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A SULPHIDE PARAGENESIS WITH PYRRHOTITE AND MARCASITE IN THE SIDERITE-CRYOLITE ORE OF IVIGTUT, SOUTH GREENLAND

BY

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WITH 23 FIGURES AND 1 TABLE IN THE TEXT
AND 5 PLATES

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Abstract

Sulphide nodules with pyrrhotite and marcasite occur enclosed in siderite masses in the siderite-cryolite ore of Ivigtut. From a detailed study of the structure of the nodules and of the textural relations of the minerals a sequence of five phases of mineral formation in the nodules is inferred. Approximate temperatures during the successive phases of mineral formation are deduced from mineralogical data, while variations in CO_2-, S_2- and O_2-fugacities are inferred from the stability relations siderite–iron sulphides at various temperatures and CO_2-pressures.

It is concluded that the pyrrhotite-marcasite nodules and associated sulphides may have crystallized from fluids entrapped in siderite during crystallization of the siderite masses. The entrapped fluids were characterized by high CO_2-pressures and relatively high S_2-pressures and certain amounts of dissolved Pb, Cu, Zn and other metals. Crystallization occurred during cooling from over 500° C to approximately 200° C under conditions of decreasing CO_2-, S_2- and O_2-pressures. The rate and amount of decrease of CO_2-pressures, as compared with the decrease in temperature and S_2-pressures, were significant in causing the stability fields of pyrite and pyrrhotite to encroache on that of siderite, so that iron sulphides could crystallize from the fluids. The development of concentric zones of pyrrhotite, chalcopyrite, sphalerite, pyrite, and galena is attributed to the control by f_{S_2}-gradients around the nodules; the f_{S_2}-isogrades shifted towards the core of the nodules in the course of time.

Marcasite is believed to be a common hypogene mineral which is formed below 300° C in the course of cooling of Fe-sulphide-carbonate parageneses. If cooling is relatively slow, a decrease in CO_2-pressures may cause the replacement of earlier carbonates by marcasite; if cooling is comparatively rapid replacement of pyrrhotite by marcasite, pyrite, and siderite may result.

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INTRODUCTION

General remarks

The main type of cryolite ore from the cryolite deposit at Ivigtut in South Greenland is a very coarse-grained siderite-cryolite rock containing appreciable amounts of sulphides and quartz and minor amounts of fluorite and other minerals.

Notwithstanding its unique character a detailed account of the deposit is still lacking. A brief review of former and current work has been given by PAULY (1960) in a paper on the paragenetic relations in the main cryolite ore from Ivigtut. In the latter ores a network of veinlets and irregular masses of cm-size of sulphides, siderite and quartz occur intergranularly between very coarse-grained cryolite crystals, which are often more than half a metre in size. Often the siderite also forms coarse-grained crystals from 10 to nearly 50 cm across. The bulk of the sulphides consists of galena, chalcopyrite, and sphalerite. Several other sulphides occur in minor amounts. Although sphalerite analyses give an average of about 15 wt per cent of FeS, pyrrhotite is not a common mineral in this sulphide paragenesis; the mineral is usually observed only as microscopic inclusions in sphalerite, chalcopyrite, and galena. However, a couple of small pieces of pyrrhotite from Ivigtut is kept in the collections at the Mineralogical Museum of the University of Copenhagen, while another small piece of pyrrhotite has once been found in a drill core. Marcasite has formerly also been observed only as small inclusions in other sulphides. Thus, pyrrhotite and marcasite are not common minerals in the cryolite-siderite ore.

Nodular sulphide aggregates with pyrrhotite and marcasite in the siderite-cryolite ore

Recently, a porous sulphide aggregate resembling a boxwork of oxidized sulphides (Plate I, fig. 1) has been investigated. The results show that this boxwork consists of a dendritically developed marcasite crystal, which is presumably a hypogene transformation product of pyrrhotite. A subsequent inspection of the quarry and the piles at Ivigtut have yielded a collection of several lumps with macroscopically visible pyrrhotite and marcasite; this collection forms the material for the present study. Coarse-grained marcasite with some pyrite and with or without pyrrhotite generally forms the more or less porous central part of a nodular sulphide aggregate, which invariably occurs enclosed in coarse-grained siderite or siderite aggregates. The largest of these nodules in our collection is about 12 cm long. The marcasite-pyrite cores of the nodules are separated from the enveloping siderite by various thin zones consisting mainly of galena, sphalerite, chalcopyrite, and pyrite, i. e. of the same sulphides which also form the bulk of the intergranular sulphide and sulphide-siderite veinlets in the siderite-cryolite rock.

The special pyrrhotite-marcasite and the main sulphide parageneses in the siderite-cryolite ore

The assemblage of sulphides in the intergranular veinlets referred to above is conveniently designated as the main sulphide paragenesis since it forms an essential part of the siderite-cryolite rock. The nodular sulphide aggregates with pyrrhotite and/or marcasite as important constituents are of less common occurrence and the sulphides in these nodular aggregates can be considered as a special pyrrhotite-marcasite paragenesis.

A close genetic relationship between the two parageneses is suggested by the association of minerals common to both parageneses, but other features suggest that they have crystallized under different environmental conditions. The association of euhedral siderite with the sulphides in the main sulphide paragenesis indicates the deposition of a siderite-sulphide assemblage from a fluid, so rich in dissolved CO_2 that pyrrhotite cannot crystallize directly from the fluid as a stable phase (GARRELS 1960, p. 158). Under these conditions siderite has a large stability region in the PT-field and the bulk of the Fe is crystallized as siderite, leaving only minor amounts of Fe to form Fe-sulphides. On the other hand, the textural relations described in the following indicate that dissolution, recrystallization and replacement of siderite have accompanied the formation of iron-sulphides in the pyrrhotite-marcasite paragenesis.

The paragenetic relations in the main sulphide paragenesis have been described by PAULY (1960); the present paper is only concerned with a description of the pyrrhotite-marcasite paragenesis and a discussion of its conditions of formation.

Acknowledgements

The authors are obliged to Mr. W. LODDER for help in taking X-ray photographs of pyrrhotite, to Miss A. M. VAN ARKEL, Mrs. P. OEN-TAN and Miss KIRSTEN JENSEN for assistance in typing the manuscript, and to Mr. J. J. WIERSMA and Mr. CHR. HALKIER for preparing some of the photographs. Mr. A. MOURITZEN has skillfully made the polished sections.

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I. MACROSCOPIC STRUCTURES

General structure of the pyrrhotite-marcasite nodules

Plate I, fig. 1 illustrates the common appearance of the pyrrhotite-marcasite nodules. The specimens mostly consist of coarse-grained euhedral siderite crystals enveloping a cavernous sulphide nodule of irregular shape and with dimensions varying usually between 3 and 12 cm. For the description the nodules can be considered as build up of a generally cavernous core surrounded by a thin mantle consisting of alternating thin zones of sulphides and recrystallized siderite.

Macroscopic structures in the core of the nodules

The cavernous structure of the core is due to the development of marcasite as one or more coarsely developed skeletal crystals or dendrites building a network of branching sheets with open spaces in between them. The branching sheets are overcrusted with fine-grained, euhedral pyrite; occasionally this infilling with pyrite is almost complete. Sometimes the marcasite occurs intergrown with pyrrhotite and forms branching dendritic sheets in the latter mineral. Under the microscope it appears that often there is only one coarse-grained pyrrhotite crystal, which is intergrown with one coarse-grained, but finely developed marcasite dendrite. Compared with the coarsely developed cavernous marcasite dendrites the dendritic marcasite networks in pyrrhotite are characterized by a more regular pattern of the dendritic sheets, suggesting a control of the orientation of the sheets by crystallographic directions of the pyrrhotite (figs. 1 and 2). In some instances cavernous, finely developed marcasite dendrites showing the same regular pattern as the dendrites in the pyrrhotite are found without being intergrown with the latter mineral. This kind of cavernous dendrites is characterized by the usual absence of conspicuous pyrite overcrustings.

The cavernous cores of the sulphide nodules often contain irregular or veinlike masses of recrystallized siderite. Furthermore, scattered patches of galena are sometimes found in the core of the nodules.

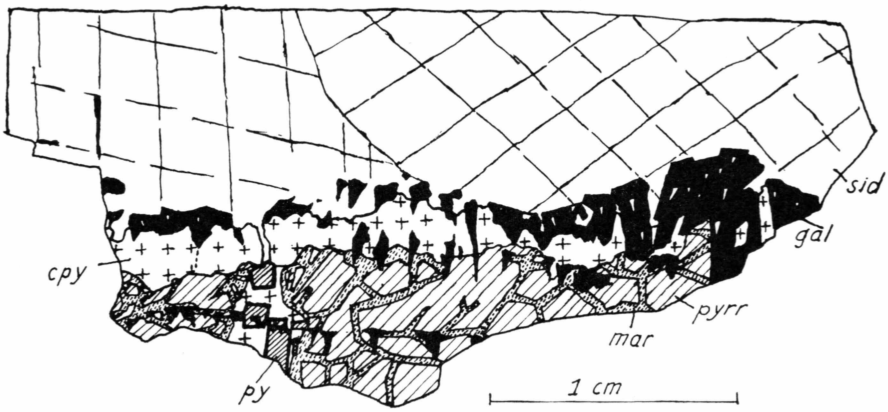

Fig. 1. Polished section 1481; sid–siderite, gal–galena, cpy–chalcopyrite, py–pyrite, pyrr–pyrrhotite, and mar–marcasite. The pyrrhotite–marcasite intergrowth in the lower half of the figure forms part of the core of a pyrrhotite-marcasite nodule in siderite. The dendritically developed marcasite sheets in the pyrrhotite show a regular, more or less hexagonal pattern, suggesting a control of the orientation of the sheets by crystallographic directions of the pyrrhotite. In the case shown here the mantle of the nodule is very thin and it consists essentially of an outer galena band and a chalcopyrite zone. Besides this outer galena band a partly developed intermediate band and an inner band of galena can be recognized. The latter two bands of galena are traceable across the boundaries of the chalcopyrite, pyrrhotite and pyrite areas; note the relict inclusions of galena in the pyrite at the place where larger pyrite crystals have grown across the thin inner band of galena.

Polished surfaces reveal a sharp boundary between the core and the mantle of the nodules; the boundary plane is usually smooth with only minor irregularities in the form of convexly outward bulging parts.

Macroscopic structures in the mantle of the nodules

The width of the mantle of sulphides and recrystallized siderite varies between a few mm and about 2 cm. Polished surfaces show radial and banded structures in the mantle.

Usually the radial structures are macroscopically not clearly visible. Figures 3 and 4 show thin, discontinuous veinlets of galena and sphalerite with a radial arrangement with respect to the core of the nodules. The siderite have also recrystallized in aggregates of radiating lamellae.

The banded structures are more obvious and they permit the division of the mantle in an inner and an outer zone. The inner zone, bordering directly to the core of the nodule, is formed by a conspicuously developed, continuous band of chalcopyrite, about 1–10 mm in width. This chalcopyrite band is always present; it often contains inclusions of minerals occurring in the outer zone of the mantle.

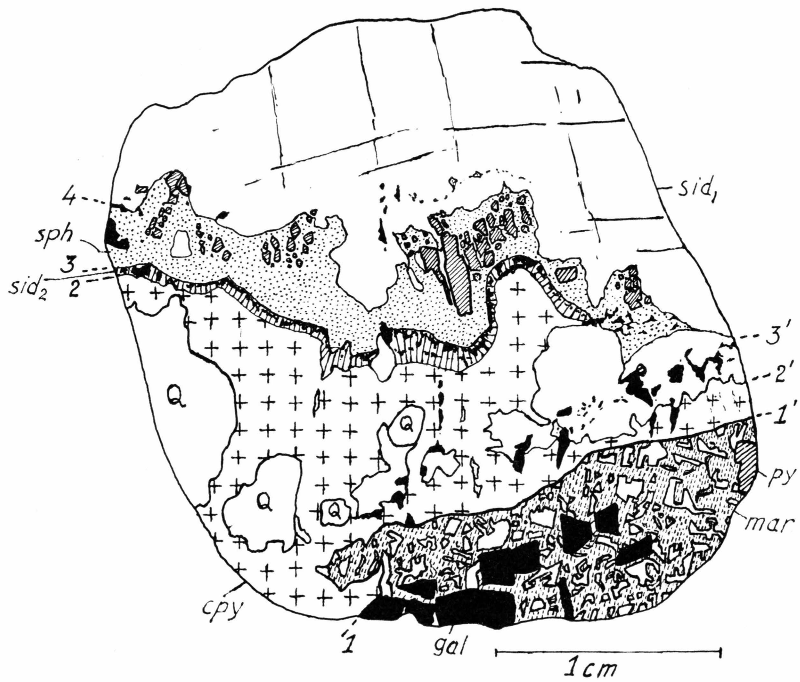

Fig. 2. Polished section 821; sid_1 – coarse-grained siderite of the envelope of the nodules, sid_2 – fine-grained recrystallized siderite of the mantle of the nodules, py-pyrite, gal-galena, sph-sphalerite, cpy-chalcopyrite, mar-marcasite, and Q-gangue. The section shows a part of a nodule with several zones as described in the text of the paper. From bottom to top of the figure the following zones can be recognized: (a) A part of the core of the nodule with its outer boundary 1–1'; the core is filled with a finely developed, cavernous marcasite dendrite showing a rectangular pattern of the dendritic sheets; inclusions of euhedral galena and pyrite in the core of the nodule have apparently crystallized as cavity fillings; (b) The chalcopyrite zone with its outer boundary 2–2'; the inclusions of siderite and galena in this zone are apparently replacement relicts; (c) A thin zone of fine-grained recrystallized, columnar siderite between 2 and 3; at the external side of this zone a very thin band of galena borders directly to the sphalerite zone, note that this galena band is concordant to the boundary of the sphalerite zone; for details in this zone see text-figures 11 and 12, plate II fig. 2 and plate III figs. 1 and 2; (d) The sphalerite zone between 3–3' and 4; this zone contains inclusions of siderite and pyrite; note the scalloped inner boundary of the sphalerite zone with convex bulgings towards the core.

The outer zone of the mantle is between 0 and in 10 mm width and it shows a finely developed banding of alternating, more or less discontinuous bands or streaks consisting predominantly of galena, pyrite, sphalerite and recrystallized siderite. Up to four thin, discontinuous, parallel galena-rich bands with a regular spacing between them have been observed (figs. 1 and 5); this banding resembles rhythmic or diffusion banding as described by Bastin (1950, pp. 47–51).

Generally an outermost galena band marks the boundary between mantle and enveloping coarse-grained siderite (figs. 1, 3, and 5). Irregular aggregates and rows of pyrite crystals also tend to be concentrated along this border zone; occasionally banded and radial structures of pyrite aggregates have been observed (figs. 2, 3, and 5). Sphalerite occurs in discontinuous bands or aggregates which mostly adjoin the galena- and pyrite-rich bands. The space between the sulphide-rich bands and streaks is occupied by recrystallized siderite.

Outside the mantle only some galena is found as very thin veinlets along cleavage directions in the enveloping coarse-grained siderite. A diagrammatic sketch of the banded and other structures in the nodules is given in fig. 19 c.

Age relations inferred from the macroscopic banding

The outer boundary of the chalcopyrite or inner zone of the mantle often show outward bulgings suggesting an outward growth of the zone. This boundary is often concordant to the banding in the outer zone, but in some instances it is clearly discordant and the chalcopyrite zone is intersecting the galena and pyrite bands of the outer zone (figs. 3, 4, and 5). In the latter case the structures in the outer zone can locally still be traced in the chalcopyrite areas as relict bands, radial veinlets or aggregates of galena. These relations indicate without doubt that the chalcopyrite or inner zone has developed later than the galena and pyrite in the outer zone.

In the outer zone pyrite aggregates sometimes enclose relict bands of galena indicating that the pyrite has crystallized later than the galena. In some samples with rhythmic bands of galena it can be shown that all galena bands are older than the pyrite and chalcopyrite (fig. 5). However, microscopic observations (chapter II) indicate that when the banding is not rhythmic galena bands of different age can often be recognized.

The inner boundary of certain sphalerite bands or streaks are characterized by corewards directed bulgings suggesting that the bands

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Figs. 3 and 4. Polished section 1483. The section shows a part of the mantle of a nodule with several zones and radial structures as described in the text of the paper. Note that the chalcopyrite zone and the zones of fine-grained columnar siderite and sphalerite are mutually concordant; they apparently represent younger zones, which cut discordantly across a set of older parallel zones of pyrite, galena, and coarse-grained recrystallized siderite. For further particulars see the text of the paper, text-figures 7, 8, 9, 10, 13, 14, 15 and 18, plate II fig. 1, and plate IV figs. 1 and 2.

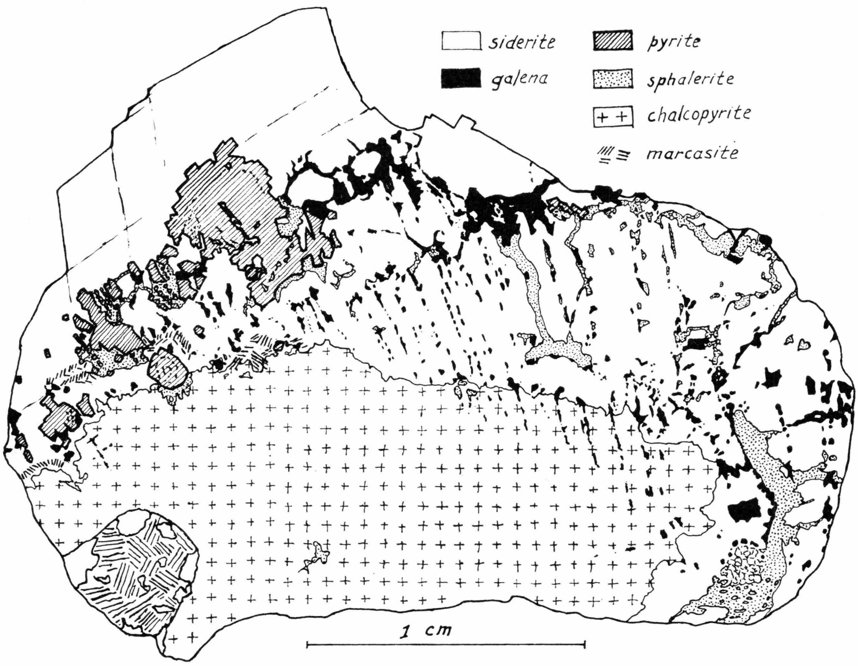
siderite
pyrite
galena
sphalerite
chalcopyrite
marcasite
1 cm

Fig. 3.

