

GEOLOGINEN TUTKIMUSLAITOS

BULLETIN
DE LA
COMMISSION GÉOLOGIQUE
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N:o 217

THE COMPOSITION AND CONDITIONS OF FORMATION
OF ARSENOPYRITE AND LÖLLINGITE IN THE
YLÖJÄRVI COPPER-TUNGSTEN DEPOSIT,
SOUTHWEST FINLAND

BY
ALAN HORRELL CLARK

WITH 15 FIGURES AND 3 TABLES IN TEXT

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ABSTRACT

X-ray diffraction analysis of 214 specimens indicates that arsenopyrite in the Ylöjärvi deposit shows a wide variation in arsenic content, from ~ 30 to 36.6 atomic per cent. The compositional variation is interpreted as suggesting that crystallization of this mineral commenced at $\sim 700^{\circ}\text{C}$, and continued to $580\text{--}600^{\circ}\text{C}$, under confining pressures probably in excess of 2000 bars. Brecciation and mineralization may have taken place at a depth of 7—11 km, the elevated temperatures of arsenopyrite deposition supporting the magmatogene, hydrothermal nature of the ore fluids. Minor Co, Ni, Sb, Bi and Se show no relation to the As:S ratios of the host arsenopyrites, and these elements did not attain equilibrium concentrations or partitioning. Minor replacement of arsenopyrite by löllingite occurred at temperatures below approximately 300°C .

PART I
MAJOR ELEMENT COMPOSITION OF THE ARSENOPYRITE

INTRODUCTION

Recent experimental studies on the phase equilibria of the more important sulphide systems have encouraged the estimation of the P-T conditions prevailing during mineralization in a considerable number of sulphide deposits. Although the sphalerite geothermometer (Kullerud, 1953) has been shown by Barton and Toulmin (1964) to be of probably dubious validity, the temperatures of formation of many sulphide assemblages may be deduced with some degree of confidence. Less is known, however, about the confining pressures under which ore deposits have formed, a factor of importance in the classification of mineral deposits, and in the detailed study of mineralized areas. Under favourable conditions, the depth at which mineralization occurred may be estimated by calculation of the thickness of the superincumbent strata, or by the study of fluid inclusions in minerals, but these approaches have generally proved successful only for deposits of shallow formation. In a general geological context a reliable mineral »geobarometer» would be of great value in the interpretation of mineral parageneses.

In the course of an experimental investigation of the Fe-As-S system, L. A. Clark (1960a, b) found that the solvus curves relating the composition of arsenopyrite to the temperature of crystallization are very steeply inclined, and are markedly affected by confining pressure. Thus, although it appeared improbable that the composition of arsenopyrite could be used as a very precise geothermometer, Clark suggested that this mineral might find application as an indicator of confining pressures if its temperature of deposition could be estimated by independent means. Arsenopyrite, though generally restricted in its occurrence to the immediate vicinity of ore deposits, is sufficiently widespread to be potentially a useful geobarometer. This mineral is a major constituent of the Ylöjärvi copper deposit, Finland, which has been the subject of a mineralogical and geochemical study by the writer (1964a). In this deposit the temperatures of ore deposition were estimated independently from analyses of pyrrhotite and sphalerite. The composition of the

arsenopyrite has been examined in some detail, in a preliminary attempt to evaluate the possible applicability of this mineral as a geobarometer for natural assemblages. A summary of the results of this study has been published (1964c).

EXPERIMENTAL BASIS

Prior to the investigations of L. A. Clark (1960a), knowledge of the phase equilibria in the ternary system Fe-As-S was negligible. Clark has summarized previous work on compositional relations between minerals in the system, and these earlier studies will not be discussed here. McKinstry (1957) tentatively proposed phase relations in the ternary system on the basis of the known natural mineral assemblages, and recently (1963) re-examined these in the light of Clark's experimental data.

Clark (1960a) determined the equilibrium phase relations in the ternary system at 600°C, and studied the changes in the stable assemblages from 400°C to 800°C. The more important conclusions of this work, as far as the study of natural assemblages containing arsenopyrite is concerned, are as follows:—

1. Arsenopyrite is stable in the presence of vapour at all temperatures to $702 \pm 3^\circ\text{C}$, above which temperature the assemblage löllingite-pyrrhotite-liquid is stable. Thus the presence of arsenopyrite is not in itself a criterion for deposition at high temperatures, as has often been assumed.

