2) Remnants of gersdorffite within the intergrowths occur in a very fine spongy or mesh structure whose margins, though rounded, have no resemblance to a eutectic. It is only between the substituting minerals that the pseudo-eutectic relationships develop. Thus, though gersdorffite is the primary replaced mineral, unlike other pseudo-eutectic intergrowths, it does not form an essential component of it.

The occurrence of the pseudo-eutectic intergrowth in gersdorffite is in harmony with Lindgren's observation that most such textures occur in cubic minerals, but differs from the view that the replaced mineral (and replacing) should be soft, particularly if the intergrowths result directly by one rather than two separate reactions. Lindgren did not, for instance, cite any examples involving pyrite group minerals, and Edwards (1954) in discussing them states: "Replacement of hard minerals like pyrite, usually results in rounded or angular residuals." This is of course true, but our observations have now shown that a harder mineral and one having a pyrite structure can be involved in some way in this type of texture.

That they should tend to develop most frequently in cubic minerals may have some structural basis. It might be expected that such unoriented arrangements would develop in isotropic substances; materials of other crystal systems, with their anisotropic structures, would probably exert much stronger directional influence over a metasome, yielding bladed and other lattice-controlled intergrowths.

The niccolite-pyrrhotite and niccolite-maucherite or chalcopyrite intergrowths, on the other hand, appear more normal with respect to softness of the replaced mineral although the host mineral involved is hexagonal and not cubic in character.

Formation of the Textures

Ideas concerning the formation of pseudo-eutectic textures in ores are too well known to need recapitulation. Lindgren, Lausen, and Anderson (1934) have shown beyond reasonable doubt that they are
generally due to replacement, and there is little doubt that the Sudbury intergrowths have also formed—at least in part—in this way. A further mechanism has, however, been demonstrated by Hawley & Hewitt (1948), who have shown that artificial niccolite-maucherite intergrowths can be formed directly at high temperatures and low pressures simply by arsenic loss. It will be shown that both processes, replacement and variations in arsenic vapour pressure, may have operated in conjunction at Sudbury.

Observational Evidence

The Sudbury intergrowths show two very persistent features—one of association, the other of constitution:

(1) Association with gersdorffite. During a very careful examination of the arsenide ores in 1957 it occurred to us that the gersdorffite did not show a simple variation in its replacement by other ore minerals—that is, there was not a simple range from uncorroded, euhedral crystals down to almost completely resorbed, irregularly shaped, residuals. There were two distinct types; one in which replacement by other minerals took the usual form and course, with embayment and replacement veining leading to the formation of normal irregular small residuals; the other in which replacement produced a distinct “sponge” texture in the gersdorffite. Furthermore, it became apparent that the first type of replacement was induced usually by single metasomes, whereas the spongy type appeared only in association with the pseudo-eutectic groupings. At the same time, the latter seldom appeared without at least some associated spongy gersdorffite. In cases where no gersdorffite was visible, its absence may be accounted for by complete replacement.

It thus became clear that the intergrowths (a) occurred in most cases in the presence of gersdorffite; (b) occurred, furthermore, in association only with spongy gersdorffite and its relicts which, conversely, only occurred in the presence of one or other of the intergrowths.

In addition, the pyrrhotite-maucherite intergrowths formed sharp pseudomorphs after euhedral and subhedral gersdorffite, indicating exclusive preference for this mineral as host. Niccolite-pyrrhotite intergrowths similarly replace gersdorffite but also occur separately in contact only with massive pyrrhotite, and, as noted above, the latter appears to be of normal replacement origin.

(2) Ubiquity of arsenide in intergrowths. No instance of an intergrowth without either niccolite or maucherite has been found—all have at least one or other of them among its constituents.

Thus from (1) and (2) it appears that: (a) the intergrowths have formed in the place of—and with the one exception noted exclusively in
the place of—gersdorffite; (b) such substitution was, as is evidenced by
the retention of nickel and arsenic in the replacing intergrowths, in the
nature of chemical reaction and breakdown, rather than simple physical
replacement; (c) substitution took place under somewhat unusual con-
ditions, leading to the development of unusual textures in both host and
guest.

Before any attempts were made to deduce the exact mechanism and
time of formation of the intergrowths further experimental work was
undertaken by the junior author (A.Y.S.) particularly to determine if,
in fact, gersdorffite could be converted artificially to intergrowths of the
types found.