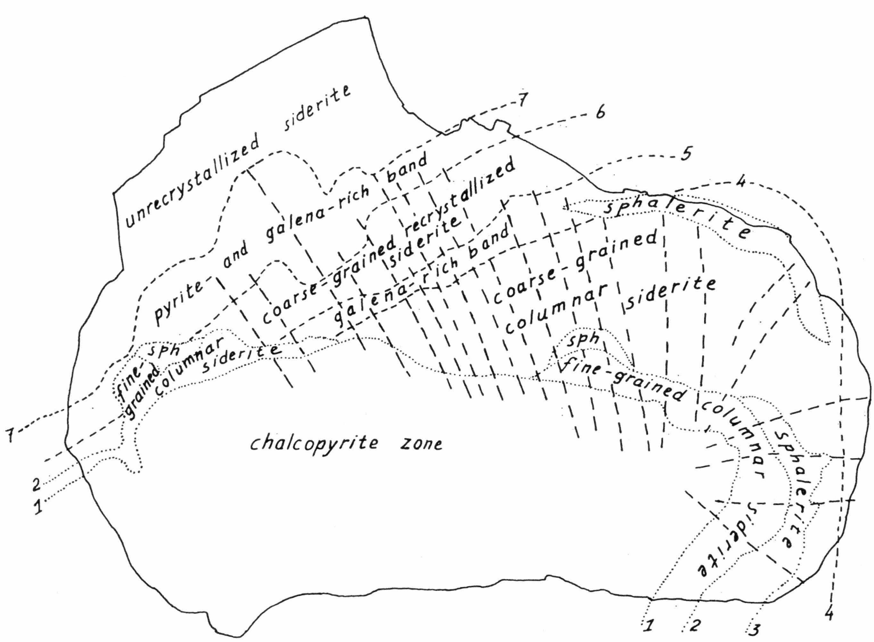
unrecrystallized siderite
pyrite- and galena-rich band
coarse-grained recrystallized siderite
galena-rich band
coarse-grained columnar siderite
sphalerite
sph
fine-grained columnar siderite
fine-grained columnar siderite
sph
chalcopyrite zone
columnar siderite
sphalerite
1
2
3
4
5
6
7

Fig. 4.

have thickened by growing in a direction towards the core of the nodules (figs. 2 and 6). This inner sphalerite boundary is always parallel to the outer boundary of the chalcopyrite zone, which suggests a contemporaneity of the sphalerite streaks and bands with the chalcopyrite zone.

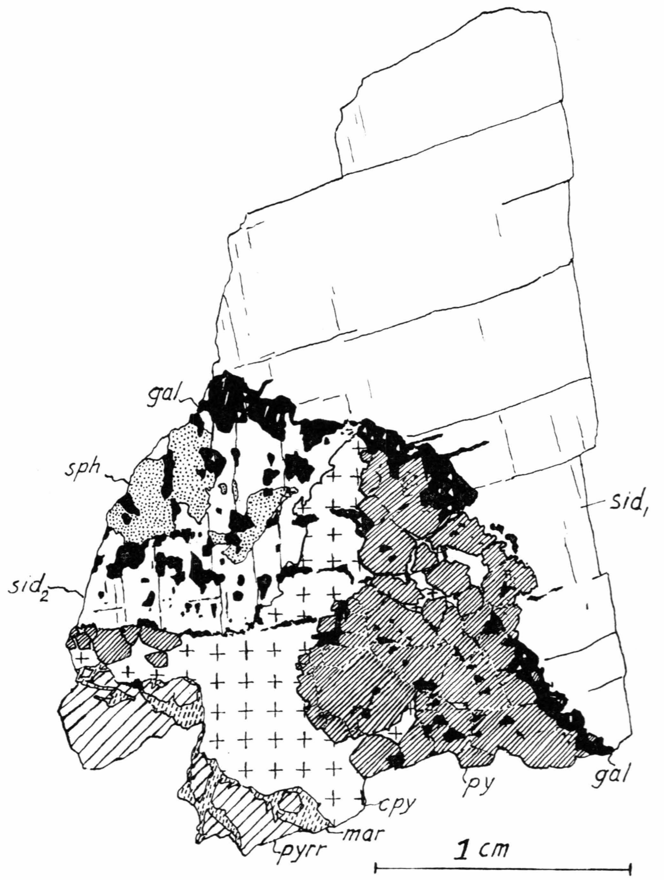

Fig. 5. Polished section 1484; sid_1 – coarse-grained siderite of the envelope of the nodule, sid_2 – recrystallized coarse-columnar siderite, gal – galena, py – pyrite, cpy – chalcopyrite, sph – sphalerite, pyrr – pyrrhotite, and mar – marcasite. The section shows rhythmic bands of galena in the outer zone of the mantle of a pyrrhotite-marcasite nodule. The galena bands are traceable as relicts in later pyrite and chalcopyrite. The chalcopyrite zone cuts discordantly across earlier bands of galena.

The coarse-grained siderite crystals surrounding the sulphide nodules are characterized by euhedral boundaries against each other, but not against the sulphide nodules. On polished surfaces the boundary line between the mantle of the nodules and the enveloping siderite appears as a smooth line transecting mutual boundaries of siderite crystals; the latter clearly appear older than the nodules.

Microscopic study shows that the different bands often interpenetrate and the resulting replacement textures, described in the next chapter, allow the establishment of more precise age relations.

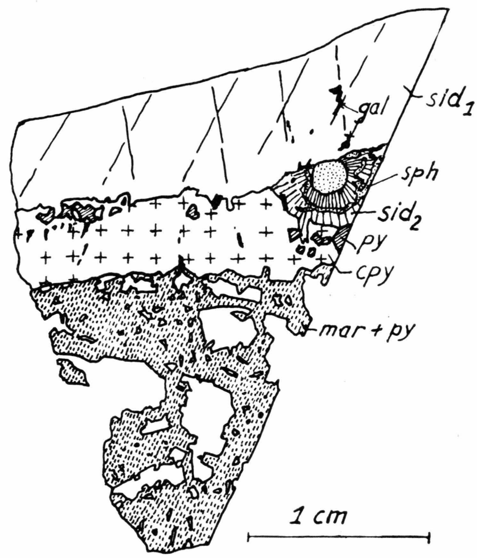

Fig. 6. Polished section 1257; sid_1 – coarse-grained siderite of the envelope of the nodule, sid_2 – fine-grained recrystallized, columnar siderite, sph – sphalerite, py – pyrite, cpy – chalcopyrite, and mar – marcasite. Note especially the radial aggregates of columnar siderite and the very thin concentric sphalerite bands around the rounded sphalerite aggregate in the right hand side of the picture.

II. MICROSCOPIC STRUCTURES

The siderite envelope of the pyrrhotite-marcasite nodules

The pyrrhotite-marcasite nodules occur enclosed in aggregates of coarse-grained siderite crystals with lengths of about 10 cm or more. Within about 2 cm from the outer boundaries of the nodules galena is often found as very thin veinlets along cleavage planes and crystal boundaries of the coarse-grained, unrecrystallized siderite. Euhedral pyrite crystals or aggregates are sometimes also found enclosed in this unrecrystallized siderite, but always within about 5 mm from the outer boundary of the nodule. Sphalerite and chalcopyrite do not occur outside the mantle of recrystallized siderite and sulphides.

Assuming that the sulphides have diffused from the core of the nodules outwardly, it follows that generally galena has penetrated farthest from the core into the siderite, pyrite has penetrated less far into the latter mineral, sphalerite does not come farther than the outer boundary of the mantle of the module, while chalcopyrite remains in the inner zone of the mantle in direct contact with the core of the nodules. Therefore, a certain zonal arrangement of minerals around the pyrrhotite-marcasite cores of the nodules is apparent.

The mantle of the sulphide nodules

Siderite

In the mantle of the nodules siderite is recrystallized in aggregates of anhedral, inequidimensional grains, which disposition often gives rise to banded and columnar textures. Sometimes the siderite grains show a random three-dimensional orientation, more often they have their longest dimension subparallel to the banding in the mantle, but most frequently the grains are arranged with their longest dimension approximately perpendicular to the banding. The latter disposition of the grains gives rise to siderite bands with columnar and radiating textures.

The lengths of the radiating siderite grains vary between less than 0.1 mm to about 2 mm; the thickness of the columnar siderite bands vary accordingly. Several bands of columnar siderite, each characterized by of specific grain size and orientation of the columnar aggregates, can often be recognized. These bands sometimes adjoin each other with sharp junctions, but usually they appear separated by intervening finer-grained bands of more granular siderite with varying proportions of galena or sphalerite. When the latter minerals predominates in amount over the siderite, these intervening bands become macroscopically visible as galena- or sphalerite-rich bands.

A zonal variation in grain size of the recrystallized siderite is often noted. The columnar siderite grains bordering directly to the chalcopyrite or inner zone of the mantle have an average length of about 0.4 mm; in an outward direction the grain size in the siderite bands first decreases rather gradually and then often increases rapidly until in the outermost parts of the mantle the siderite grains have average lengths of about 2 mm. Sphalerite is usually found as an important band in and along the intermediate zone of finest-grained siderite, whereas galena is often found associated with bands of coarser- as well as finer-grained siderite. However, sometimes a rather irregular distribution of coarser- and finer-grained siderite aggregates have also been noted; here too, the sphalerite tend to occur associated with the more fine-grained siderite aggregates.

Adjoining grains of the relatively coarser-grained siderite in the outermost part of the mantle often differ only slightly in their optical orientations, indicating only an incipient degree of recrystallization. In the latter case the columnar textures are often less well developed. In general, the recrystallization of siderite in distinct columnar bands is limited to a narrow zone (1–4 mm) of finer-grained siderite bordering directly to the inner or chalcopyrite zone of the mantle.

If grain size and difference in optical orientation of adjoining grains are taken as measures of the degree of recrystallization of the siderite it appears that galena occurs in zones of slightly as well as strongly recrystallized siderite, whereas sphalerite occurs mostly in zones of strongly recrystallized siderite. As will appear from the following descriptions the sphalerite is later than the galena. The existence of more than one phase of siderite recrystallization may already be suggested here.

In the following descriptions zones of fine-grained siderite, generally with columnar structures and occurring in the inner part of the outer zone of the mantle, are referred to as zones of strongly recrystallized siderite; zones of coarser-grained siderite in the mantle are referred to as zones of slightly recrystallized siderite. A complete development of a zone of strongly recrystallized siderite surrounded by a zone of slightly recrystallized siderite is not always observed.

Galena

The galena bands and radiating veinlets do not form continuous bands and veinlets of galena, but they are formed by different proportions of galena and recrystallized siderite. Thin streaks consisting entirely of galena are sometimes observed, but they always grade laterally into bands of galena and siderite. The radiating veinlets consist of discontinuous, veinlike stretches of galena occurring aligned along certain straight directions (figs. 7, 8 and 9). The veinlets are less than 0.1 mm thick.

Under the microscope the radiating galena veinlets are seen crossing several grains of recrystallized siderite without showing obvious relations to cleavage directions in the siderite. In this respect the galena veinlets in the mantle differ from the galena veinlets along cleavage directions of the siderite in the envelope of the nodules.

Apparently the galena bands and radiating veinlets could develop unrelated to the siderite crystal structures only within the mantle of the nodules where the recrystallization of the siderite have also resulted in banded and radial structures, and where cleavage directions of the siderite, owing to the small grain size, do not continue for appreciable distances. This inference indicates that the galena bands and veinlets cannot have formed earlier than the first recrystallization of the siderite in the mantle.

The relationships between galena and recrystallized siderite differ depending on whether the galena occurs in zones of slightly or strongly recrystallized siderite. Therefore, the two cases will be described separately.

a) Galena in zones of slightly recrystallized siderite

1) Rhythmic bands of galena characterized by regular spacings between the parallel bands are usually associated with relatively coarse-grained, inequigranular, slightly recrystallized siderite (fig. 5). The siderite grains are sometimes several mm in size and the optical orientations of the grains appear to differ only slightly from that of the adjoining large crystal of unrecrystallized siderite that belongs to the envelope of the nodules.

The galena bands are formed by rows of small galena patches, each consisting of one or two anhedral galena crystals. A preferred crystallographic orientation of the galena crystals is apparent from the approximately parallel orientation of the triangular cleavage pits in the galena of all the patches. The outermost of the rhythmic bands of galena is usually situated along the border between recrystallized and unrecrystallized siderite. The galena in this band sometimes forms crystals of 2 mm and more; in the inner bands the galena tends to be finer-grained.

In relatively coarse-grained fragments of recrystallized siderite the galena patches often figure as inclusions bounded by cleavage directions in the siderite, but in somewhat finer-grained siderite the galena patches are clearly interstitial to the siderite grains.

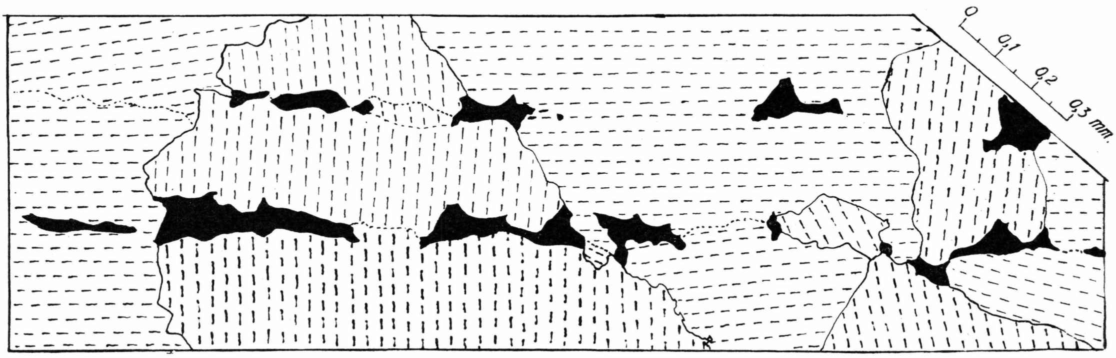

Fig. 7. Galena veinlets in the coarse-grained recrystallized siderite zone of polished section 1483 (see text-figure 4). The discontinuous veinlets consist of short stretches of galena (black), which abut against grain boundaries of the recrystallized siderite. The siderite is shown with different directions of striation, which indicate schematically different extinction directions of the grains. Some adjoining grains of siderite (with boundaries indicated by a dotted line) differ only very slightly in their optical orientations. The short stretches of galena veinlets are characterized by scalloped contacts showing concave embayments with sharp protuberances in between two embayments.

The latter observations suggest that the galena is later than the recrystallization of the siderite. However, these observations are specific only for samples showing an incipient degree of recrystallization of the siderite; therefore, this inference should not be generalized.

As described earlier the rhythmic bands of galena are older than the pyrite and chalcopyrite, which enclose relicts of galena bands. The rhythmic pattern and the tendency to a preferred orientation of the galena crystals suggest that all bands have formed about contemporaneously by a process of rhythmic deposition from fluids diffusing outwardly from the core of the nodules (Bastin 1950, pp. 47–51).

2) Radiating veinlets of galena mostly occur in comparatively broad zones of slightly recrystallized siderite with columnar textures (figs. 3, 4, 7, 8 and 9). The elongated siderite grains are mostly between 1 and 3 mm long.

Relatively coarse, anhedral grains of siderite are sometimes traversed by two or more parallel galena veinlets; the siderite grain boundaries and crystallographic directions show no relation to the direction of the veinlets. However, locally aggregates of finer grained siderite show siderite grains bounded by stretches of galena veinlets or by rectilinear grain boundaries parallel to the general direction of the radiating veinlets. The siderite grains on either side of a rectilinear boundary or a galena veinlet often differ only slightly in optical orientations. The delimitation of the grains by rectilinear boundaries gives rise to a kind of columnar textures, which by their regularity differ from the siderite columnar textures usually observed (figs. 8 and 9).

The observations just described suggest that in siderite aggregates with galena veinlets and rectilinear grain boundaries the recrystallized siderite have adapted its forms to the pattern of radiating galena veinlets. Therefore, since the galena veinlets are not earlier than the recrystallization of the siderite, it must be concluded that recrystallization of siderite has outlasted the formation of the galena veinlets. Presumably, the siderite first recrystallized in coarser, anhedral grains, which were then traversed by galena veinlets; after this the siderite continued to recrystallize in finer grains with forms adapted to the pattern of veinlets.

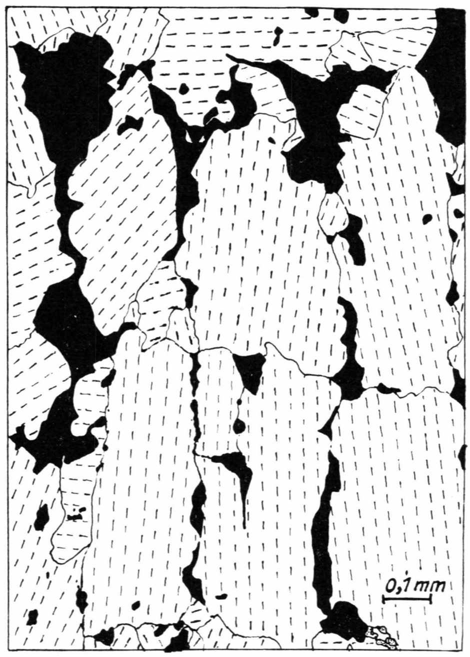

Fig. 8. Galena veinlets (black) in the galena-rich band of polished section 1483 (see text-figure 4) The different extinction directions of the siderite are schematically indicated in the drawing by different directions of striation. The recrystallized siderite grains show rectilinear boundaries controlled by the presence of the galena veinlets. Note the concave embayments and sharp protuberances characterizing the boundaries of the galena areas in the figure. At places (top of the figure) the galena veinlets spread out laterally to form a thin galena band.

As stated before, the galena veinlets consist of short, veinlike stretches of galena aligned along the direction of the veinlet, which crosses several grains of recrystallized siderite. Although the siderite grain boundaries and the direction of the veinlets intersect, detailed observations show that the short veinlike stretches of galena rarely, if ever, traverse undisturbedly across siderite grain boundaries. The veinlike galena stretches in a siderite grain occasionally protrude a very short distance in the adjoining siderite grain, but a far more common picture is provided by veinlike galena stretches abutting abruptly against siderite grain boundaries. After this interruption at the siderite grain boundaries the galena veinlet often continues in the same direction in the next grain of siderite (figs. 7 and 8).