2. The assemblage native arsenic-arsenopyrite, rare in nature, is unstable above $\sim 688^\circ\text{C}$.

3. Pyrite and arsenopyrite cannot coexist in equilibrium with vapour above $491 \pm 12^\circ\text{C}$. If these minerals are in contact, and equilibrium is assumed to have obtained during deposition, one or both minerals must have been deposited below this temperature. It is often difficult to decide whether equilibrium conditions were achieved, however, and the composition of the arsenopyrite must be taken into account in interpreting such assemblages.

The composition of arsenopyrite, which shows a variation in arsenic:sulphur ratio on either side of ideal FeAsS, is dependent on the temperature and confining pressure during deposition, as well as on the nature of the co-existing minerals — whether sulphides or arsenides. Morimoto and Clark (1961) have reviewed the more reliable chemical analyses of arsenopyrite, and conclude that the Fe:As+S ratio of this mineral is consistently 1:2, the iron content remaining constant at $33 \frac{1}{3}$ atomic per cent. The arsenic:sulphur ratio, the most important parameter in the study of arsenopyrite compositions and phase relations, may be estimated rapidly by measurement of the 131 spacing of the metrically monoclinic unit-cell (Clark 1960a; Morimoto and Clark, 1961).

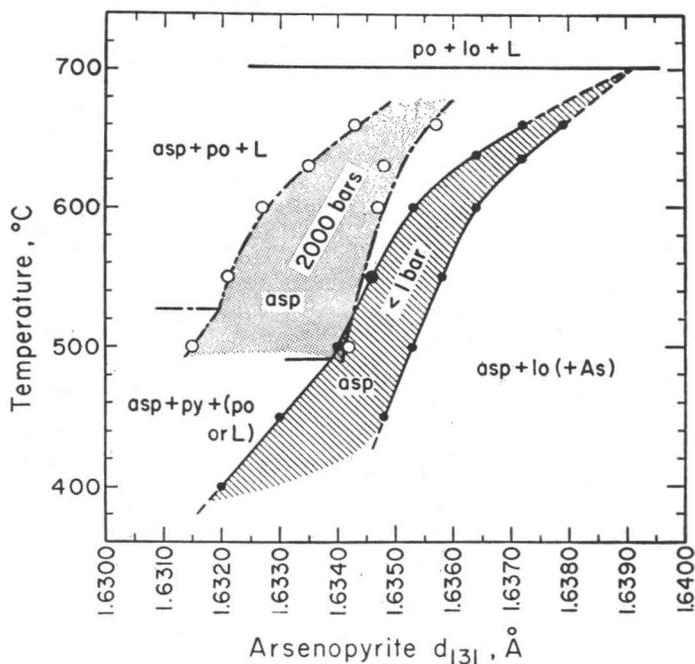


Fig. 1. T-X plot showing the fields of stability of arsenopyrite at < 1 bar and 2000 bars confining pressure; the section at 1000 bars, occupying an intermediate position, has been omitted. The phase relations are projected from P-T-X space onto a part of the FeS_2 - FeAs_2 pseudobinary T-X section. The 131 spacing of arsenopyrite varies as a function of the arsenic: sulphur ratio. Abbreviations: asp, arsenopyrite; po, pyrrhotite; py, pyrite; lo, löllingite; and L, liquid. (After L. A. Clark, 1960 b).

In an extension of the original work on the Fe-As-S system, Clark (1960b) examined in more detail the dependence of the composition of arsenopyrite on temperature and confining pressure. This study has been the basis of the present work. Clark determined the variations of arsenopyrite composition in equilibrium with sulphur- and arsenic-rich fluids at confining pressures of < 1 , 1 000, and 2 000 bars, and at temperatures from 702°C to below 500°C (Fig. 1). The data for the sulphur-rich P-T-X surface are redrawn on the P-T plot of Fig. 2, the 131 spacing contours representing lines of constant As:S ratio. This diagram facilitates the application of the compositional data to the estimation of temperatures and confining pressures of arsenopyrite deposition. In order to make an estimate of confining pressure, it is necessary to ascertain that the arsenopyrite was deposited in association with sulphides as opposed to arsenides, and that the combined minor

element content in the arsenopyrite does not exceed 1.0 weight per cent. It was suggested by Clark that determination of the temperature of deposition to within 40°C would permit the estimation of confining pressure to within 400 bars.