Experimental Evidence

Experiments by Hawley & Hewitt have already confirmed that nicco-
seite-maucherite intergrowths, at least, may be produced artificially by
loss of arsenic from niccolite, and it seems clear that such a reaction (as
No. 1) may have taken place in

\[ 11\text{NiAs} \rightarrow \text{Ni}_{11}\text{As}_{8} + 3\text{As} \]

niccolite maucherite

some natural niccolite under conditions allowing a loss of arsenic as
might occur during fracturing prior to the introduction and deposition
of later copper and iron sulphides.

To test the role of gersdorffite in the development of such textures
four experiments were carried out involving heat treatment of gers-
dorffite alone, or with chalcopyrite in one case and pyrrhotite in another,
in an atmosphere of either arsenic or sulphur.

Gersdorffite used was from fairly pure material from Falconbridge.
Chalcopyrite, used as a major constituent was from the Hardy Mine,
and pyrrhotite from the Bluebell Mine, B.C. The gersdorffite was well
crystallized in grains up to 3 mm. with minor amounts of interstitial
pyrrhotite, chalcopyrite, and chlorite gangue. Chalcopyrite contained
only a few euhedral magnetite grains. Pyrrhotite impurities in gersdorf-
fite were probably nickeliferous, but that from the Bluebell Mine con-
sisted of pure, nickel-free crystals.

Specimens of the minerals were cut into small cubes, \( \frac{1}{2} \) inch to the
side, one face of which was ground smooth with emery 305 on a glass
plate. Samples to be heat-treated were made up of a cube of gersdorffite
and either a cube of chalcopyrite or pyrrhotite, the flattened sides being
placed together and bound with iron wire. (This technique was devised
to test particularly the diffusion of constituents from one mineral into
the other.) Samples were then placed in pyrex tubes with either powdered
Fig. 9. Artificial niccolite-maucherite pseudo-eutectic intergrowth developed from and surrounding gersdorffite in an arsenic atmosphere. Gersdorffite (white, centre and lower right). In intergrowth white phase is niccolite and grey is maucherite. Experiment No. 1. Refl. light in oil, \( \times 158 \).

Fig. 10. Artificial niccolite-maucherite intergrowth and massive grey maucherite
sulphur or arsenic, the tubes evacuated and sealed off. Heatings were carried out in a tube furnace regulated by a Bristol controlling pyrometer. In each case the temperature was raised rapidly to 750°C and held for 24 hours. At the end of the heating period samples were allowed to cool to room temperature, usually in about two hours.

The samples were removed from the pyrex tubes, mounted in plastic, and polished for microscopic examination. Some of the products were removed for x-ray determination. Table I outlines the experimental conditions.

**Table I**

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<tr>
<th>Sample #</th>
<th>Material</th>
<th>Temp.</th>
<th>Atmos.</th>
<th>Products</th>
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<tbody>
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<td>1</td>
<td>Gersdorffite</td>
<td>750°C</td>
<td>Arsenic</td>
<td>Niccolite-maucherite intergrowth, arsenic mirror on tube</td>
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<td></td>
<td></td>
<td></td>
<td>vapour</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Gersdorffite plus</td>
<td>750°C</td>
<td>Arsenic</td>
<td>Niccolite-maucherite intergrowth, minor pentlandite (?), arsenic mirror on tube</td>
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<tr>
<td></td>
<td>chalcopyrite</td>
<td></td>
<td>vapour</td>
<td></td>
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<td>Gersdorffite plus</td>
<td>750°C</td>
<td>Sulphur</td>
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<td></td>
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<tr>
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<td>chalcopyrite</td>
<td></td>
<td>vapour</td>
<td></td>
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</tbody>
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**Results**

*Sample 1.* Gersdorffite alone; heated 24 hours at 750°C in arsenic vapour at approximately 3 atmospheres. Small, oval, porous patches developed in the gersdorffite. Within these patches a two-phase pseudo-eutectic intergrowth resembling a fingerprint developed (Fig. 9). One (centre) developed from gersdorffite (top, white). Entire area was originally gersdorffite. On right niccolite predominates. Experiment No. 1. Refl. light in oil, × 100.

*Fig. 11.* Artificial niccolite-chalcopyrite intergrowth developed from artificial niccolite-maucherite intergrowth formed from original gersdorffite. White phase is niccolite. Dark grey, centre top, and within intergrowth is chalcopyrite. Lower right, grey phase is likely maucherite but is indistinguishable from chalcopyrite. Lower centre, chalcopyrite preferentially replaces maucherite and encloses niccolite. Experiment No. 2. Refl. light in oil, × 550.