The observation that the galena veinlets maintain a constant direction across several siderite grains, but appear intersected and divided into discontinuous stretches by the siderite grain boundaries is consistent with the earlier inference that the

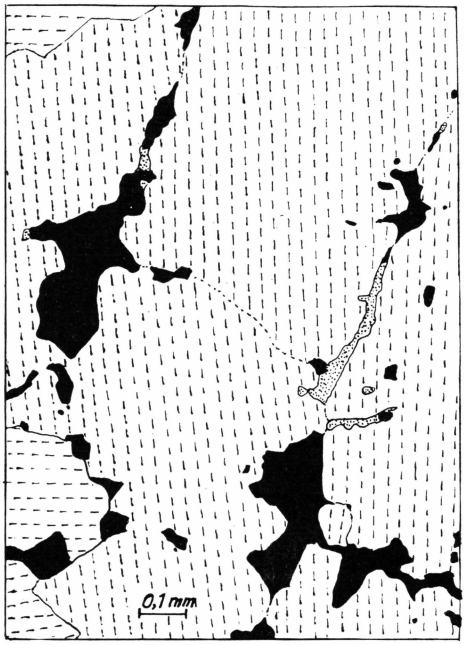

Fig. 9. Galena veinlets in the coarse-grained recrystallized siderite of polished section 1483 (see text-figure 4). The figure shows essentially the same features as text-figure 8. Some sphalerite has developed along the same directions as the galena veinlets.

veinlets are later than the beginning of recrystallization of siderite, but that the latter process has outlasted the formation of the veinlets, or have recurred at a later period.

The grains of recrystallized siderite adjoining the galena veinlets often tend to develop rounded forms with convex bulgings directed towards the galena. The irregular thickness and forms of the galena veinlets appear adapted to the form of the adjacent siderite grains; where the siderite bulges towards the galena, the veinlet is reduced in thickness or even eliminated. Thus, the galena veinlets are characterized by scalloped contacts showing concave embayments with sharp protuberances in between two embayments (figs. 7, 8 and 9).

The scalloped siderite-galena contacts indicate that the siderite grains are later than the galena (HARVEY 1931). This conclusion is consistent with the inference that recrystallization of siderite outlasted the formation of the galena veinlets.

Where the radiating galena veinlets reach the outer boundary of the mantle they spread out laterally into a fine interstitial network of thin galena veinlets in recrystallized siderite; locally the galena also penetrates along cleavage directions into the surrounding large crystals of unrecrystallized siderite (figs. 3 and 5). Other thin bands of interstitial galena occur in streaks of finer-grained siderite, which traverse aggregates of coarser-grained siderite; this interstitial galena also appears connected to the galena in the radial veinlets (figs. 8 and 9).

The interstitial galena veinlets are obviously later than the siderite grains between which they occur. However, they appear connected to radiating veinlets, which relationships to adjoining siderite grains indicate that the siderite grains are later than the galena (see above). These ambiguous and seemingly conflicting textural evidences are specific for zones of slightly recrystallized siderite. In fact, such reverse relationships between galena and recrystallized siderite are to be expected if the galena crystallized after the siderite has begun to recrystallize and as the formation of the galena is outlasted by the recrystallization of the siderite.

Sometimes short veinlike stretches of galena occur at very regular intervals along the direction of the veinlet, while in a direction across the veinlets the discontinuous stretches of galena also appear to show a regular arrangement in parallel bands.

The latter regular disposition of the veinlike galena stretches suggests that the galena in the veinlets may also have crystallized by a process of rhythmic deposition from fluids diffusing outwardly from the core of the nodules.

b) Galena and sphalerite in zones of strongly recrystallized siderite

A narrow zone of strongly recrystallized siderite usually occurs between the inner or chalcopyrite zone of the mantle and a prominent band or streak of sphalerite in the outer zone of the mantle. Occasionally, another rudimental zone of strongly recrystallized siderite occurs at the external side of prominent sphalerite bands. Where the sphalerite does not occur as a prominent band the strongly recrystallized zones of siderite are less conspicuous or even absent. Where a sphalerite band wedges out the adjoining zones of strongly recrystallized siderite also disappear (fig. 10 and Plate II, fig. 1).

The strongly recrystallized siderite has commonly developed distinct columnar structures and sometimes several bands of columnar siderite are found. The siderite columns rarely exceed 0.5 mm in length; they are longest and broadest in the parts adjoining the chalcopyrite zone and decrease in size towards the sphalerite band.

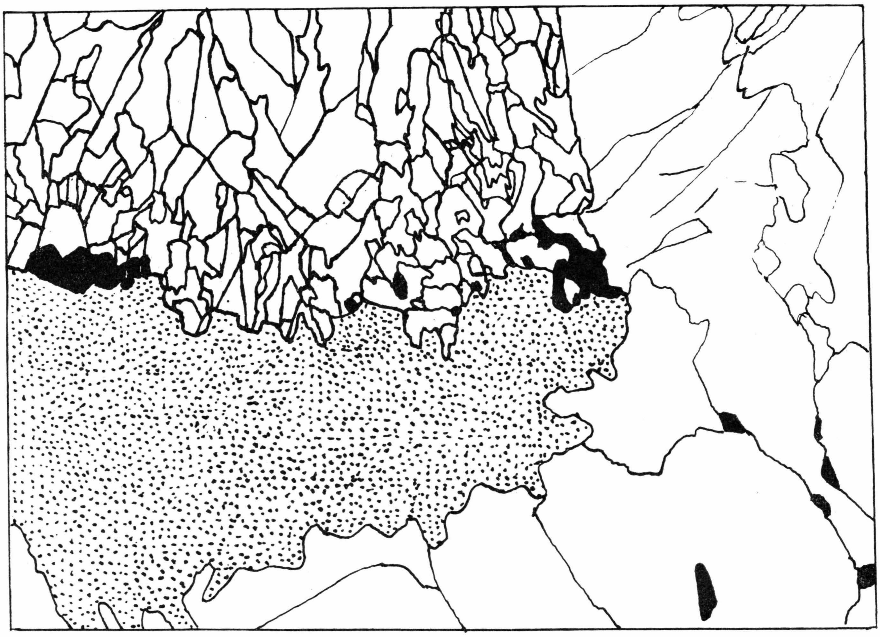

Fig. 10. Key to the photograph plate II fig. 1. The dotted area is part of a sphalerite streak in polished section 1483 (text-figure 4). On the photograph plate II fig. 1 the sphalerite area appears dark and numerous inclusions of siderite and chalcopyrite can be seen in the sphalerite. Grains of galena (black) occur along the inner (upper in the figure) boundary of the sphalerite streak. Fine-grained recrystallized, columnar siderite aggregates (upper left hand side of picture) occur along the sphalerite streak. Where the latter wedges out the fine-grained, columnar siderite also disappears. The coarser grained siderite at the upper right hand side of the picture shows incipient recrystallization into finer grained siderite columns, which tend to show a kind of radial arrangement around the end of the sphalerite streak. The rest of the picture is occupied by coarser grained, columnar siderite.

The sphalerite bands or streaks, sometimes up to 4 mm thick, contain numerous rounded inclusions of siderite. The regular decrease in grain size of the siderite in a direction from the chalcopyrite zone towards the sphalerite band is continued in the latter by a decrease, but at a much more rapid rate, in the size of the siderite inclusions (fig. 11). The siderite inclusions along the inner border of the sphalerite band are mostly about half the size of the siderite grains outside the sphalerite and often the inclusions still show the same extinction directions as the nearest siderite grain outside the sphalerite. Locally, streaks of columnar siderite occur enclosed in the sphalerite areas (fig. 11). Towards the external border of the sphalerite band the siderite inclusions decrease rapidly in size, while the streaks of columnar siderite disintegrate into rows of rounded inclusions in sphalerite. Thus, in this stage the arrangement of the siderite inclusions still reflects the derivation of the in-

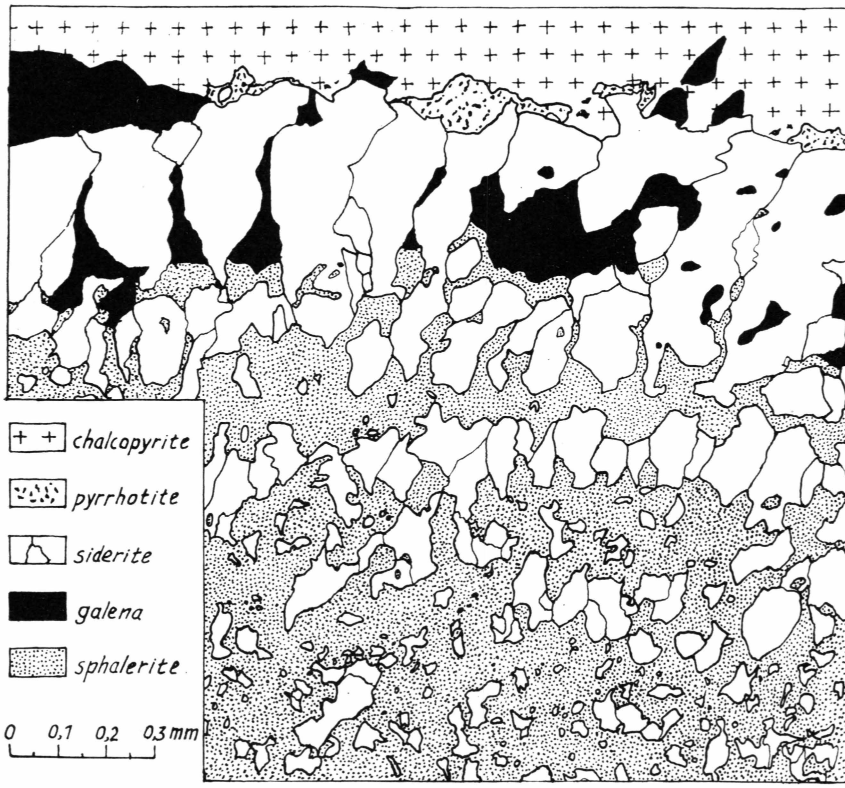

Fig. 11. Detail of the zone of fine-grained recrystallized, columnar siderite in polished section 821 (see text-figure 2). Note the regular decrease in grain size of the siderite in a direction from the chalcopyrite zone towards the sphalerite band. The arrangement of siderite inclusions in the sphalerite still reflects their derivation from columnar siderite bands. The sphalerite areas have apparently grown inwardly in the direction of the chalcopyrite zone. Galena appears concentrated in a thin zone in front of the sphalerite band. A characteristic texture is formed by the tapering sphalerite cogs fitting into notches between adjacent grains of columnar siderite; note especially the typical cogs with a sphalerite base and a galena tip and the scalloped sphalerite-galena boundaries. Pyrrhotite is preferentially developed along chalcopyrite-siderite boundaries. The sphalerite contains numerous small inclusions of chalcopyrite, pyrrhotite, and marcasite, which are not indicated in the figure.

clusions from columnar siderite bands. About in the central part of the sphalerite band the siderite inclusions have been reduced to very small rounded blebs, less than 0.01 mm in diameter. Eventually, the siderite inclusions disappear leaving a siderite free zone near the outer margin of the sphalerite band. However, along this outer margin some siderite inclusions, apparently derived from the rudimental external zone of strongly recrystallized siderite, are again found.

The textural relations described here indicate a replacement of part of the strongly recrystallized columnar siderite by sphalerite. In agreement with earlier conclusions (p. 12) the asymmetrical distribution of siderite inclusions in the sphalerite band suggests that the broadening of the sphalerite band at the expense of the siderite has mainly taken place in an inward direction towards the inner zones of the nodule.

The close spatial relationship of sphalerite and strongly recrystallized siderite suggest that the crystallization of sphalerite is related to a renewed recrystallization of the siderite.

Galena occurs in the zones of strongly recrystallized siderite along the borders with the sphalerite bands. The galena grains, rarely

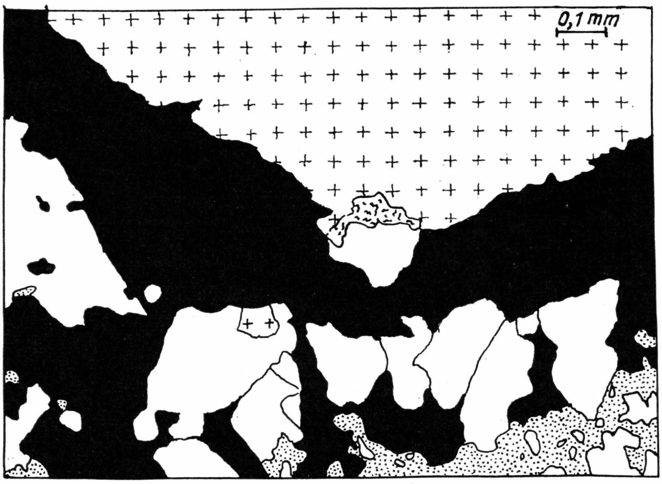

Fig. 12. Detail of the zone of fine-grained, columnar siderite in polished section 821 (text-figure 2). For explanation see fig. 11. Note especially the preferential development of pyrrhotite along chalcopyrite-siderite boundaries.

larger than 0.4 mm, are interstitial to the columnar siderite and they occur arranged in one or two bands. The interstitial galena shows thin, veinlike forms; also characteristic are triangular and Y-forms (figs. 11 and 12; Plate II, fig. 2; Plate III, fig. 1 and 2). The amount of galena in the galena bands increases or decreases in a lateral direction. With the increase of galena in a band the interstitial galena veinlets thicken and tend to develop outward bulgings at the expense of the adjoining siderite grains. Where the galena predominates over siderite the galena forms equant grains, about 0.3 mm in diameter, which partly or completely enclose rounded grains of siderite. The latter galena-rich bands sometimes pass laterally into thin bands consisting entirely of galena (Plate II, fig. 2; Plate III, fig. 2).

According to the above observations the galena bands are later and have replaced the strongly recrystallized siderite. Thus, the galena-siderite relationships in zones of slightly and strongly recrystallized siderite are reversed: in the slightly recrystallized zones the recrystallization of siderite has outlasted the formation of galena, whereas in the strongly recrystallized zones recrystallization of siderite is earlier than the galena. It follows as a logical conclusion that the galena in the strongly recrystallized zones is later than the galena in the slightly recrystallized zones. There has been either an introduction of new galena or a remobilization and recrystallization of older galena.

On polished surfaces the trace of the sphalerite boundary appears macroscopically as a smooth line characterized by convex bulgings directed towards the core of the nodule (fig. 2). However, in detail this boundary line is irregular and sometimes characterized by a typical texture with tapering sphalerite cogs fitting into notches between adjacent grains of columnar siderite (fig. 11; Plate III, fig. 1). The ends of the siderite columns between the interstitial sphalerite cogs usually appear rounded. Where a galena band intervenes between the sphalerite and columnar siderite the galena often truncates the sphalerite cogs at their base, so that the notches between the columnar siderite grains are filled with interstitial galena instead of with sphalerite. Sometimes the sphalerite cogs are truncated at their tips, so that the cogs consist of a sphalerite base with a galena tip (figs. 11 and 12; Plate II, fig. 2; Plate III, figs. 1 and 2). In the latter case the stretches of the sphalerite-galena boundary line in the cogs can be connected across contiguous siderite grains to form a regular curve. The sphalerite-galena boundary plane, of which the latter curve is the trace, is apparently a curved plane perforated by siderite columns protruding into the sphalerite. On a still smaller scale the sphalerite-galena boundaries are characterized by scalloped outlines with convex bulgings of the sphalerite and corresponding concave embayments in the galena (fig. 11; Plate II, fig. 2; Plate III, figs 1 and 2). The sphalerite areas near these boundaries are usually full of siderite inclusions, but strikingly devoid of galena inclusions.

The convex bulgings of the sphalerite boundaries, directed towards the interior of the nodule, suggest an inward growth of these bands. The scalloped sphalerite-galena boundaries points to an expansion of the sphalerite areas at the expense of galena. However, as it has been shown that sphalerite has replaced siderite and as sphalerite adjoining galena is full of siderite inclusions but free of galena inclusions, metasomatic replacement of galena by sphalerite is not likely to have occurred. The concentration of galena just in front of the sphalerite boundaries is a remarkable feature, which suggests that during the formation of the sphalerite band and the renewed recrystallization of siderite in and along these bands, the older galena in the space now occupied by the sphalerite band has been dissolved, remobilized and redeposited in front of the inwardly expanding sphalerite band. This interpretation seems consistent with all other observations and inferences described in this paper; it conveniently explains: (1) the occurrence of galena along sphalerite-siderite boundaries in zones of strongly recrystallized siderite, (2) the absence of galena inclusions in the sphalerite although the scalloped boundaries indicate that the sphalerite areas have expanded in the direction of the galena, (3) the typical cogs with sphalerite base and galena tip protuding into the zone of strongly recrystallized siderite in a way which suggests that the interstices between the columnar siderite were penetrated first by galena and then by sphalerite, (4) the reversed galena-recrystallized siderite relationships in zones of slightly and strongly recrystallized siderite respectively, (5) the fact that in the zones of strongly recrystallized siderite the greatest concentrations of galena occur where the sphalerite bands are broadest (see below).

Thin streaks of galena sometimes occur along sphalerite-siderite boundaries at the external side of streaks of columnar siderite enclosed in the sphalerite bands; the galena is typically absent at the internal or coreward side of the enclosed siderite streaks. Two thin galena streaks sometimes merge laterally into a single galena band, whereby the thickness of the band is about equal to the thickness of the two streaks together.

The inner boundary of the sphalerite bands are not exactly parallel to the outer boundaries of the chalcopyrite zone. Where the sphalerite areas bulge inward towards the chalcopyrite zone the intervening zone of strongly recrystallized columnar siderite is very reduced in thickness. In these relatively narrow zones of strongly recrystallized siderite the amount of galena is proportionally increased at the expense of siderite and in extreme cases the galena band along the sphalerite-siderite boundaries is pressed against the chalcopyrite zone; the siderite has disappeared completely, leaving a band consisting entirely of galena between the sphalerite band and chalcopyrite zone (Plate III, fig. 2).

The observation that more galena occurs where the sphalerite band is broadest supports the view that remobilized galena was deposited in front of the inwardly expanding sphalerite band. The amounts of both sphalerite and galena vary inversely to the width of the zone of strongly recrystallized siderite; this suggests that siderite has been concurrently replaced by sphalerite and galena, since such quantitative relations would not be expected if there has been successive steps of replacement siderite-galena-sphalerite or siderite-sphalerite-galena.