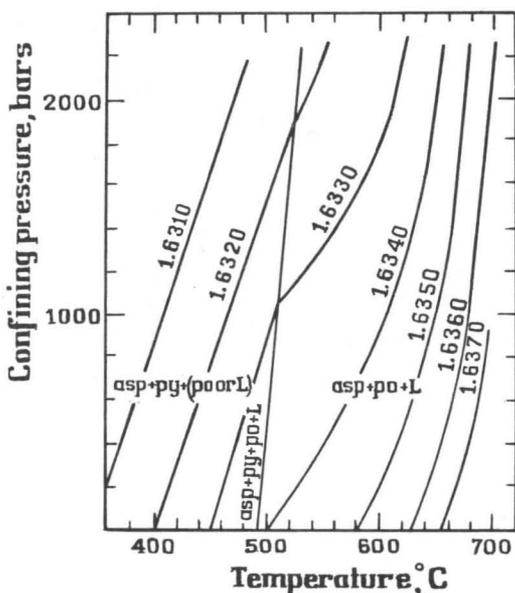


Fig. 2. Lines of constant 131 spacing, and As:S ratio, projected from the sulphur-rich P-T-X surface of the arsenopyrite stability field, and plotted as contours on the P-T projection. The upper stability curve of the pyrite-arsenopyrite assemblage (L. A. Clark, 1960 a) is also shown; the contour positions on the low-temperature side of this curve are approximate because pressure data were not obtained below 500°C. (After L. A. Clark, 1960 b).

PREVIOUS APPLICATIONS OF THE DATA

Clark (1960b) briefly discussed the application of the arsenopyrite geobarometer, and estimated the confining pressures affecting sulphide deposition in the Giant Yellowknife (Northwest Territories) and Parrex prospect, Hansen Lake (Saskatchewan) deposits. Pressures of approximately 2 500 and 1 100 bars were obtained for these parageneses, where the temperatures of deposition could be estimated using the sphalerite geothermometer. In each case only one arsenopyrite was examined, and no attempt was made to determine the range of composition of this mineral.

Other applications of the phase relations in the Fe-As-S system have generally been restricted to the observation that, where arsenopyrite and pyrite coexist, mineralization evidently took place below ~ 491°C (e.g., Markham, 1961; Kalliokoski, 1961; Priem, 1962; Arnold, Coleman and Fryklund, 1962; Boyle and Jambor, 1963). In these studies equilibrium between pyrite and arsenopyrite was assumed, although the paragenetic relations between these two minerals were often ill-defined. The compositions of the arsenopyrites were not estimated. In the Nigadoo deposit, New

Brunswick (Kalliokoski, 1961) arsenopyrite with $d_{131} = 1.6321 \pm 0.0003 \text{ \AA}$ (L. A. Clark, written communication) is associated with sphalerite whose iron content indicates a temperature of deposition of up to $\sim 670^\circ\text{C}$. Kalliokoski considered that the arsenopyrite was deposited later than the sphalerite, and concluded that »the temperature must have dropped about 180°C by the time that arsenopyrite was crystallizing» (*op. cit.*, p. 1450). Roy (1961), however, suggested, on the basis of textural studies, that arsenopyrite preceded sphalerite, and the significance of the arsenopyrite/pyrite relationships in this paragenesis cannot be evaluated.¹

Gottardi (1962), in an interesting study of the Ortano sulphide deposit, Isle of Elba, suggested that arsenopyrite with a 131 spacing of 1.634 \AA was deposited at $\sim 500^\circ\text{C}$, while later hexagonal pyrrhotite crystallized at $\sim 375^\circ\text{C}$. The writer has carried out a preliminary re-examination of arsenopyrite and pyrrhotite from this deposit (1963) and has shown that the arsenopyrite apparently has a widely variable composition. Although it is probable that deposition of this mineral took place at temperatures above 450°C , more data are needed before a reliable estimation of the conditions of ore deposition in the Ortano deposit may be made.