*Fig. 12.* Artificial chalcopyrite-like phase (darker grey) surrounding central grain of previously non-nickeliferous pyrrhotite in which flames of pentlandite (off-white) have developed along parting by diffusion of nickel from arsenides. The "chalcopyrite" also replaces gersdorffite (white, top and bottom right). On top, left, mottled intergrowth of niccolite-maucherite is also replaced by "chalcopyrite." Experiment No. 2. Refl. light in oil, × 158.
phase of this intergrowth was identified by optical properties and by x-ray diffraction methods as niccolite. The second phase of the intergrowth was a pinkish brown, slightly anisotropic mineral identified as maucherite by optical means. The intergrowth will be described more fully later.

Sample 2. Gersdorffite in contact with chalcopyrite; heated 24 hours at 750° C in arsenic vapour at approximately 3 atmospheres. As in Sample 1, the gersdorffite became very porous, and the same two-phase intergrowth of niccolite and maucherite developed. Next to the gersdorffite-chalcopyrite contact a considerable amount of a chalcopyrite-like phase developed within the gersdorffite. This clearly replaced the gersdorffite, the niccolite-maucherite intergrowth, the pyrrhotite originally interstitial to gersdorffite, and veined and replaced the chloritic gangue.

Where chalcopyrite formed in contact with the niccolite-maucherite intergrowth it preferentially replaced the maucherite rather than niccolite (Fig. 11). In one place, replacement of maucherite by chalcopyrite had progressed far enough to be considered a niccolite-chalcopyrite intergrowth. Where the newly formed chalcopyrite replaced pyrrhotite, originally present in the gersdorffite portion of the sample, small white flames of an isotropic mineral developed within the remnant of pyrrhotite. These flames (Fig. 12) stained blue with chromic acid and were identified as pentlandite.

Sample 3. Gersdorffite in contact with pyrrhotite; heated 24 hours at 750° C in sulphur vapour at approximately 4 atmospheres. Chalcopyrite, originally present in the gersdorffite portion of the sample interstitial to gersdorffite, replaced gersdorffite to a very minor extent, leaving small remnants of gersdorffite unreplaced within the chalcopyrite. With this exception, no significant changes took place and no pseudo-eutectic textures developed. There is no indication of what happened to the replaced constituents of gersdorffite, which on the whole, however, remained stable under the sulphur pressure developed.

Sample 4. Gersdorffite in contact with chalcopyrite; heated 24 hours at 750° C in sulphur vapour at approximately 4 atmospheres. Chalcopyrite migrated into the gersdorffite part of the sample and replaced both gersdorffite and pyrrhotite originally present in the gersdorffite part of the sample, and veined and replaced the chloritic gangue. Where gersdorffite was replaced by chalcopyrite the relationship was as in Sample 3, with no development of the niccolite-maucherite intergrowth. Where pyrrhotite was replaced by chalcopyrite no mineral resembling pentlandite developed in the unreplaced remnants of pyrrhotite as it had in No. 2.
The pseudo-eutectic intergrowths of niccolite-maucherite, and niccolite-chalcopyrite which developed in Samples 1 and 2, closely resemble in many respects the natural ones described in the first part of this paper.

The main mass of the gersdorffite remained relatively unchanged, although it was somewhat fractured by the heating. Within and around this gersdorffite, oval, porous patches, up to 1.5 mm. across, developed. These patches consisted of the niccolite-maucherite intergrowth. In contact with gersdorffite about equal proportions of niccolite and maucherite occur in oriented, bladed "fingerprint" textures (Fig. 9). Within these intergrowths, the niccolite phase is optically continuous, suggesting a development of fairly large grains of niccolite. The maucherite of this intergrowth is also optically continuous but over even larger areas than the niccolite, and may cover several "grains" of niccolite. This is somewhat at variance with the natural intergrowths.

Away from the original gersdorffite contact, two situations occur. In the first, niccolite becomes more continuous, with smaller patches of maucherite within it. This type of relation rather closely resembles the natural niccolite-maucherite intergrowths. In the second situation, often following closely upon the first (Fig. 10), maucherite becomes more massive, in patches up to 0.5 mm. across. Occasional remnants of niccolite may be present in this maucherite.

Very little of the spongy type of gersdorffite noted in natural ores occurs in the artificial textures, owing possibly to the fact that replacement progresses on a broad, smooth front extending inward from the original gersdorffite boundary, rather than developing projections or cusps.