At some places the chalcopyrite zone is in contact with a band of contiguous grains of galena and siderite. The boundary of the chalcopyrite zone appears as a smooth line; where in contact with galena this boundary often show scalloped outlines with convex bulgings of chalcopyrite fitting into concave embayments in the galena, but the reverse relation has sometimes also been observed; where in contact with siderite a narrow rim of pyrrhotite has often developed along the chalcopyrite-siderite boundaries (figs. 11 and 12; Plate II, fig. 2; Plate III, fig. 1).

When the pyrrhotite formed along the chalcopyrite-siderite boundaries the galena is presumably already *in situ*, for otherwise a continuous pyrrhotite rim would have been formed instead of the present one which appears interrupted by stretches of galena-chalcopyrite contacts without pyrrhotite. The scalloped galena-chalcopyrite boundaries equally points to an earlier presence of the galena relative to chalcopyrite.

Again, seemingly contradicting evidence are noted: the galena seems earlier than the chalcopyrite but the inward displacement of the galena zone in front of the sphalerite bands seems halted by the presence of a chalcopyrite zone. However, an approximately contemporaneous deposition of sphalerite, galena and chalcopyrite, largely overlapping in time but not in space, can be conceived; the outward growth of the chalcopyrite zone has taken place contemporaneously with the inward displacement of the galena band in front of the inwardly expanding sphalerite band. When the galena and chalcopyrite zones have met and the dissolution of all siderite interspersed between the sulphide bands is completed, an apparently stable association sphalerite-galena-chalcopyrite is formed.

Pyrite

The pyrite mostly occurs in aggregates of euhedral to subhedral crystals, smaller than 0.5 mm to about 2 mm in cross-section, usually in the outer portions of the mantle. Streaky pyrite aggregates, sometimes characterized by serrate textures, are often subparallel to galena bands or radial veinlets. Pyrite aggregates in zones of slightly recrystallized, relatively coarse-grained siderite frequently enclose small siderite areas, which by their uniform extinction directions can be related to coarse grains of siderite outside the pyrite aggregates. Quite often a kind of breccia texture is observed with pyrite occurring embedded in a matrix of interstitial siderite or siderite and sphalerite. The interstitial sphalerite mostly contains numerous very small, rounded inclusions of siderite with mutually differing extinction directions contrasting against the uniform extinction directions of the interstitial siderite. The form of the interstitial sphalerite and siderite areas are determined by the shape of the pyrite crystals. At some places pyrite crystals are apparently broken and traversed by dilatation veinlets of sphalerite characterized by conformable walls, i.e., each protuberance on one of the walls fits exactly into a corresponding embayment in the opposite wall. These dilatation veinlets never contain siderite. The sphalerite in the dilatation veinlets is devoid of siderite inclusions, although it is contiguous with the interstitial sphalerite containing numerous siderite inclusions.

The dilatation veinlets of sphalerite in pyrite indicate that the formation of sphalerite was accompanied by local fragmentation of pyrite crystals. The sphalerite is thus later than the pyrite. Since pyrite crystals in contact with sphalerite maintain their euhedral forms and as the sphalerite is full of siderite inclusions but devoid of pyrite inclusions, it is concluded that the sphalerite, besides occurring as fracture fillings in pyrite crystals, has selectively replaced siderite between the pyrite crystals. The replacement of siderite was accompanied by recrystallization of siderite as indicated by the different optical orientations of the siderite inclusions in sphalerite.

Pyrite aggregates transecting galena bands in zones of slightly recrystallized siderite sometimes still contain the relicts of galena in traceable bands (fig. 5). The pyrite crystals which have developed in siderite areas usually do not contain any inclusions, but the pyrite which has crystallized in galena bands generally show beautiful poikilitic textures. Sometimes the galena inclusions in these pyrite poikiloblasts show a distinct zonal arrangement parallel to the pyrite crystal faces (Plate I, fig. 2); the inclusions are largest and most numerous along the borders of the pyrite crystals adjoining galena areas. Frequently the pyrite poikiloblasts have developed in the central parts of galena aggregates, leaving an irregular rim of galena around them.

The textures just described clearly indicate that the pyrite is later than the galena.

In the zones of strongly recrystallized siderite pyrite occurs as sparsely disseminated euhedral to subhedral crystals rather than in aggregates. Bands of strongly recrystallized columnar siderite are not interrupted by the pyrite crystals, but the columnar siderite bands wrap around the pyrite crystals, whereby the siderite columns tend to assume an orientation perpendicular to the crystal boundaries of the pyrite.

This adaption of the course and structure of the columnar siderite bands to crystal boundaries of pyrite indicate that the pyrite is earlier than the strongly recrystallized columnar siderite. Thus, there has been at least two periods of recrystallization of siderite: the first recrystallization of siderite is associated with galena and earlier than pyrite, the second recrystallization of siderite is associated with sphalerite and later than the pyrite.

Arsenopyrite

Euhedral to subhedral crystals of arsenopyrite (Plate V, fig. 1) are occasionally found in association with pyrite aggregates.

Because of its close association with pyrite and similar textural habit the arsenopyrite is considered as contemporaneous with the pyrite.

Sphalerite

The sphalerite bands, streaks or irregular aggregates in the outer zone of the mantle always contain a multitude of microscopic exsolution blebs of chalcopyrite. The distribution of these blebs along crystallographic directions of the sphalerite and sometimes along grain boundaries show that the grain size of the sphalerite in the bands and streaks vary between about 0.1 mm and 2 mm.

Siderite inclusions are very common in the sphalerite. Less common inclusions are formed by exsolution blebs of pyrrhotite and by blebs of marcasite (see pp. 34–35).

Many of the textural features of the sphalerite has already been described, e.g., the association of sphalerite with strongly recrystallized siderite (pp. 20–25), the sphalerite-galena-chalcopyrite strongly recrystallized siderite relationships (pp. 24–26), and the sphalerite-pyrite relationships.

Sphalerite streaks or aggregates sometimes occur along the outer boundary of the mantle in contact with the enveloping unrecrystallized siderite. At their internal sides these sphalerite streaks or aggregates are often bounded by a band of columnar siderite in which the columns tend to be oriented perpendicular to the boundary of the sphalerite streak. Somewhat rounded sphalerite aggregates sometimes act as centres from which siderite columns arranged in several concentric bands radiate (fig. 6). The bands are the finer grained the closer they are to the sphalerite centre, sometimes thin concentric streaks of sphalerite intervene between the columnar siderite bands of different grain size.

Locally, a central area of sphalerite with few small siderite inclusions grades towards the border of the sphalerite area into poikilitic sphalerite full of siderite inclusions. These poikilitic border zones of the sphalerite sometimes grade into a cellular intergrowth in which rounded recrystallized siderite grains form the cells separated by very thin walls of interstitial sphalerite (fig. 13).

The above observations confirm the inference that sphalerite formation is accompanied by recrystallization of siderite and that the sphalerite has replaced the recrystallized siderite.

Prominent bands of sphalerite occurring in zones of slightly recrystallized siderite are characterized by outward radiating apophysae of tapering sphalerite veinlets, which sometimes follow the same paths as the radiating galena veinlets (figs. 9, 14 and 15). In the latter instances composite veinlets of galena and sphalerite in slightly recrystallized siderite are formed. The sphalerite in these veinlets is often full of siderite inclusions, whereas the galena is devoid of inclusions. The sphalerite has developed along galena-siderite boundaries and sometimes they enclose stretches of galena veinlets (figs. 14 and 15) and small rounded galena blebs. The sphalerite boundaries generally show convex bulgings fitting into corresponding concave embayments in the galena, but the reverse relation has sometimes also been noted (fig. 15). The veinlike stretches of galena abut against siderite grain boundaries (p. 18), whereas the sphalerite veinlets are continuous across several siderite grains. Some thin sphalerite veinlets are clearly dilatation veinlets with congruent walls, few or no inclusions of siderite, and uniform extinction of siderite

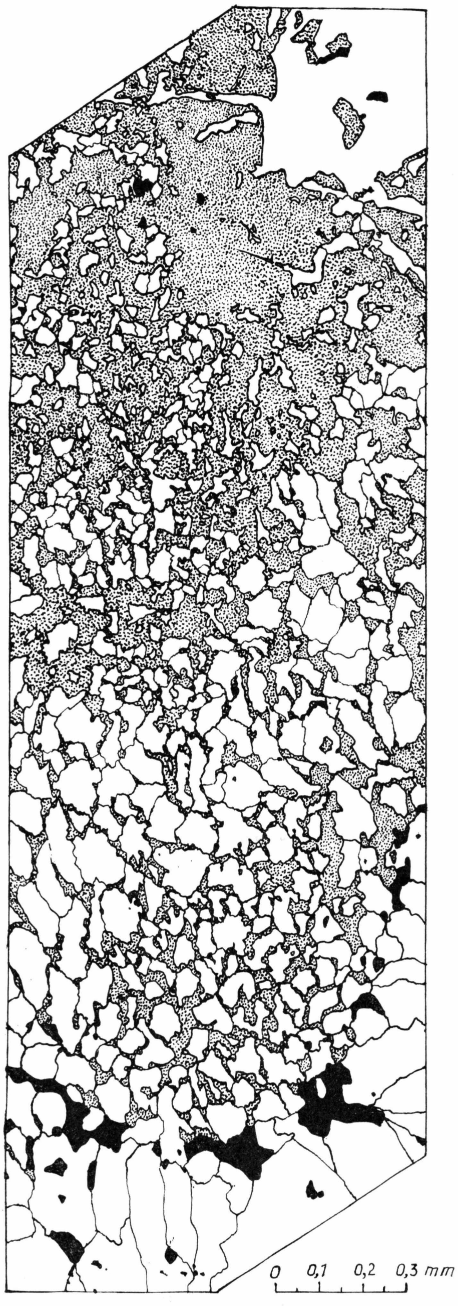

Fig. 13. Detail of the sphalerite band shown in the lower right hand corner of text-figure 3, polished section 1483. The sphalerite band consists of an external zone with very few siderite inclusions (top half of the figure), an intermediate zone of poikilitic sphalerite with numerous siderite inclusions, and an internal zone consisting of a cellular intergrowth of siderite grains with interstitial sphalerite. Note also the galena grains along the internal border of the sphalerite band. Dotted areas—sphalerite, black—galena, white—siderite.

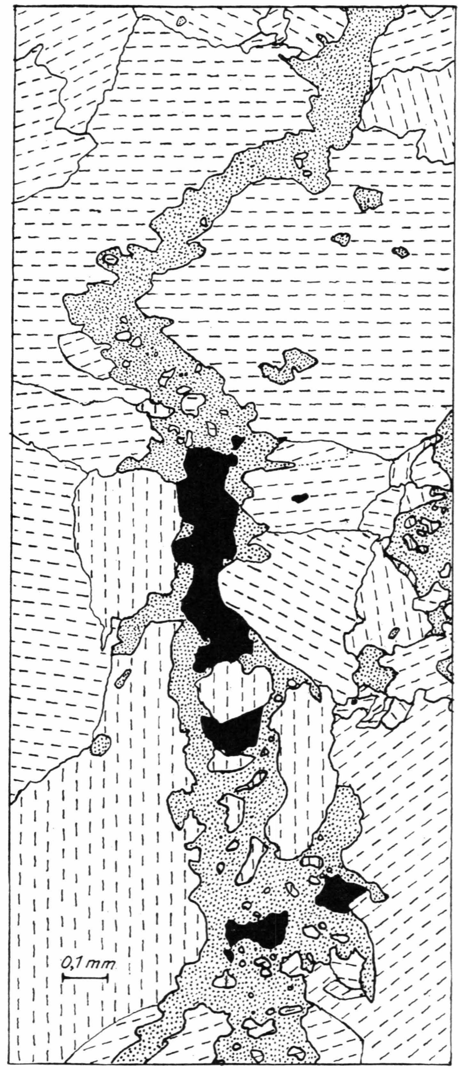

Fig. 14. A composite galena-sphalerite veinlet in polished section 1483 (text-figure 3). Galena is indicated in black, sphalerite by the dotted areas, and siderite by the striations indicating schematically the different extinction directions of the siderite grains. The stretches of galena are discontinuous and abut against siderite grain boundaries as also shown in text-figures 7 and 8. The sphalerite forms more continuous veinlets across several siderite grains. Sometimes cleavage directions in the siderite are followed by the sphalerite veinlets (upper half of the figure). Certain stretches of sphalerite veinlets are dilation veinlets with congruent walls, e.g., the small veinlet below the scale-mark in the figure. Note also the development of the sphalerite along galena-siderite boundaries and the inclusions of galena and siderite in the sphalerite.

fragments on both sides of the veinlet. Thicker veinlets contain numerous inclusions, while the vein walls are no longer congruent. Stretches of sphalerite veinlets sometimes follow cleavage directions in siderite grains. Exsolution blebs of chalcopyrite in sphalerite are concentrated along the sphalerite-galena and sphalerite-siderite grain boundaries.

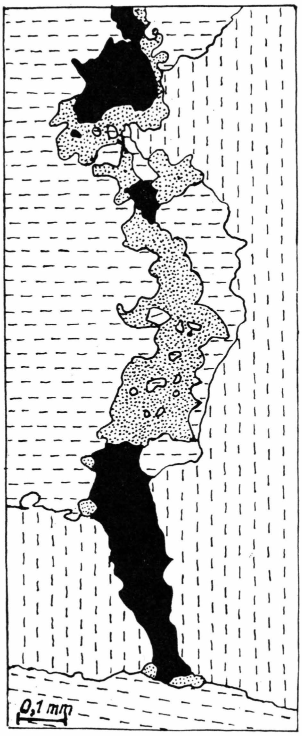

Fig. 15. A composite galena-sphalerite veinlet in polished section 1483 (text-figure 3). For explanation see fig. 14. Note especially the scalloped sphalerite boundary at the right hand side in the middle part of the figure; this boundary is partly characterized by convex bulgings of the sphalerite areas fitting into concave embayments in the siderite, and partly by concave embayments in the sphalerite into which convex bulgings of the siderite fit.

The latter observations clearly show that the sphalerite is later than the radiating galena veinlets. Sphalerite formation is accompanied by fracturing of siderite and pyrite; dilatation veinlets of sphalerite have broadened by replacement of the adjoining siderite walls. Galena and pyrite appear only slightly corroded by the sphalerite; the latter mineral have grown mainly by selective replacement of siderite.

Larger areas of galena frequently contain small, irregularly shaped grains or aggregates of sphalerite interstitial to the galena; however, sometimes this sphalerite has also developed as small granular crystals with porphyroblastic habit.

Chalcopyrite

The inner or chalcopyrite zone of the mantle is usually formed by a few large crystals of chalcopyrite, which show distinct anisotropy effects and a commonly developed grid twinning consisting of polysynthetic twin-lamellae occurring in two directions under an angle of about 90°.

Outside the chalcopyrite zone chalcopyrite occurs as exsolution blebs in sphalerite. In one instance a band of interstitial sphalerite in strongly recrystallized siderite has been observed to grade laterally into a band of interstitial chalcopyrite.

The latter observation is consistent with the inference that sphalerite and chalcopyrite have crystallized about contemporaneously.

The chalcopyrite zone is surrounded by zones of strongly recrystallized siderite only in those cases where appreciable quantities of sphalerite or marcasite (p. 35) are found in the outer zone of the mantle. In other cases the chalcopyrite zone is bounded by a zone of slightly recrystallized, relatively coarse-grained siderite with galena and pyrite or directly by the unrecrystallized siderite of the envelope of the nodules. Where in contact with coarser grains of slightly recrystallized siderite the chalcopyrite boundary is scalloped with convex chalcopyrite bulgings fitting into concave embayments in the siderite grains. However, where the chalcopyrite zone is bounded by strongly recrystallized columnar siderite seemingly reverse relations are observed: concave embayments in the chalcopyrite enclose the rounded tips of the columnar siderite grains and the cusps between adjacent chalcopyrite embayments penetrate interstitially between the grains of columnar siderite (fig. 16).

In the chalcopyrite-siderite boundary zones the chalcopyrite is at least partly later than the second recrystallization of siderite.

Galena inclusions in the chalcopyrite zone are often aligned in rows parallel to or in the direct continuations of galena veinlets and bands in the outer zone of the mantle. The inclusions have rounded shapes if they lie in the directions of galena bands; they form thin, elongated bodies with rounded tips if they occur in the direction of galena veinlets. Occasionally, veinlike stretches of galena are aligned along a direction which can be traced from in the core of the nodules, across the chalcopyrite zone, into the outer mantle. These veinlike stretches are broadest in the chalcopyrite zone and thinnest in the outer zone of the mantle. When the chalcopyrite zone is bounded by slightly recrystallized siderite the veinlike stretches of galena in the chalcopyrite often continue in the siderite, forming the radial galena veinlets described before (pp. 17–20, fig. 3); when the chalcopyrite zone is bounded by strongly recrystallized siderite the veinlike stretches of galena, after crossing the chalcopyrite boundary, usually dissolve into a very fine galena network interstitial to the siderite grains.

The galena veinlets have presumably formed as outwards tapering radial veinlets during the first phase of recrystallization of siderite in the mantle (p. 27). The chalcopyrite zone has formed later by selective replacement of the siderite, whereby stretches of galena veinlets originally contained in the siderite became incorporated

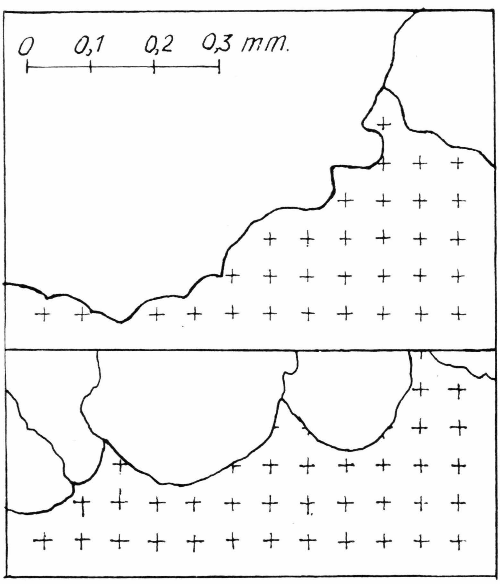

Fig. 16. Scalloped chalcopyrite-siderite boundaries. In the upper figure chalcopyrite (crosses) is in contact with a coarse grain of siderite and the boundary is characterized by convex bulgings of chalcopyrite fitting into concave embayments in the siderite. In the lower figure the chalcopyrite is in contact with a juxtaposition of columnar siderite grains and the boundary is characterized by concave embayments in the chalcopyrite enclosing the rounded tips of the columnar siderite grains.

in the chalcopyrite zone as mineral and textural relicts. Generally, no sphalerite is found along the galena inclusions in the chalcopyrite; this is consistent with the inference that the sphalerite along the galena veinlets in the outer zones of the mantle (see above) is also later than the galena and broadly speaking contemporaneous with the chalcopyrite: the chalcopyrite formed in the inner zone of the mantle at the same time that sphalerite crystallized in the outer zone. The dissolution of veinlike stretches of galena into an interstitial network in strongly recrystallized siderite is in agreement with the inference that part of the galena is remobilized during a second phase of recrystallization of siderite, which took place in association with the formation of the sphalerite bands and chalcopyrite zone after the formation of the original galena veinlets.