On the basis of the compositions of coexisting arsenopyrite, pyrrhotite and sphalerite in the apical zone of the greisenized Panasqueira granite, Portugal, the writer has suggested that the emplacement of the granite and of the associated wolframite- and cassiterite-bearing quartz vein system took place under confining pressures in the range 500—1000 bars, and at a temperature of $\sim 700^\circ\text{C}$ (1964b).

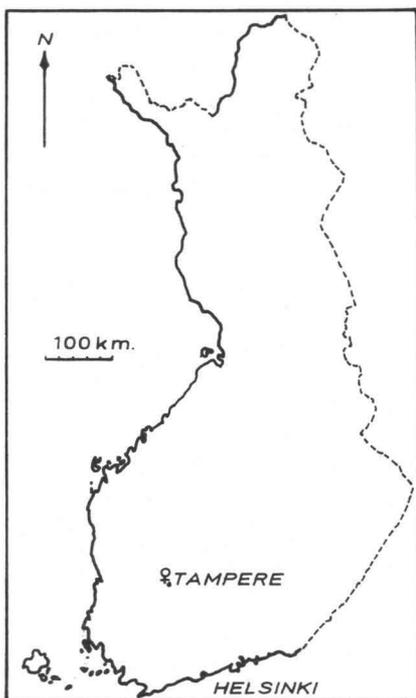
Prior to the above-mentioned and the present studies no detailed work has been carried out on the variations in composition shown by arsenopyrite in individual deposits or orebodies. Studies of this nature are clearly a necessary preliminary to the evaluation of the arsenopyrite geobarometer. In view of the wide variations in the concentration of minor elements in this mineral it was, furthermore, felt that a careful study of the distribution of both minor and major elements in the arsenopyrite of the YlÖjärvi deposit might yield significant data on the spatial and geochemical evolution of the ore solutions.

THE YLÖJÄRVI DEPOSIT

Copper has been mined since 1943² from the YlÖjärvi mine (Outokumpu Oy), situated at Paroinen, some 23 km northwest of Tampere, in southwest

¹) The writer is at present examining the compositions of arsenopyrite and pyrrhotite in the Nigadoo deposit.

²) Production ceased towards the end of 1964.



Finland (Fig. 3). Production has been moderate, but at present averages some 300 000—350 000 tons of ore per annum. In 1961, 8821 tons of chalcopyrite concentrate, containing 22.4 per cent Cu, and 390g/t Ag, were obtained from 325.583 tons of ore. In addition, up to 400 tons of scheelite concentrate are produced yearly.

Fig. 3. Index map of Finland showing Ylöjärvi mine.

GEOLOGICAL SUMMARY

Himmi (1954, 1960) has concisely described the geology of the Ylöjärvi deposit. A detailed account of the mineralogy of the ore zones is in the course of preparation by the present writer, and only a brief summary of the relevant details will be given here.

The orebodies at Ylöjärvi occur in a steeply plunging brecciated zone, with an irregular lenticular plan, which cuts metamorphosed Svecofennian (Bothnian) basic-intermediate tuffs («tuffites»), agglomerates, and intermediate-acid lavas («porphyrites») (Fig. 4). The deposit is the largest of a series of tourmaline-cemented breccia bodies developed around the eastern and northeastern margins of the Hämeenkyrö quartz-diorite intrusion (Simonen, 1952), which constitutes a possible source of the mineralizing solutions. Brecciation closely followed amphibolite-grade regional metamorphism and later retrograde alteration to the epidote-amphibolite facies. The earliest stage of the mineralization included the crystallization of blue-green hornblende, almandine-spessartine garnet, biotite, magnetite and apatite in the country rocks in the immediate vicinity of the breccias. Intense silicification and local chloritization followed.