Where the chalcopyrite-like phase developed within gersdorffite it replaced, in every case, the maucherite of the niccolite-maucherite intergrowth so that eventually a niccolite-chalcopyrite intergrowth resulted. Neither a niccolite-pyrrhotite nor a maucherite-pyrrhotite intergrowth developed in these experiments.

**SUMMARY OF EXPERIMENTAL RESULTS AND INTERPRETATIONS**

Several interesting facts emerge from these experiments.

(1) Niccolite-maucherite, pseudo-eutectic intergrowths, resembling those of natural ores to a considerable extent, form from gersdorffite alone or with chalcopyrite when heated in an atmosphere of arsenic but not in an atmosphere of sulphur. In the first case the partial pressure of arsenic and of sulphur must have been sufficiently low to allow the decomposition of the gersdorffite and the formation of under-saturated maucherite. In
the second case the partial pressure of sulphur must have been sufficient
to stabilize the gersdorffite at the temperatures involved. It is likely the
two-phase intergrowth developed directly according to the reaction:

$$12\text{NiAsS} \rightarrow \text{NiAs} + \text{Ni}_{11}\text{As}_{8} + 3\text{As} + 12\text{S}.$$  \hspace{1cm} (2)

gersdorffite → niccolite + maucherite and vapour

There is no indication in the experiments as to the behaviour of the
iron or cobalt contained in the gersdorffite. It seems likely that sulphur
was expelled ahead of arsenic, but loss of both immediately next to un-
replaced gersdorffite gave rise first to niccolite-maucherite, in about equal
proportions, then to more abundant niccolite (some in single grains),
perhaps as a result of arsenic reacting with maucherite, and still farther
away to even massive maucherite, by further loss of arsenic. Such an
assemblage suggests that equilibrium conditions had not been obtained
throughout the entire specimen. In any case these several products have
clearly developed from original gersdorffite and the question may be
raised as to how much niccolite and maucherite in the deposits may have
had such an origin.

(2) Heat treatment of gersdorffite in contact with chalcopyrite or
pyrrhotite in an atmosphere of sulphur yielded no pseudo-eutectic inter-
growths, but whether chalcopyrite was present as a major or minor
phase, a chalcopyrite-like phase replaced gersdorffite to a greater or
lesser extent, but in an entirely normal manner.

(3) In an arsenic atmosphere, however, with the development of the
niccolite-maucherite intergrowth from gersdorffite, in the presence of
chalcopyrite (and minor pyrrhotite), a chalcopyrite-like phase was found
to selectively replace maucherite giving rise to niccolite-chalcopyrite
intergrowths, similar to natural occurrences. Such a preferential replace-
ment may be ascribed to the defect type of lattice of maucherite. The
substance of the replaced maucherite, plus arsenic vapour, may have
added to the niccolite phase of the niccolite-chalcopyrite intergrowth and
similarly, original iron and sulphur from the gersdorffite may have found
their way into the replacing chalcopyrite phase.

(4) Though not of immediate concern, it may also be noted that when
pyrrhotite was present, intergrown with gersdorffite, heat treatment in
an arsenic atmosphere gave rise to fine flames of “ex-solution type”
pentlandite in pyrrhotite, suggesting diffusion of nickel into the pyrrhotite.
This was confirmed by other experiments using non-nickeliferous pyrrho-
tite. In a sulphur atmosphere, however, no such intergrowth of pentlan-
dite in pyrrhotite was found, a logical result as nickel can form a stable
solid solution with pyrrhotite under some sulphur pressure.

(5) In none of the experiments was there any development of either
niccolite-pyrrhotite or maucherite-pyrrhotite intergrowths, though favourable experimental conditions may not have been found for these. Their explanation then must be deduced from observational evidence alone.

Conclusions on the Origin of the Textures

Both the observed associations in natural ores and experimental results confirm the direct development of niccolite-maucherite pseudo-eutectic intergrowths from gersdorffite at elevated temperatures and under suitable partial pressures of arsenic and sulphur. The reaction is inhibited by high sulphur vapour pressure, but apparently proceeds even in the presence of considerable arsenic vapour pressure, if the temperature is sufficiently high.

Earlier experiments confirmed the development of similar textures by loss of arsenic from niccolite, so, though gersdorffite appears to have been the original host for most such intergrowths and may alter directly to niccolite and maucherite, a two-stage alteration, first to niccolite and then of niccolite (in part) to maucherite, may, in some cases, more correctly portray the mechanism of the development of such textures.