Sphalerite inclusions in the chalcopyrite zone occur irregularly distributed as irregular, sometimes more or less rounded, blebs and as skeletal crystals bounded by composition planes of the polysynthetic grid twinning in the chalcopyrite. Other small sphalerite inclusions are occasionally found along boundaries of the chalcopyrite with inclusions of siderite or galena. The sphalerite inclusions always contain very small exsolution blebs of chalcopyrites.

The sphalerite inclusions in the chalcopyrite are apparently not replacement relicts because they are later than or contemporaneous with the twinning in the chalcopyrite. The possibility of a later introduction of sphalerite is unlikely because there is no later generation of sphalerite outside the chalcopyrite. Therefore, the sphalerite inclusions presumably originated by segregation after exsolution from chalcopyrite.

Inclusions of siderite aggregates are found in the chalcopyrite zone, but they are not frequent, usually very small, and often for a considerable part replaced by marcasite (p. 37).

Pyrrhotite

The sphalerite bands in the mantle often contain very small exsolution blebs of pyrrhotite besides similar blebs of chalcopyrite. The exolution blebs tend to segregate around inclusions of siderite (fig. 17).

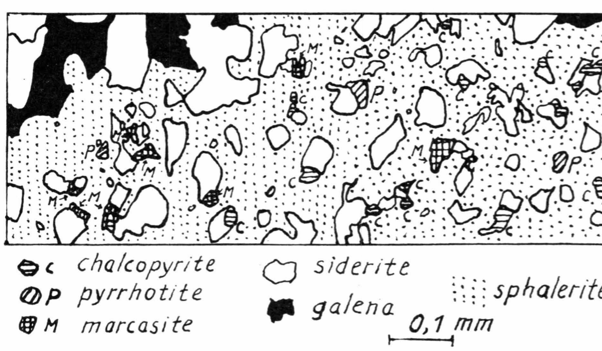

Fig. 17. Inclusions of chalcopyrite, pyrrhotite, marcasite, and siderite in sphalerite. The chalcopyrite and pyrrhotite inclusions are presumably exsolution blebs, which tend to segregate around siderite inclusions. Pyrrhotite blebs occurring attached to siderite inclusions have in most instances apparently been transformed into marcasite.

Some pyrrhotite is found in the chalcopyrite, and rarely in the siderite, along the boundaries of the chalcopyrite zone with strongly recrystallized siderite, in particular when the chalcopyrite boundary is in contact with a juxtaposition of siderite and galena grains (p. 25). Along the chalcopyrite-siderite contacts a narrow rim of pyrrhotite, often in symplectic intergrowth with the chalcopyrite, and sometimes larger blebs of pyrrhotite are found in the chalcopyrite (figs. 11 and 12); Plate II. fig. 2; Plate III. fig. 1). The pyrrhotite sometimes contains extremely small inclusions of galena. The pyrrhotite blebs and symplectic intergrowths are sometimes veined by the chalcopyrite. In very few instances are pyrrhotite crystals found in the siderite along the chalcopyrite boundary.

The restricted occurence of pyrrhotite in the border zones of chalcopyrite, siderite and galena suggests that the pyrrhotite in these zones was formed by the interaction of chalcopyrite with siderite and galena.

Marcasite

Small grains of marcasite are always found in the sphalerite bands which contain exsolutions blebs of pyrrhotite and siderite inclusions. The marcasite inclusions have the same size and form as the pyrrhotite blebs and they invariably occur attached to siderite inclusions in the same way as chalcopyrite and pyrrhotite exsolution blebs frequently occur attached to the siderite inclusions (fig. 17). When only chalcopyrite blebs and/or siderite inclusions are present without pyrrhotite, the marcasite inclusions are not found.

The relationship described suggests that the marcasite in the sphalerite bands has been formed by replacement of exsolved pyrrhotite blebs in contact with siderite inclusions.

Marcasite is also found in the siderite and exceptionally in the chalcopyrite along certain siderite-chalcopyrite boundaries. This marcasite is developed as small skeletal or dendritic crystals composed of groups of parallel lamellae with regular spacings between them (fig. 18; Plate IV, figs. 1 and 2). The lamellae, mostly 0.1–1 mm long, show polysynthetic twinning with the twin planes perpendicular to the elongation of the lamellae. When the lamellae occur in relatively coarse-grained siderite, the siderite grain boundaries are usually intersected by the lamellae (fig. 18). Hovever, sometimes the marcasite lamellae occur in a matrix of fine-grained siderite, whereby the size and form of the siderite grains appear adapted to the width of the spacings between the lamellae.

Frequently there are two systems of parallel marcasite lamellae. The lamellae of one system often touch the lamellae of the other system, but intersection of lamellae has not been observed (Plate IV, fig. 2). The sharp angle between the directions of the two systems of lamellae are mostly near 30°, 60°, or 90°. The directions of the lamellae are not related to crystallographic directions of the siderite matrix because the lamellae traverse several differently oriented siderite grains; they

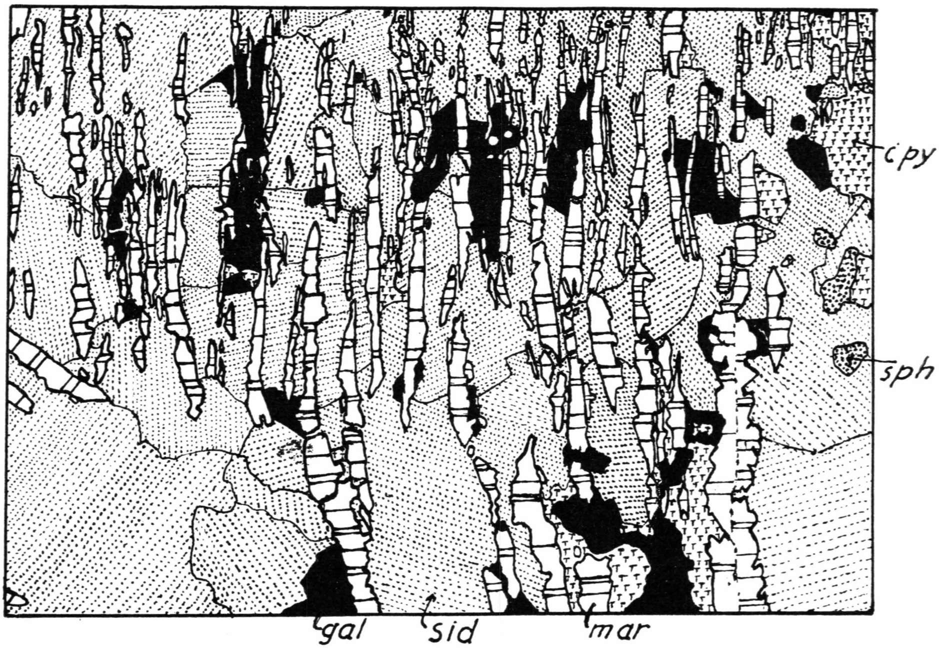

Fig. 18. Marcasite lamellae in siderite along the boundary of the chalcopyrite zone in polished section 1483 (see text-figure 3); gal – galena, cpy – chalcopyrite, sph – sphalerite, mar – marcasite, and sid – siderite. See also plate IV fig. 1.

rather represent crystallographic directions of the marcasite dendrite itself.

Along the siderite-chalcopyrite border zones marcasite and pyrrhotite tend to exclude each other: if pyrrhotite is present in the chalcopyrite along this border zone marcasite is rarely found, if appreciable marcasite is present in the siderite the bordering chalcopyrite is devoid of or poor in pyrrhotite. Only occasionally have the two minerals been found together; in these cases pyrrhotite grains in chalcopyrite are sometimes traversed by marcasite lamellae.

Sometimes marcasite lamellae occur partly in siderite and partly in the chalcopyrite zone (Plate IV, fig. 2).

Grains of galena interstitial to the siderite are frequently traversed by the marcasite lamellae (fig. 18). Pyrite idioblasts are not traversed by the marcasite, but the marcasite lamellae often surround the pyrite crystals. Locally, marcasite lamellae show fractures filled with fine dilatation veinlets of siderite, which also cross chalcopyrite and galena grains (fig. 18; Plate IV, fig. 1).

Usually the boundaries of the marcasite lamellae are rather smooth but also quite often the lamellae show serrated boundaries due to the development of outgrowths of marcasite replacing the siderite between the lamellae. This infilling of the marcasite dendrites has often reached an advanced stage in the marcasite which has developed in siderite aggregates enclosed in the chalcopyrite zone. In the latter case, the outer serrated margins of the lamellae sometimes consist of pyrite rather than marcasite.

Inclusions of siderite aggregates in the chalcopyrite zone are always for a considerable part replaced by chalcopyrite and marcasite. Sometimes the chalcopyrite spreads out along the marcasite lamellae and partially fills the space between the lamellae. Galena grains interstitial to the siderite are traversed by the marcasite lamellae and corroded by the chalcopyrite; sometimes the galena shows a mottled appearance due to the development of chalcopyrite blebs in the galena. Furthermore, occasionally occurring sphalerite areas in siderite-marcasite-chalcopyrite aggregates also appear affected by the chalcopyrite, which forms a typical pattern of blades in the sphalerite. Pyrite idioblasts in the siderite inclusions often merge into surrounding granular marcasite aggregates.

Very rarely fine-grained lamellar marcasite has been observed to form a band in the outer margin of a narrow zone of strongly recrystallized siderite which adjoins to the chalcopyrite zone.

The lamellar marcasite here described may show some resemblances to lamellar marcasites described by Edwards (1954), Oen (1958), Ramdohr (1960), Oelsner and Starke (1964), etc., which are believed to represent replacement of pyrrhotite by marcasite. However, in the present case the marcasite dendrites formed mainly in siderite along boundaries of the siderite with chalcopyrite, whereas pyrrhotite is formed mainly at the chalcopyrite side of the same boundaries. This difference in site of deposition, together with differences in grain sizes and crystal habits, indicate that the marcasite has not been formed by replacement of pyrrhotite. The structures described in the above indicate that the marcasite dendrites have developed mainly at the expense of siderite.

The intersection of siderite and galena grains by the marcasite lamellae indicates that galena was already present and the siderite at least partially recrystallized when the lamellae formed; the adaptation of grain size and shape of strongly recrystallized siderite to the inter-lamellar spacings of the marcasite dendrites and the recementation with siderite of fractures in the lamellae show that a later recrystallization of siderite has at least locally taken place after or contemporaneous with the formation of the marcasite.

Where siderite is replaced by marcasite some chalcopyrite locally spreads out along the marcasite lamellae, while mottled galena-chalcopyrite and bladed sphalerite-chalcopyrite intergrowths apparently indicate replacements of galena and sphalerite by chalcopyrite. Thus, the formation of marcasite at the expense of siderite have locally been accompanied by enlargement of the chalcopyrite areas, so that marcasite lamellae are sometimes enclosed in chalcopyrite. It is interesting to note that these local enlargement of chalcopyrite, which presumably formed contemporaneous with the marcasite below 300° C (p. 41) also show polysynthetic grid twinning and is in optical continuity with the main part of the chalcopyrite, which is believed to have formed between 400° and 500° C (p. 44). However, the chalcopyrite which has formed by enlargement of areas of earlier chalcopyrite do not contain sphalerite inclusions.

Stannite

Stannite is very rarely found in the chalcopyrite zone as very small inclusions of irregular shape.

The core of the sulphide nodules

Pyrrhotite. galena, and siderite

The pyrrhotite in the core of the nodules is usually composed of one large crystal, which always occurs intergrown with marcasite.

Galena is regularly found in the pyrrhotite as veinlike stretches or patches which often continue into the chalcopyrite zone. Whereas these galena stretches in the chalcopyrite zone are relatively thin and characterized by rounded outlines, those in the pyrrhotite are thicker and have remarkably straight boundaries parallel to the (100) direction of the galena. The orientation of triangular cleavage pits often indicate an approximately parallel crystallographic orientation of groups of veinlike galena stretches in the pyrrhotite. The galena areas often wedge out with a sharp point towards the interior of the nodule. Sometimes the galena patches show an arrangement in diffusion bands as described before (p. 16). Some of the bands are enclosed partly in pyrrhotite and partly in chalcopyrite. In other instances aggregates of relatively large (5 mm) euhedral crystals of galena occur enclosed in the pyrrhotite near the boundary with the chalcopyrite zone (fig. 2). Pyrite poikiloblasts with galena inclusions are often found protruding from the chalcopyrite zone into the pyrrhotite.

The aggregates of relatively coarse-grained galena enclosed in the pyrrhotite along the borders of the chalcopyrite zone are apparently earlier than the pyrrhotite. Galena is presumably the first sulphide that crystallized in the mantle as well as in the core of the nodules. The difference in textural habit of the coarse-grained euhedral galena in the core and the finer-grained galena in diffusion bands and radial cracks in the mantle may be due to the fact that the galena in the core has crystallized in cavities, whereas the galena in the mantle has replaced siderite.

The pyrrhotite in the core of the nodules presumably has also crystallized mainly as open space fillings. However, the galena diffusion bands presumably originated in the mantle of recrystallized siderite, so that the enclosure of galena bands in the pyrrhotite suggests that some replacement of the siderite mantle by pyrrhotite must have taken place (fig. 1).

Chalcopyrite and sphalerite are very rarely found as small irregularly shaped inclusions in the pyrrhotite or marcasite in the core of the nodules.

Sometimes irregular aggregates and veinlike masses of siderite are found in the core of the nodules; the veinlike siderite masses traverse the pyrrhotite and marcasite in the core of the nodules.

The latter observations indicate the existence of a very late stage of siderite recrystallization.

Marcasite and pyrite

The pyrrhotite in the core of the nodules always occur intergrown with marcasite. The marcasite has developed as a one-crystal dendrite consisting of branching marcasite sheets which have replaced the pyrrhotite along crystallographic directions of the latter mineral. In some sections the sheets form a hexagonal network in the pyrrhotite (fig. 1), in other sections the marcasite sheets form a rectangular pattern (fig. 2), therefore, the marcasite dendrites have apparently developed along the prismatic and basal planes of the pyrrhotite.

The marcasite sheets in pyrrhotite are usually less than 0.5 mm thick. Often the sheets show an untwinned central part with straight outlines surrounded by irregularly shaped marcasite areas, which appear attached in twin relation to the central parts of the marcasite sheets.

Infilling with pyrite of the marcasite dendrites in pyrrhotite is not common. Only in a few cases have small pyrite grains been observed as linings along the marcasite sheets in pyrrhotite.

Some specimens contain cavernous marcasite dendrites instead of pyrrhotite-marcasite intergrowths; pyrrhotite is either absent or present only as relictic patches. There are two kinds of cavernous marcasite dendrites. One kind is represented by fine-cavernous marcasite dendrites in which the branching sheets have the same size and structure as those of the marcasite dendrites occurring intergrown with pyrrhotite; pyrite infillings are absent or scarce (fig. 2).

These fine-cavernous marcasite dendrites are so similar to the marcasite dendrites in pyrrhotite that it may reasonably be assumed that they also originated in pyrrhotite; the latter mineral is later apparently completely dissolved.

The other kind of cavernous marcasite dendrites are formed by coarse-cavernous marcasite-pyrite dendrites, which show bigger caverns and thicker dendritic sheets, sometimes 1 mm or more in width. The branching sheets are often slightly curved and a regular pattern in the branching network of marcasite sheets is mostly not discernible. Twinning is more complex than in the marcasite sheets in pyrrhotite. The branching sheets are built up of a skeleton of thin, finely twinned and straightly bounded marcasite sheets, which have apparently grown thicker by the attachment along their sides of granular marcasite in twin relation to the central marcasite sheets. The coarse-cavernous marcasite dendrites always show pyrite overcrustings on all their branches; often pyrite even predominates over marcasite. The degree of pyrite infilling of the dendrites increases from the central part of the nodules outward; in the peripheral parts of the core the infilling with pyrite is often nearly complete.

The marcasite in the coarse-cavernous dendrites frequently contain groups of extremely small (0.01 mm) pyrrhotite inclusions. These inclusions are sometimes of irregular shape, but more often they form short laths, parallelly arranged along a crystallographic direction of the marcasite (Plate V, fig. 2). All pyrrhotite inclusions extinguish simultaneously. Some of the lath-shaped inclusions protrude from the marcasite into the overcrusting pyrite without being corroded by the pyrite; the latter mineral do not contain pyrrhotite inclusions.

The pyrite infillings of the coarse-cavernous dendrites apparently have not developed in a pyrrhotite matrix because where the latter matrix is still present pyrite infillings are generally absent. Dendritic growth is highly favoured, among others, by rapid deposition in open spaces (BUCKLEY 1951, pp. 479–488). Presumably the marcasite skeleton and the pyrite infillings formed by one continuous process of dendritic crystallization in the open spaces created by the dissolution of pyrrhotite.

The former presence of pyrrhotite at the sites now occupied by the coarse-cavernous marcasite-pyrite dendrites is witnessed by the lath-shaped pyrrhotite inclusions in the marcasite. These inclusions cannot be considered as later replacements because they are apparently earlier than the pyrite infillings. Simultaneous deposition of marcasite and pyrrhotite seems also precluded for in the pyrrhotite-marcasite intergrowths pyrrhotite is replaced by marcasite. The pyrrhotite inclusions presumably represent relicts of the dissolved pyrrhotite, which due to the rapid dendritic growth of the marcasite have been incorporated in the latter mineral.