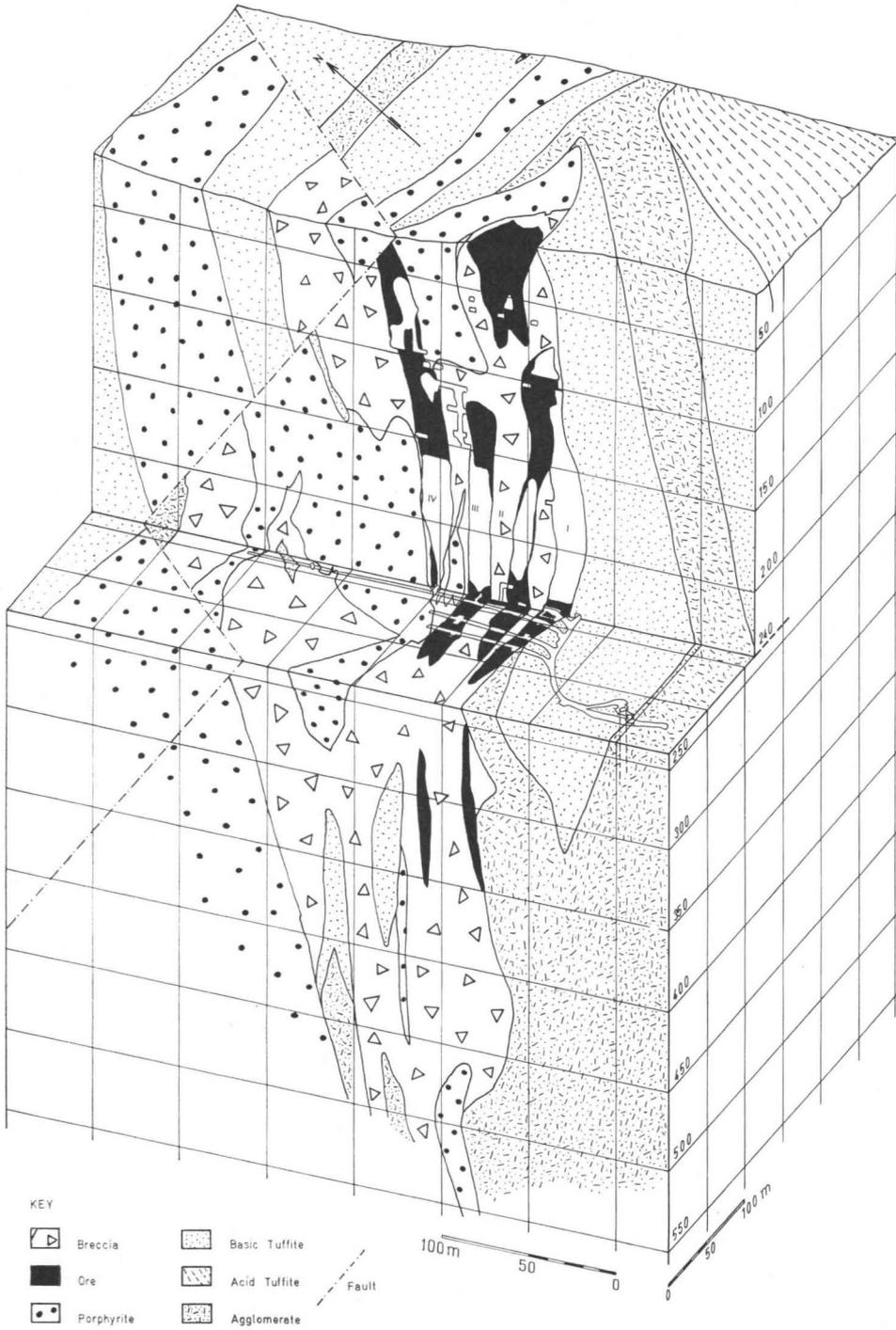


Fig. 4. Block diagram of the Ylöjärvi deposit. (After R. Himmi, 1960, 1961).