The three-phase intergrowth of niccolite-maucherite-chalcopyrite has been shown to form by replacement of maucherite by remobilized chalcopyrite. Complete replacement of such maucherite gives rise to the niccolite-chalcopyrite intergrowth, but it is not implied that maucherite always participated in the development of the latter pair. (Otherwise maucherite would probably be much more common than it seems to be.)

There remains to explain the niccolite-pyrrhotite and maucherite-pyrrhotite pseudo-eutectic textures, both of which have been observed forming from gersdorffite, although the former also develops directly as a replacement feature in niccolite along contacts with pyrrhotite. In so far as distinctly ferroan gersdorffite has participated in their development, part or all of the pyrrhotite component of the intergrowths may have arisen by dissociation to form niccolite and pyrrhotite according to the reaction:

\[
\text{Ni}_{1-y}\text{Fe}_y\text{AsS} \rightarrow (1-y)\text{NiAs} + y\text{FeS} + y\text{As} + (1-y)\text{S}. \quad (3)
\]

ferroan gersdorffite → niccolite + pyrrhotite

In such a case partial pressure of arsenic would have to be sufficient to prevent the breakdown of niccolite to maucherite, but where this was not the case, intergrowths of maucherite-pyrrhotite would form either directly from the gersdorffite, as seems to have happened in the case of
a natural ore according to Reaction (4), or indirectly, from first-formed niccolite, according to Reaction (1), noted above.

\[ 11\text{Ni}_{1-y}\text{Fe}_y\text{AsS} \rightarrow (1-y)\text{Ni}_{11}\text{AsS} + 11y\text{FeS} + (3+8y)\text{As} + 11(1-y)\text{S} \]

ferroan gersdorffite → maucherite + pyrrhotite

(4)

Conditions under which such natural pseudo-eutectic intergrowths will form, as interpreted from experimental results, clearly require elevated temperatures and a lowering of the vapour pressure of sulphur and at times also of arsenic, below those required for the continued existence of gersdorffite and niccolite respectively. Experiments also indicate that such intergrowths may form in the presence of such sulphides as chalcopyrite and pyrrhotite and that diffusion of copper from the former may bring about the development of the chalcopyrite phase of the intergrowth, possibly directly with niccolite, or by replacement of maucherite.

What conditions in nature would best explain a lowering of sulphur (and possibly also arsenic) vapour pressure, and at what stage in the mineralization history did this occur?

Experiments suggest that for the pseudo-eutectic textures to form, temperatures were still relatively high. Progressive, deep fracturing during the mineralization, a feature common in many ore deposits, might well allow escape of sulphur and arsenic and thus affect the stability of gersdorffite and any niccolite.

It has been shown that in places the arsenides, and particularly gersdorffite, have been deposited prior to the common Sudbury sulphides, and it was suggested by Hawley & Hewitt that possibly the development of niccolite-maucherite-chalcopyrite intergrowths occurred before and during the introduction of the latter. If however, all of these minerals were crystallized from a single, sulphide-rich liquid or melt, as seems probable, a decrease in sulphur pressure would be hard to explain. In fact it is clear that chalcopyrite, pyrrhotite, and even pentlandite were deposited around gersdorffite crystals with no effect, or where some fracturing of gersdorffite had occurred the sulphides simply filled these fractures and replaced the gersdorffite in an entirely normal manner.

The association of the pseudo-eutectic intergrowths both with quartz-carbonate veins of the type noted by Lausen and also with pyrrhotite containing fine, secondary cube pyrite and marcasite suggests the intergrowths may in fact have developed at a late stage after deposition of the common sulphides. The apparently late chalcopyrite in some intergrowths may be simply remobilized chalcopyrite from close at hand. Again deep fracturing and faulting of still hot, mineralized zones; introduction of quartz and carbonates; and remobilization and diffusion of constituents already present may have allowed such textures, which so
much resemble late-stage granophyric alterations in metamorphic rocks, to form in the ores. At a still later time, possibly along the same deep fracture zones, development of supergene millerite and violarite, often also associated with cube pyrite in pyrrhotite, took place, but these must not be allowed to confuse the hypogene characteristics of the pseudo-eutectic intergrowths. Further field investigations may aid in establishing more clearly the actual locus and time of formation of these interesting textures of the Sudbury ores.

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