It follows from the above that the cores of the nodules were presumably first completely filled with pyrrhotite. The latter mineral was then dissolved, but in most cases the formation of the marcasite dendrites had set in before the dissolution of the pyrrhotite was completed. This has resulted in the formation of the pyrrhotite-marcasite intergrowths at places where the pyrrhotite was not yet dissolved, and in the coarse-cavernous marcasite-pyrite dendrites at the sites where the pyrrhotite was already dissolved. The fine-cavernous marcasite dendrites originated by dissolution of the pyrrhotite after the formation of the marcasite dendrites.

The pyrite infillings in the coarse-cavernous marcasite dendrites indicate a change in environmental conditions favouring the formation of pyrite rather than that of marcasite (chapter III). This change may also have arrested the dissolution of pyrrhotite; the latter mineral is not replaced by pyrite infillings.

III. THE CONDITIONS OF FORMATION OF THE PYRRHOTITE-MARCASITE NODULES IN THE SIDERITE-CRYOLITE ORE

Sequence of mineral formation

In the preceding chapters the sequence of crystallization of the minerals have been inferred from their textural relations. In Table I the conclusions are summarized and arranged in a logical order. Five suc-

Table I

Phase		Temperature	f_{CO_2}
1	dissolution of siderite........................		
2	cavity linings, rhythmic bands and radial veinlets of galena; recrystallization of siderite....	± 500° C	> $10^{2.6}$ atm.
3	idioblasts and poikiloblasts of pyrite replacing galena and siderite, locally the pyrite is accompanied by arsenopyrite....................	< 500° C	
4	crystallization of coarse-grained pyrrhotite as cavity fillings in the core of the nodules and partly also as replacements of siderite; formation of a chalcopyrite zone by replacement of siderite around the pyrrhotite core of the nodule; formation of sphalerite bands, streaks, and radial veinlets by replacement of siderite in the outer zone of the siderite mantle of the nodules; remobilization of galena; recrystallization of siderite in fine-grained columnar aggregates..........	> 400° C	> $10^{1.1}$ atm.
4a	exsolution of chalcopyrite and pyrrhotite from sphalerite...............................	± 400°–350° C	
	formation of pyrrhotite along chalcopyrite-siderite boundaries..........................	± 400°–300° C	
5	formation of small marcasite dendrites along chalcopyrite-siderite boundaries; enlargement of chalcopyrite areas; replacement of exsolved pyrrhotite in sphalerite by marcasite along contacts with siderite inclusions in sphalerite....	< 300° C	
	dissolution of pyrrhotite in the core of the nodules, formation of coarse dendrites of marcasite with pyrite infillings, and of siderite veinlets crossing the marcasite-pyrite dendrites..............	± 200° C	> $10^{-1.8}$ atm.

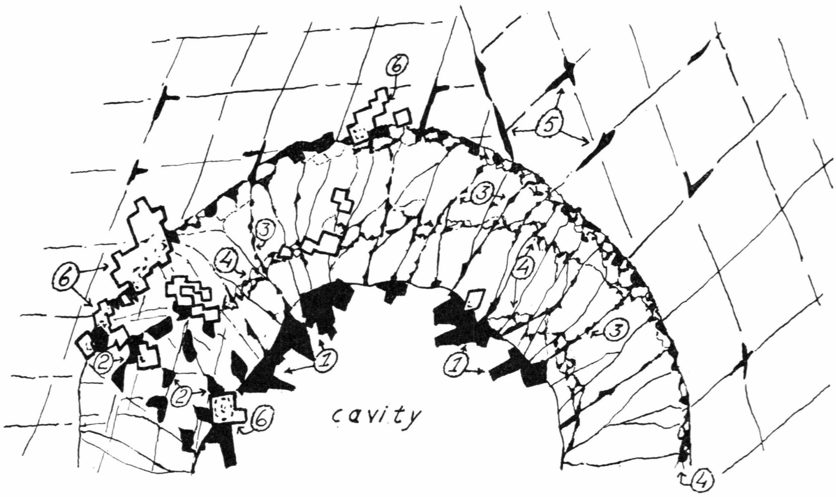

Fig. 19 a.

Fig. 19 a, b, c. Diagrammatic representation of the development of the pyrrhotite-marcasite nodules.

(a) In phase 1 the siderite in a thin zone around the fluid-filled cavity recrystallized. In phase 2 galena crystallized as cavity linings on the cavity walls (1), as concentric diffusion bands (2) and (4) and radial veinlets (3) in the mantle of recrystallized siderite, and along cleavage directions in the envelope of unrecrystallized siderite (5). In phase 3 pyrite crystallized in the mantle of recrystallized siderite and partly replaced the galena (6). Fig. 19 a shows the situation after phase 3.

(b) In phase 4 pyrrhotite crystallized in the core of the nodules, while in the mantle of the nodules replacement zones of chalcopyrite and sphalerite were formed. Between these two zones siderite recrystallized again in fine-grained columnar aggregates. The galena in the siderite areas which were replaced by sphalerite was remobilized and migrated inward in front of the inwardly expanding sphalerite bands (1). The recrystallization of siderite simultaneous with the deposition of sphalerite appears among others from textures as shown at (4). In phase 4 a pyrrhotite developed along the chalcopyrite-siderite boundaries and in phase 5 small dendrites of marcasite formed locally along the same boundaries (2) and (3). Fig. 19 b shows the situation at the beginning of phase 5.

(c) In phase 5 the pyrrhotite in the core of the nodule partly dissolved and marcasite formed instead. Fig. 19 c shows the present appearance of the pyrrhotite-marcasite nodules. Core of the nodule: 1a – cavernous coarse-grained marcasite dendrites with pyrite infillings, 1 b – pyrrhotite, intergrown with and partly replaced by marcasite. Mantle of the nodules: 2 – chalcopyrite zone with relicts of radial veinlets of galena, 3 – outer mantle of the nodules with zones of galena, pyrite, sphalerite, and recrystallized siderite. Envelope of the nodules: 4 – unrecrystallized coarse-grained siderite with galena along cleavage directions.

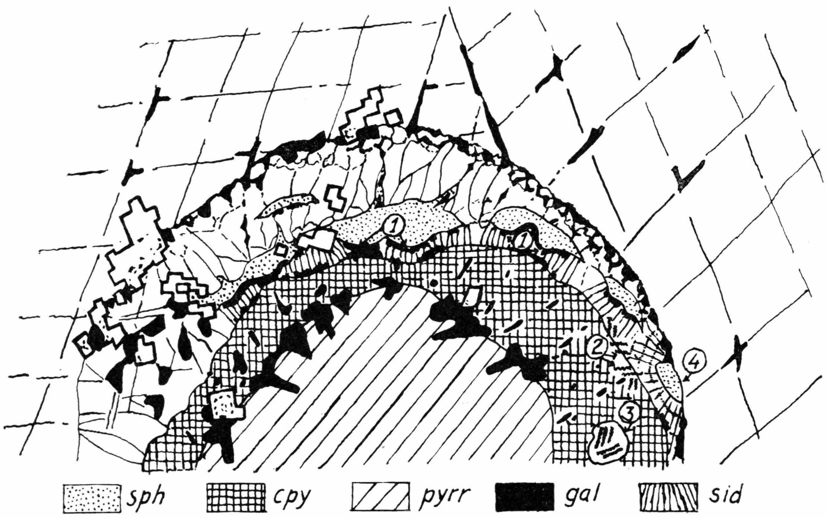

Fig. 19 b.

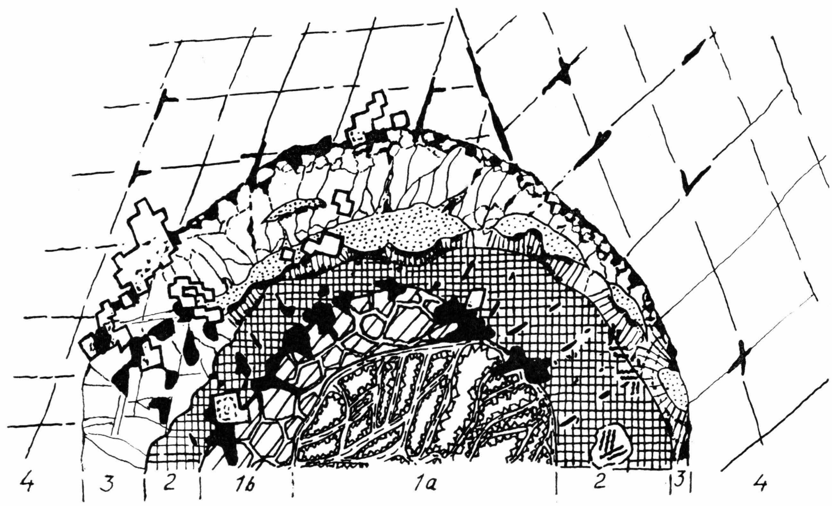

Fig. 19 c.

cessive, but more or less overlapping phases of mineral formation are recognized. An idealized diagrammatic representation of the development of the pyrrhotite-marcasite nodules during successive phases of their formation is given in figs 19 a, b, c.

Temperatures of crystallization

According to Clark (1961) the mineral pair pyrite-arsenopyrite must have been deposited below $491° \pm 12°$ C if the combined partial pressures of sulphur and arsenic are lower than the confining pressure. Thus, the formation of pyrite and arsenopyrite in phase 3 presumably occurred below 500° C.

Although in phase 4 simultaneous deposition of pyrrhotite and pyrite is not demonstrated, the pyrrhotite is at places in surface equilibrium (Barton, Bethke and Toulmin 1963, pp. 172–173) with earlier pyrite and may provide a potential geothermometer (Arnold 1962). However, the X-ray diffraction photographs of pyrrhotites from four of the investigated samples all show the characteristic reflections of monoclinic pyrrhotite at $d = 5.77 \pm 0.05$ Å, $d = 5.22 \pm 0.05$ Å, $d = 4.63 \pm 0.05$ Å, and $d = 2.049$–2.068. Only one of the diffraction patterns shows a splitting of the strongest peak into two lines, a more intense one at $d = 2.052$ Å and a less intens one at $d = 2.048$ Å, which may be due to the presence of a mixture of hexagonal and monoclinic phases of pyrrhotite. In the latter case the $d = 2.052$ Å reflection may represent the d_{102}-reflection of the hexagonal phase, and application of the d_{102} versus composition curve for hexagonal pyrrhotites and of the pyrrhotite solvus as established by Arnold (1962) indicate a temperature of formation of approximately 550° C for the pyrrhotite in question. According to von Gehlen and Kullerud (1962) the presence of chalcopyrite in equilibrium with pyrrhotite necessitates a positive correction of about 50° C to be applied to the results obtained from the pyrrhotite-pyrite geothermometer, so that one arrives at a crystallization temperature of about 600° C for the pyrrhotite considered. This temperature is apparently too high to be accepted uncritically since in phase 3 temperatures were presumably already below 500° C. As pointed out, e.g., by Carpenter and Desborough (1964) the pyrrhotite-pyrite geothermometer should be used with the utmost caution as several factors limit its applicability.

The polysynthetic grid twinning in the chalcopyrite has been interpreted as due to the inversion of high-temperature cubic chalcopyrite into the tetragonal modification. This inversion occurs near 550° C (Hiller and Probsthain 1956; Yund and Kullerud 1961; Shima 1962), but solid solutions may effect the inversion temperature and, e.g., tetragonal chalcopyrite in equilibrium with cubanite inverts to the cubic polymorph at about 480° C (Yund and Kullerud 1961).

The alleged exsolution of sphalerite from the chalcopyrite occurred after the formation of the grid twinning. Based on the early work of

Borchert (1934) this exsolution is often considered as indicating temperatures above 550° C. However, the chalcopyrite considered contains only very few sphalerite exsolution blebs, and it is very probable that a limited extent of sphalerite solid solution in chalcopyrite is possible at temperatures well below 550° C.

It is believed that there are no reliable grounds for assuming that the chalcopyrite of phase 4 has formed at temperatures above that of phase 3, i.e., above 500° C.

Exsolution of pyrrhotite from sphalerite indicates crystallization temperatures above 140° C for the mixed crystal (Kullerud 1953, 1959). Unmixing of chalcopyrite from sphalerite is generally believed to occur between 350°–400° C (Buerger 1934). The abundance of chalcopyrite exsolution blebs in our sphalerite suggests that this sphalerite crystallized above 400°–350° C.

It is concluded from the above that in phase 4 temperatures were probably between 500° C and 400° C.

In phase 5 temperatures were presumably below 300° C as marcasite is generally believed to form only below 300° C (Kullerud and Yoder 1959; Kullerud 1964, p. 223).

The temperature estimates summarized in Table I are rough approximations, which presumably will not be influenced if pressures are taken into account (Ingerson 1955, p. 349).

Pressure variables

Assuming that the cryolite deposit at Ivigtut has consolidated at a depth of about 5 km the load pressure during the mineralization may be of the order of roughly 1500 bars.

As a first approximation the total fluid pressures P_f and the load pressures P_l may be considered as about equal (Fyfe, Turner and Verhoogen 1958, p. 50; Smith 1963, p. 455). However, the siderite in the cryolite deposit has probably crystallized above 500° C and a consideration of the stability of the siderite at high temperatures indicate that, e.g., at 550° C the partial pressures of CO_2 must already have amounted to several thousand bars to stabilize siderite (fig. 20). Therefore, at least during the earlier stage of mineralization fluid pressures were probably in excess of load pressures.

Considering the mineralogy of the nodules the partial pressures, or more correctly the fugacities, of CO_2, S_2 and O_2 would be important variables determining the stable mineral associations.

Possible variations in the CO_2-fugacities (f_{CO_2}) may be depicted by considering the stability of siderite at various temperatures. However, as HOLLAND (1959, 1965) has pointed out, reliable data on the stability of siderite are at present not sufficiently available. Some recent data are provided by ROSENBERG (in HOLLAND 1965), FRENCH (1965), and WEIDNER and TUTTLE (1965). ROSENBERG has determined the breakdown of siderite at $322 \pm 4°$ C, 0.95 atm. CO_2 and 0.05 atm. CO; FRENCH

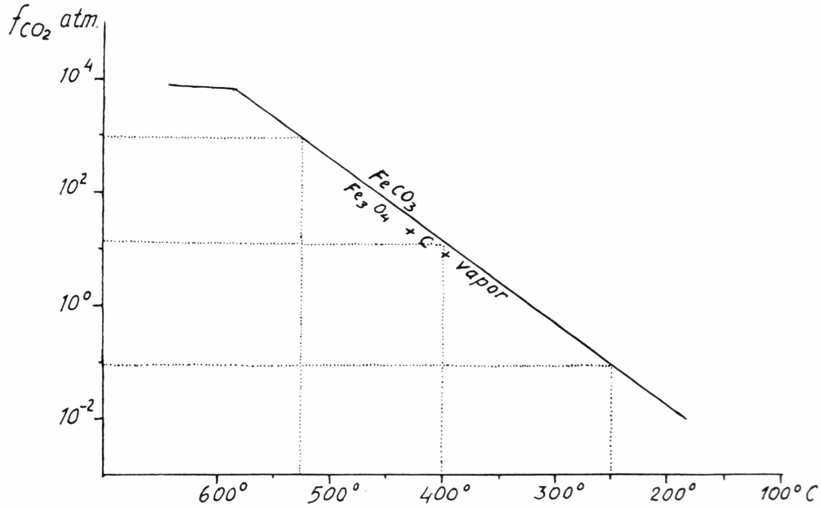

Fig. 20. Tentative curve showing at different temperatures the minimum CO_2-fugacity that is necessary for siderite to have a stability field in the system Fe-S-C-O; for details see the text of the paper.

and WEIDNER and TUTTLE have studied the equilibrium siderite $\rightleftarrows$ magnetite + C + vapor in the higher temperature ranges; WEIDNER and TUTTLE noted a change of slope in the PT-curve for the reaction studied at $P > 5000$ bars, which they suggest is due to the existence of a non-quenchable high-pressure polymorph of siderite. From these scanty data a tentative T-f_{CO_2} diagram has been constructed (fig. 20), which shows in a rather qualitative way the variation with temperature of the minimum values of f_{CO_2} that are necessary to stabilize siderite. Thus, in phase 2 (Table I) temperatures were about 500° C and the recrystallization of siderite in this phase indicates that f_{CO_2} was $> 10^{2.6}$ atm.; similarly, at the end of phase 4 f_{CO_2} must have been $> 10^{1.1}$ atm.

It may be noted here that three analyses of siderites from Ivigtut, cited by BØGGILD (1953) show a $FeCO_3$-content of 93.49 % to 95.9 % and a $MnCO_3$-content of 4.1 % to 5.16 %.

Fig. 20 shows that in the temperature interval of formation of the nodules considerable variation of f_{CO_2} is possible. The limits of variation of f_{S_2} and f_{O_2} are generally much narrower (HOLLAND 1959, 1965). Therefore, temperature and f_{CO_2} are presumably the most important variables determining the sequence of phases of mineralizations and replacements in the sulphide nodules; besides that f_{S_2} and f_{O_2} are important in determining the stable minerals in each phase.

Origin of the fluids

The occurence of the pyrrhotite-marcasite nodules and associated sulphides always as small isolated aggregates enclosed in coarse siderite crystals or aggregates suggests that the nodules may have crystallized from S-rich fluids, which have been entrapped as inclusions in the siderite masses during crystallization of the latter. Assuming that this be the case, the observed sequence of mineral formation and replacements in and around the nodules can be explained as a result of cooling of the system and decreasing f_{CO_2}, which disturbed the equilibrium fluid-siderite and caused reactions to take place. This will be discussed in the following section.

Alternative hypotheses assuming that the nodules crystallized from later-introduced fluids in the siderite encounter the difficulty that no conduits are known along which the fluids may have circulated. Moreover, the introduction of later high-temperature fluids should presumably also effect other minerals in the deposit and not only the siderite.

Stability relations of minerals in the system Fe-O-S-C and the sequence of mineral formation

The stability relations of the minerals in the system Fe-O-S-C as presented in terms of fugacities of CO_2, S_2 and O_2 by HOLLAND (1959, 1965) allow us to gain some insight in the changes in T, f_{CO_2}, f_{S_2} and f_{O_2} that have presumably controlled the crystallization sequence in the sulphide nodules in the siderite.

1) Fig. 21 shows these stability relations as functions of f_{S_2} and f_{O_2} at 525° C and CO_2-fugacities lower than 10^3 atm., higher than 10^3 atm., and much higher than 10^3 atm., respectively. If f_{CO_2} is lower than 10^3 atm. siderite is not stable and the stability relations are represented by the solid lines in fig. 21. During crystallization of the siderite masses above 500° C siderite must have a considerable stability field. e.g., such as bounded by the bar-point line in fig. 21; this necessitates a f_{CO_2} much higher than 10^3 atm. The fluids entrapped in the crystallizing siderite

masses were presumably in equilibrium with the latter mineral and, therefore, they must have f_{S_2} and f_{O_2} falling within the stippled area in fig. 21. With decrease of f_{CO_2} the siderite stability field is reduced, e.g., to the area bounded by the broken line in fig. 21 ($f_{CO_2} > 10^3$ atm.). A fluid "a" (fig. 21) with high f_{S_2} will then not be in equilibrium with siderite. Thus, in phase 1 a decrease of f_{CO_2} may cause siderite in contact with the enclosed fluids to dissolve by reaction with these fluids. The enrichment of the fluids with dissolved CO_2 may cause f_{CO_2} in the fluid-containing cavities to rise again until equilibrium is re-established and the dissolution of the siderite-walls of the cavities is automatically arrested; instead the siderite may then recrystallize. In this phase f_{CO_2} and total fluid pressures in the cavities in the siderite may be temporarily higher than the corresponding pressures outside the siderite.

2) In phase 2 the crystallization of galena is accompanied by the formation of radial cracks; this possibly indicates the escape of CO_2-rich gases or fluids from the cavities, which may result in an additional dissolution and recrystallization of siderite as in phase 1.

3) Fig. 22 shows the relation at 400° C and CO_2-fugacities of 10^4 atm. and of 10^2 atm. respectively. Comparison with fig. 21 suggests that as f_{CO_2} is high, e.g., near 10^4 atm. (bar-point lines in fig. 22) a decrease in temperature from 525° to 400° C will not affect the stability of the siderite. In this temperature interval pyrite can crystallize in phase 3 in equilibrium with the siderite from fluids with relatively high f_{S_2} as represented by "a" in the figure. From fluids in the stippled area with lower f_{S_2} only siderite can crystallize at temperatures around 400° C and high f_{CO_2} near 10^4 atm., not pyrrhotite or other Fe-sulphides.

4) A consideration of figs. 21 and 22 shows that with decreasing temperature and/or f_{CO_2} pyrrhotite can crystallize in phase 4 from the entrapped fluids only if f_{S_2} and f_{O_2} also decrease, i.e., if the point representing the fluids shifts from "a" in the direction of, e.g., "b" or "c". Cooling and crystallization of sulphides presumably have progressively lowered f_{S_2} in the fluids and the succession of concentric zones of sulphides around the nodules may be related to the shrinking of f_{S_2}-gradients around these nodules.

Galena, pyrite and sphalerite crystallized in phases 2, 3, and 4 respectively; the galena has penetrated farthest into the enveloping siderite, pyrite less far, while sphalerite usually remains closest to the core of the nodules (p. 14). Thus, the outermost boundary of sulphide deposition shifts with time and decreasing temperature towards the core of the nodules; thereby a kind of zonal pattern is developed. The

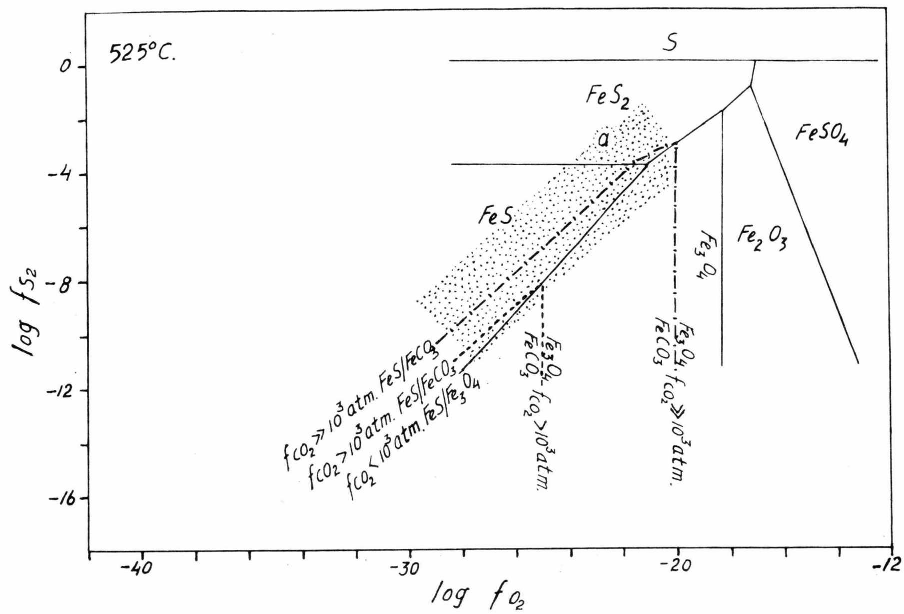

Fig. 21. Stability relations of iron minerals in the system Fe-S-C-O as functions of S_2- and O_2-fugacities at 525° C and fixed values of the CO_2-fugacities. For particulars see the text of the paper. Data after Holland 1959, 1965.

successive zones appear "telescoped", i.e. zones deposited in a later phase occur closer to the core of the nodules than zones deposited in a earlier phase. This "telescoping" cannot be adequately explained by assuming shrinking isotherms around the nodules because the fluids in the cavities and the enclosing siderite have presumably cooled together and have the same temperatures during each phase. However, the phenomenon is conveniently explained by the decrease of f_{S_2} with time. In phase 2 the fluids had comparatively high f_{S_2} and the cavities in the siderite were surrounded by an aureole of high f_{S_2}. Within this aureole siderite recrystallized and as the saturation point of PbS was reached galena is deposited at the same time. The diffusion of PbS farthest away from the cavities is easily accomplished at elevated temperatures when PbS is more soluble than, e.g., ZnS (Czamanske 1959, Kuz'mina 1961); furthermore, galena can crystallize in the outermost parts of the high-f_{S_2} aureole at lower values of f_{S_2} than, e.g., pyrite (Holland 1959, 1965). In phase 3 pyrite crystallized closer to the core of the nodules because higher f_{S_2}-values are needed for the crystallization of pyrite. In phase 4 f_{S_2} of the fluids had decreased so far that at the prevailing temperatures f_{S_2} was too low for the formation of pyrite and only pyrrhotite could crystallize. The concentric zones of pyrrhotite, chalcopyrite, and sphalerite formed in phase 4 are apparently due to steep f_{S_2}-gradients around

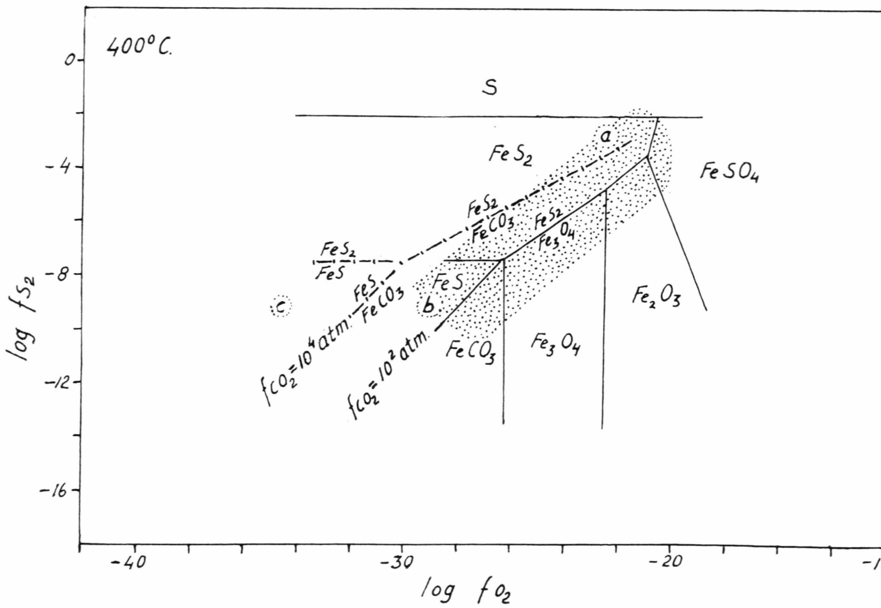

Fig. 22. Stability relations of iron minerals in the system Fe-S-C-O as functions of S_2- and O_2-fugacities at 400° C and fixed values of the CO_2-fugacities. For particulars see the text of the paper. Data after HOLLAND 1959, 1965.

the nodules; f_{S_2} was highest in the cavities where pyrrhotite crystallized and lowest in the sphalerite zone. At a given temperature sphalerite can crystallize at lower f_{S_2} than galena and much lower f_{S_2} than pyrrhotite (HOLLAND 1959, 1965). The inward shifting of the f_{S_2}-gradients also explains why the sphalerite zones apparently grew inward and why remobilized galena is redeposited at the inward side of the sphalerite zones.

Fig. 22 also shows that at temperatures around 400° C a decrease in f_{CO_2} shifts the FeS/$FeCO_3$ boundary towards the siderite field. Thus, with decrease of f_{CO_2} some pyrrhotite may be formed at the expense of siderite; this may explain the recrystallization of siderite in phase 4 and the formation of pyrrhotite along the chalcopyrite-siderite boundaries in phase 4 a.

5) At lower temperature, e.g. 250° C (fig. 23), and f_{CO_2} still near 10^2 atm. (bar-point line in fig. 23), siderite and pyrite have large stability fields, whereas pyrrhotite is stable only at very low f_S and f_{O_2}. The absence of sulphates and oxides in phase 5 indicates that f_{O_2} of the residual fluids was reduced, so that the fluid corresponds, e.g., to "c" in fig. 23. At the temperatures considered the residual fluid "c" may be in equilibrium with siderite at f_{CO_2} approximately 10^2 atm., but any decrease

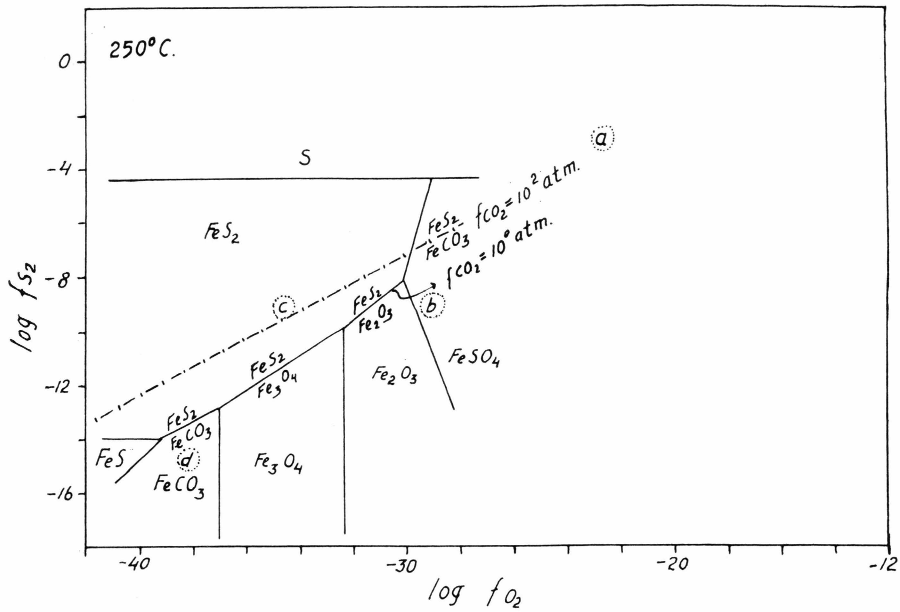

Fig. 23. Stability relations of iron minerals in the system Fe-S-C-O as functions of S_2- and O_2-fugacities at 250 C_2 and fixed values of the CO_2-fugacities. For particulars see the text of the paper. Data after Holland 1959, 1965.

in f_{CO_2} will cause the FeS_2-field to encroache on the $FeCO_3$-field (fig. 23), and this may result in the formation of FeS_2 at the expense of siderite. Thus, the formation of small marcasite dendrites at the expense of siderite in phase 5 may be caused by a continued reduction of CO_2-pressures at lower temperatures than in phase 4 a. The replacement by marcasite of pyrrhotite drops in sphalerite, where these drops are in contact with siderite, is also explained by the instability of pyrrhotite and siderite relative to FeS_2 under the same conditions as conceived for the formation of the small marcasite dendrites just describes.

At temperatures near 250° C the residual fluid "c" is also not in equilibrium with pyrrhotite. Therefore, in phase 5 pyrrhotite dissolved; the dissolved Fe and S were reprecipitated almost instantly as FeS_2, first in the form of coarse-grained marcasite dendrites, and later as pyrite infillings of these dendrites. Marcasite is apparently the stable form of FeS_2 at lower temperatures and under acid conditions (Allen and Crenshaw 1914; Rosenthal 1956); the pyrite infillings presumably indicate a shift towards more alkaline conditions with the decrease in temperature and CO_2/H_2O-ratio (Smith 1963, p. 346). Further lowering of f_{S_2} with the precipitation of sulphides caused the composition of the residual liquids to move in the direction of "d" in the siderite field of fig. 23. Thus, excess iron was precipitated in the last stages of phase 5 as siderite in late siderite veinlets crossing the marcasite dendrites.

OELSNER and STARKE (1964) have shown experimentally that at 200° C and a few atm. CO_2-pressure Fe-rich pyrrhotite breaks down into Fe-poor pyrrhotite and Fe, which latter is removed by CO_2-bearing solutions to become fixed as siderite.

General remarks on the replacement of siderite and of pyrrhotite by marcasite

Two stages of marcasite formation have been recognized:

1) In a first stage marcasite has replaced siderite along the boundaries of siderite with Fe-sulphides and chalcopyrite. This replacement is mainly related to a decrease in CO_2-pressures, which causes the FeS_2 stability field to encroache on the siderite field. Decrease in temperature is not essential (compare figures 22 and 23), although temperatures should be below 300° C to enable the formation of marcasite.

2) In a second stage the dissolution of pyrrhotite and the formation of marcasite dendrites with pyrite infillings and of late siderite veinlets seem causally related processes, occurring mainly as a result of cooling of high-temperature pyrrhotite in the presence of CO_2-rich solvents. Decrease of f_{CO_2} will delay rather than accelerate the dissolution of the pyrrhotite (see figs. 22 and 23).

Marcasite may be a very common hypogene or primary mineral which is formed in the course of cooling of Fe-sulphide-carbonate parageneses. In most recorded instances of replacement of pyrrhotite by marcasite carbonates form part of the paragenesis (EDWARDS 1954). If cooling is relatively slow a decrease in CO_2-pressure (e.g. by escape of CO_2 or crystallization of carbonates) may cause the replacement of earlier carbonates by marcasite; if cooling is comparatively rapid replacement of pyrrhotite by marcasite may result.

In the main sulphide paragenesis of the cryolite ore marcasite has also been observed as small dendrites along chalcopyrite-siderite boundaries. These marcasite dendrites often occurs closely associated with stannite replacing cassiterite (Plate V, fig. 3). The latter replacement is presumably induced by or related to similar conditions as those which governed the formation of the marcasite dendrites, i.e., acid environment, temperatures below 300° C, and a significant lowering of O_2-pressures, presumably related to a lowering of CO_2-pressures. Similar replacements of cassiterite by stannite along boundaries with pyrrhotite and chalcopyrite have been described by NOVÁK, BLÜML and TACL (1962).

Conclusion

The pyrrhotite-marcasite aggregates and associated sulphides occurring as nodules in coarse-grained siderite in the siderite-cryolite ore of Ivigtut may be considered as crystallization products of fluids, which were entrapped in the siderite during crystallization of the siderite masses. The entrapped fluids were characterized by high CO_2-pressures and relatively high S_2-pressures and contained certain amounts of dissolved Pb, Cu, Zn and other metals. Crystallization from the fluids occurred during cooling of the system from over 500° C to approximately 200° C under conditions of decreasing CO_2-, S_2-, and O_2-pressures. The rate and amount of the decrease in CO_2-pressures were significant in causing the stability fields of the iron-sulphides to encroache on that of siderite, so that iron-sulphides could crystallize from the fluids. The concentric zonation of sulphides around the nodules is explained by the control of f_{S_2}-gradients around the nodules; the f_{S_2}-isogrades shifted with time toward the core of the nodules.

The rare occurrence or absence of Fe-sulphides in the main sulphide paragenesis of the siderite-cryolite ore of Ivigtut may indicate that in all phases of crystallization of the latter paragenesis S_2-pressures were always too low for the formation of Fe-sulphides. The main sulphide paragenesis probably crystallized from differentiated and diluted fluids, whereas the pyrrhotite-marcasite nodules are derived from fluids entrapped in the siderite in an early stage of the differentiation process.

In a recent paper Rose (1965) has described pyrite nodules from the Timagami copper-nickel deposit, which in some respects may show similarities with the nodules described in this paper.

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Færdig fra trykkeriet den 4. februar 1967.

PLATES

Plate I

Fig. 1. A pyrrhotite-marcasite nodule in coarse-grained siderite 15 cm across. The cavernous marcasite dendrites is traversed by a siderite veinlet (centre of figure). The thin mantle of sulphide bands and fine-grained recrystallized siderite surrounding the marcasite core of the nodule is not well visible on the photograph. HALKIER phot.

Fig. 2. Pyrite idioblast with zonally arranged inclusions of galena. 185 x.

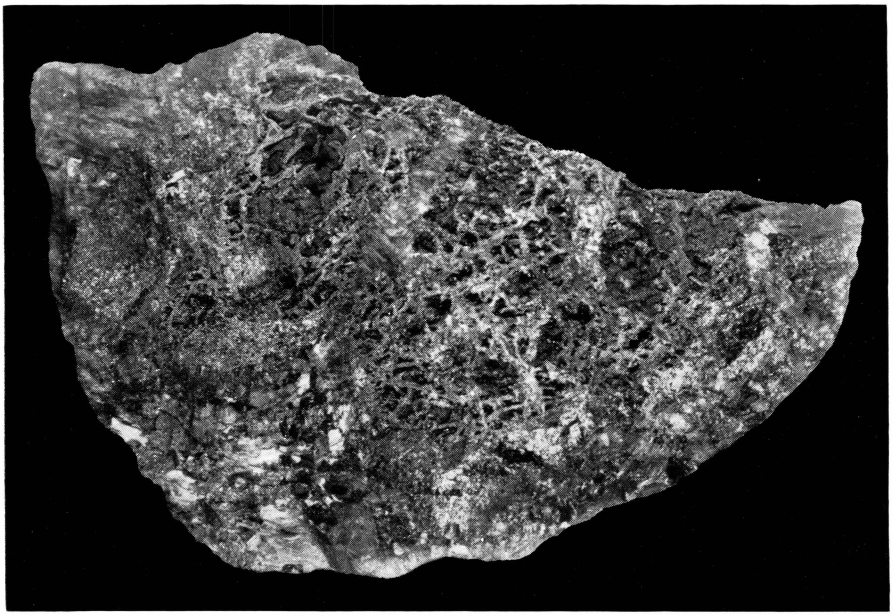


Fig. 1.

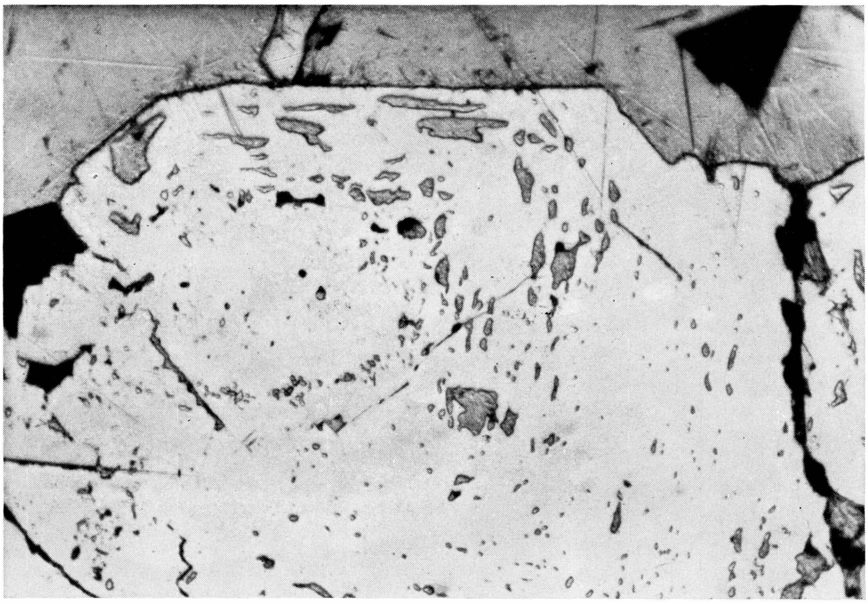
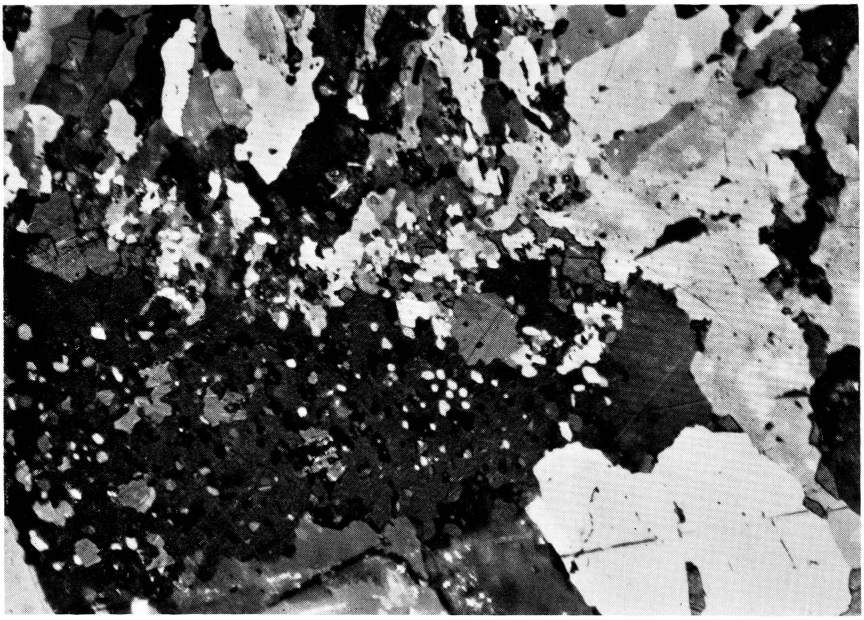


Fig. 2.

Plate II

Fig. 1. A sphalerite streak with adjoining zone of fine-grained recrystallized, columnar siderite. Where the sphalerite streak wedges out the adjoining zone of columnar siderite also disappears. See text-figures 10 for further explanation of the photograph. Crossed nicols, 85 x. WIERSMA phot.

Fig. 2. Detail of the zone of fine-grained recrystallized, columnar siderite in polished section 821 (text-figure 2). Chalcopyrite appears white (top half of the picture). Galena also appears white, but the mineral is characterized in the picture by heavier outlines. Siderite is dark grey and sphalerite light grey. The small, irregular white areas along the chalcopyrite-siderite boundaries consist of pyrrhotite. For more details see the description of text-figure 11 and the text of the paper. 85 x. WIERSMA phot.



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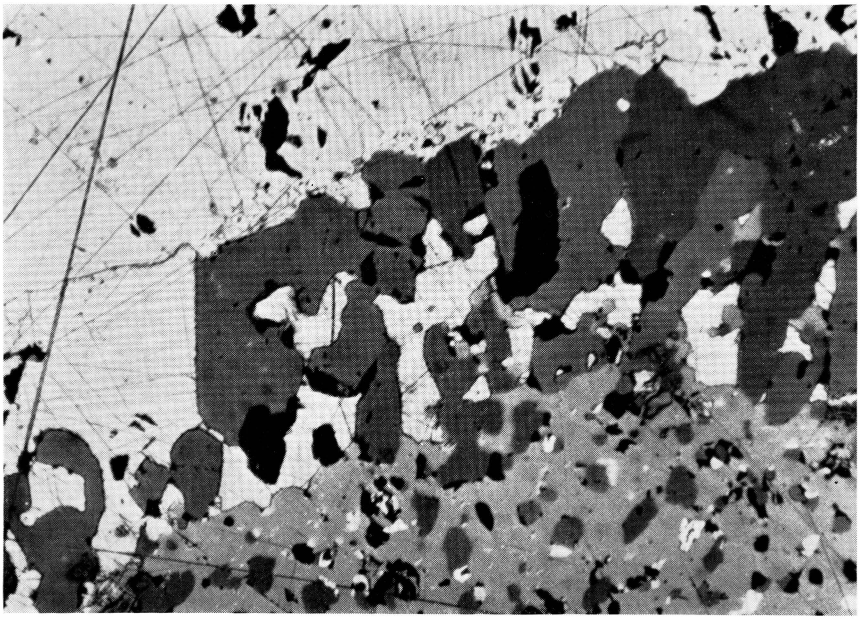


Fig. 2.

Plate III

Figs 1 and 2. Details of the zone of fine-grained recrystallized, columnar siderite in polished section 821 (text-figure 2). For explanation see the description of plate II, fig. 2, and the text of the paper. Fig. 1 shows two thin galena bands in the zone of columnar siderite between the sphalerite and chalcopyrite zones; in fig. 2 the sphalerite band has approached the chalcopyrite zone more closely and the two thin galena bands of fig. 1 have here merged into one thicker band of galena. In the latter case the zone of columnar siderite has disappeared almost completely. 85 x. WIERSMA phot.

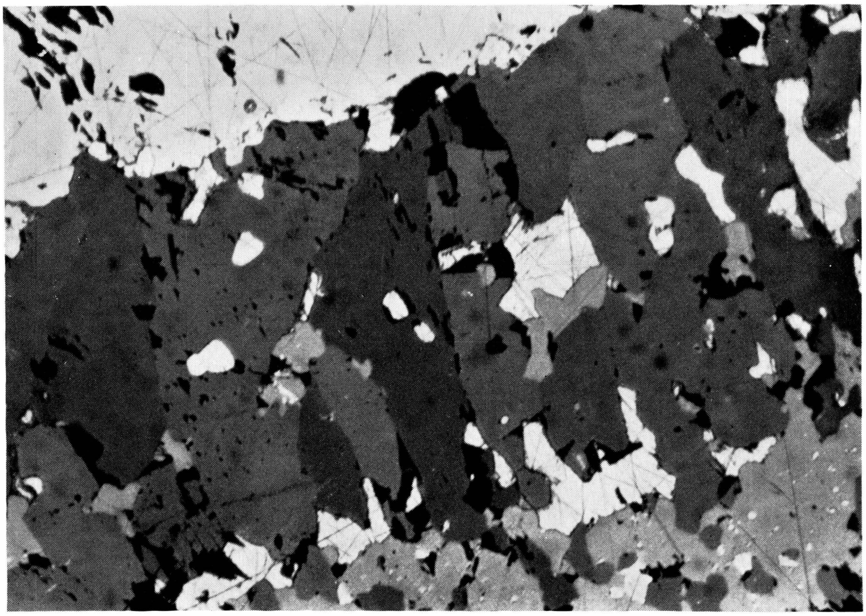


Fig. 1.

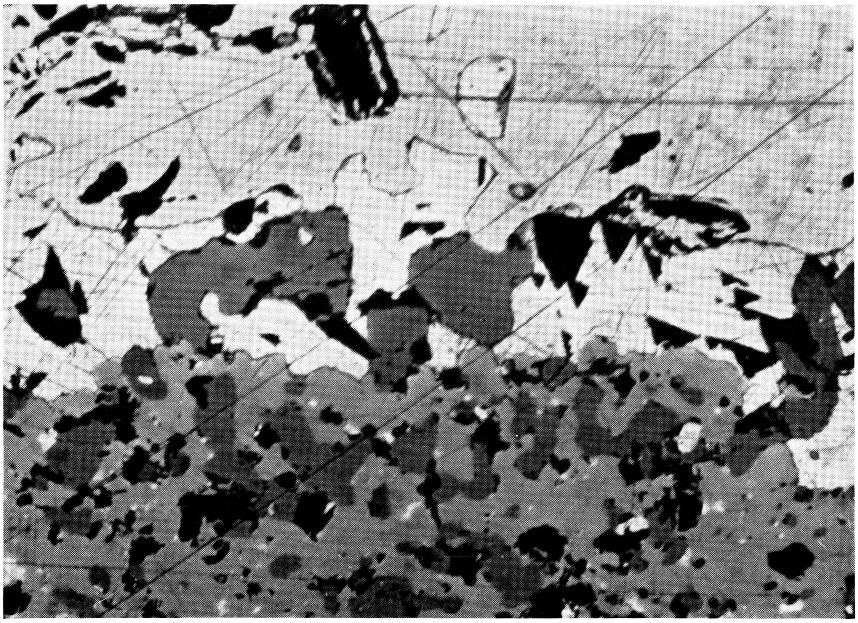
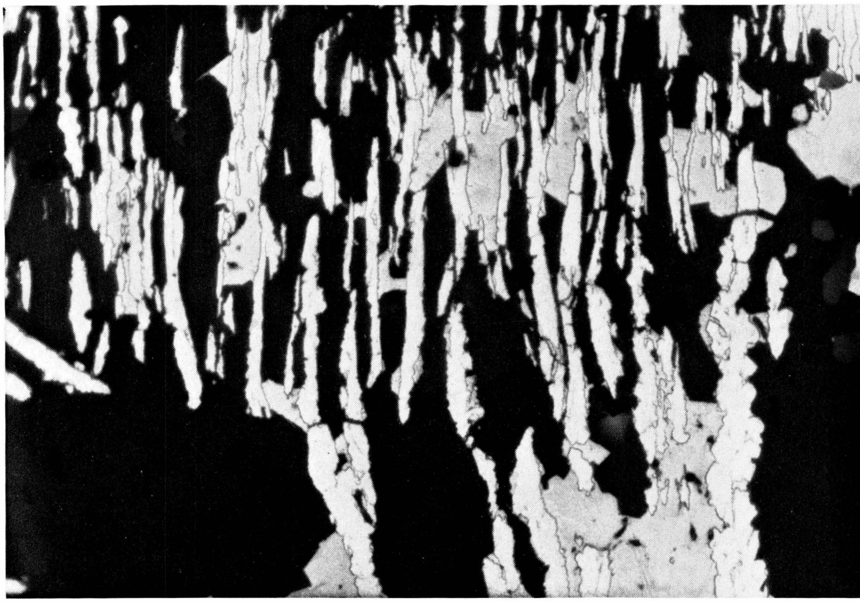


Fig. 2.

Plate IV

Fig. 1. Marcasite lamellae in siderite. See text-figure 18 for explanation. Note the fractured marcasite lamella, which is traversed by a siderite veinlet (upper right hand side of the picture). 185 x.

Fig. 2. Marcasite lamellae along the boundary of the chalcopyrite zone in polished section 1483. The lamellae occur partly in chalcopyrite (white) and partly in siderite (dark). 185 x.



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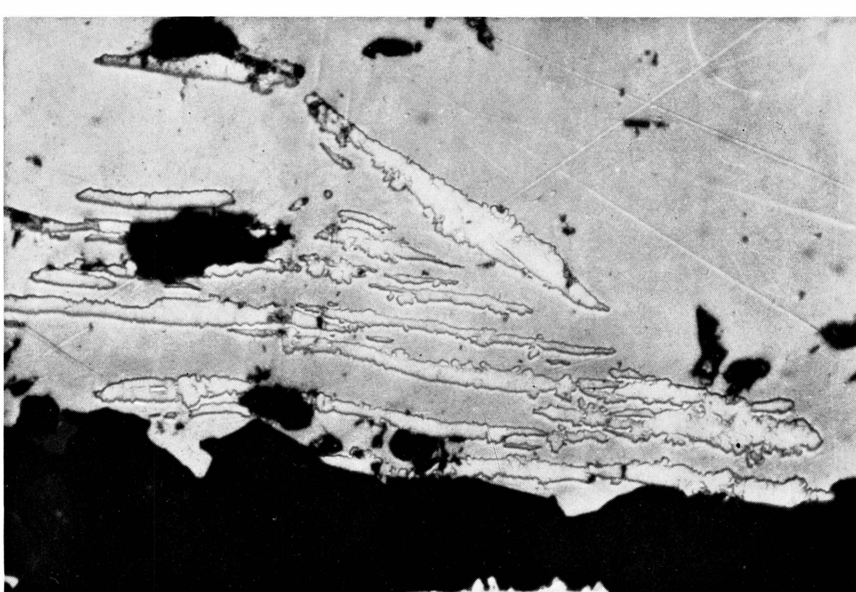

Fig. 2.

Plate V

Fig. 1. Arsenopyrite idioblast in galena. 185 x.

Fig. 2. Inclusions of pyrrhotite, small dark grey areas, in marcasite. 185 x.

Fig. 3. Marcasite lamellae along chalcopyrite-siderite boundaries in the main sulphide paragenesis. Note the association with stannite (grey) containing numerous small, relict inclusions of cassiterite. 200 x.

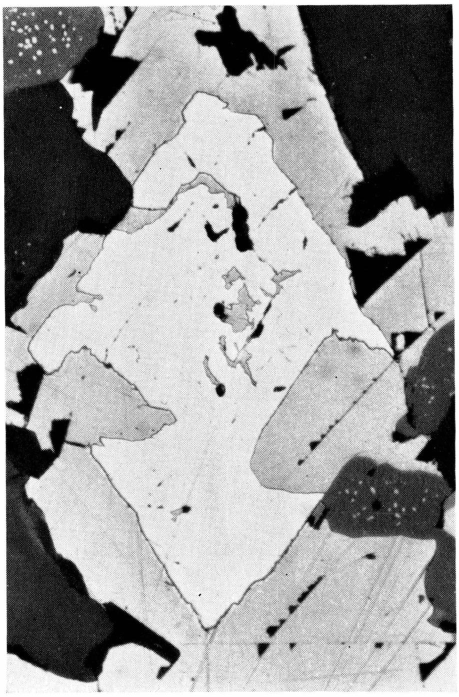

Fig. 1.

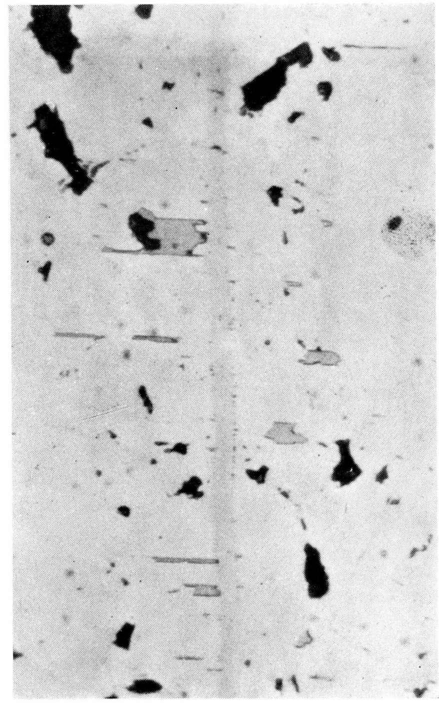

Fig. 2.

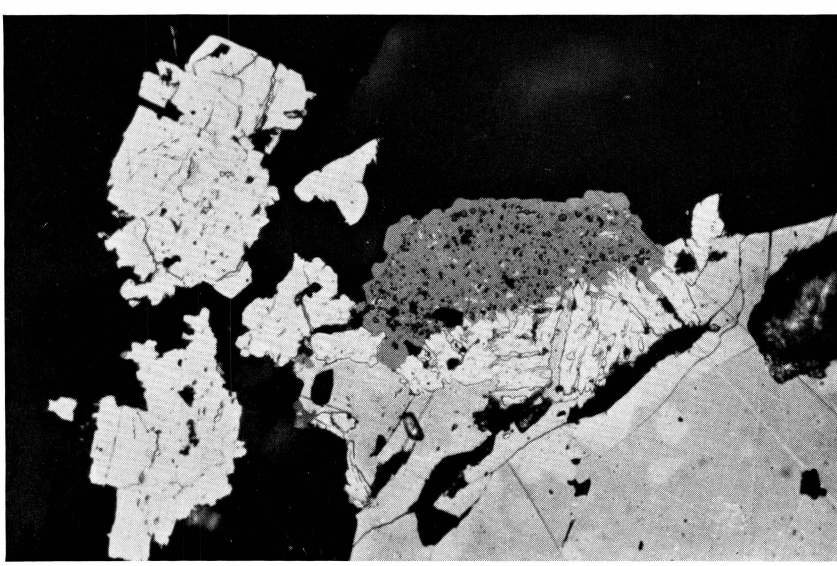

Fig. 3.