PARAGENESIS OF MAIN STAGE OF MINERALIZATION, YLÖJÄRVI DEPOSIT

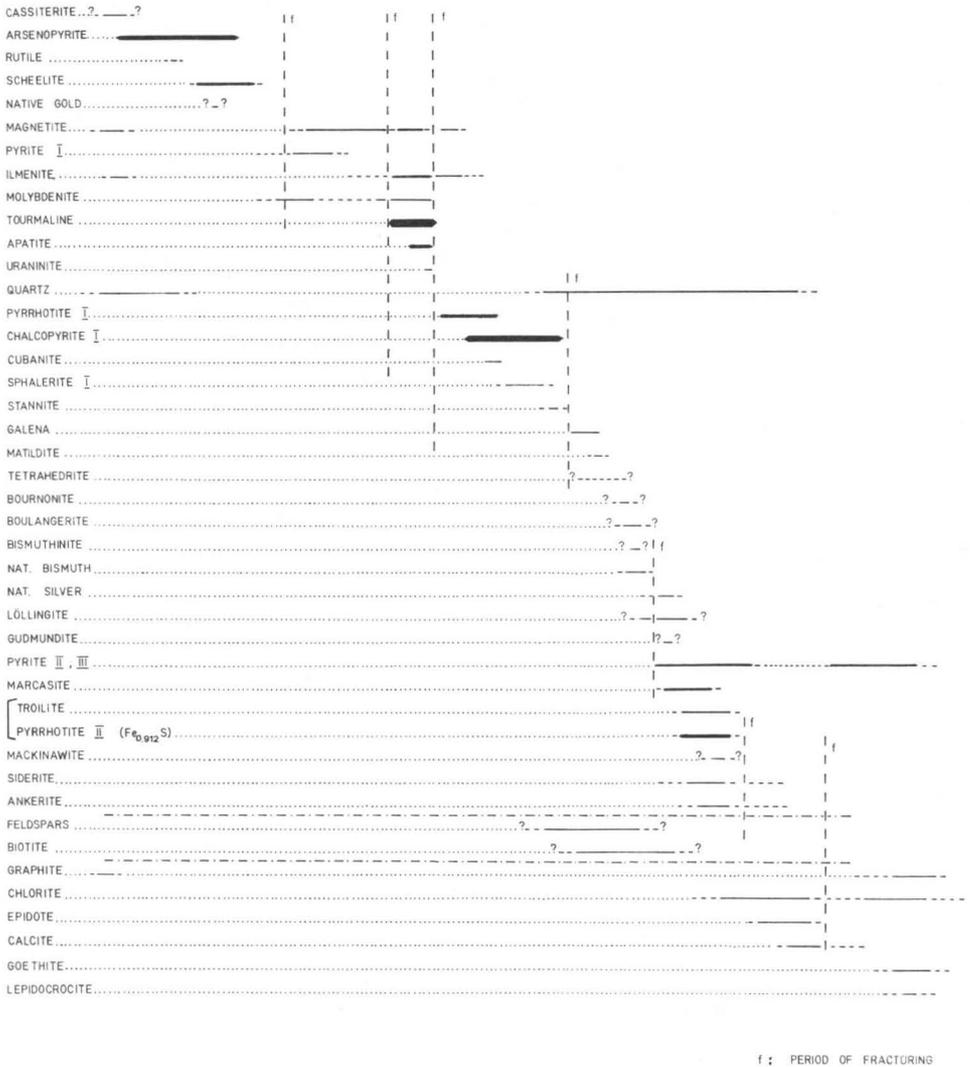


Fig. 5. Generalized paragenesis of the main stage of mineralization, Ylöjärvi deposit. Major minerals represented by broad lines. Feldspar and biotite of the flat-lying pegmatitic veins are enclosed within the dashed-dotted lines.

The ore and gangue minerals occur predominantly in the matrix of the breccias, although arsenopyrite and minor molybdenite, ilmenite, and magnetite were metasomatically introduced into the silicified wall-rocks. A generalized paragenetic scheme for the ore and gangue minerals is given in

Fig. 5. Several of the relations are uncertain, but the overall sequence of deposition is clear. Some 176 polished sections were examined microscopically in the course of this paragenetic study.

Arsenopyrite was probably the first sulphide to crystallize and was approximately contemporaneous with cassiterite, some magnetite, scheelite, quartz, and rutile. The paragenetic relations of the arsenopyrite will be described in the following section. Fracturing continued, albeit sporadically and with decreasing intensity, throughout the duration of the mineralization. The effects of some periods of cataclasis may be traced in all zones of the orebodies, and are invaluable in the clarification of the depositional sequence, but others affected only restricted zones.

Four main orebodies, henceforth designated »orebodies I, II, III, and IV», from southeast to northwest (Fig. 6), have been delimited within the main breccia zone for the purposes of mining, and are more or less continuous from the surface to a depth of about 300 m. Below this level the overall width of the breccia pipe decreases, and zones of high-grade mineralization are sporadic and irregular. Although the limits of the orebodies are economic (cut-off grade, ca. 0.5—0.6 per cent Cu), the four zones have been shown to be mineralogically and geochemically distinct in several respects. Scheelite of economic grade is restricted to orebody I.

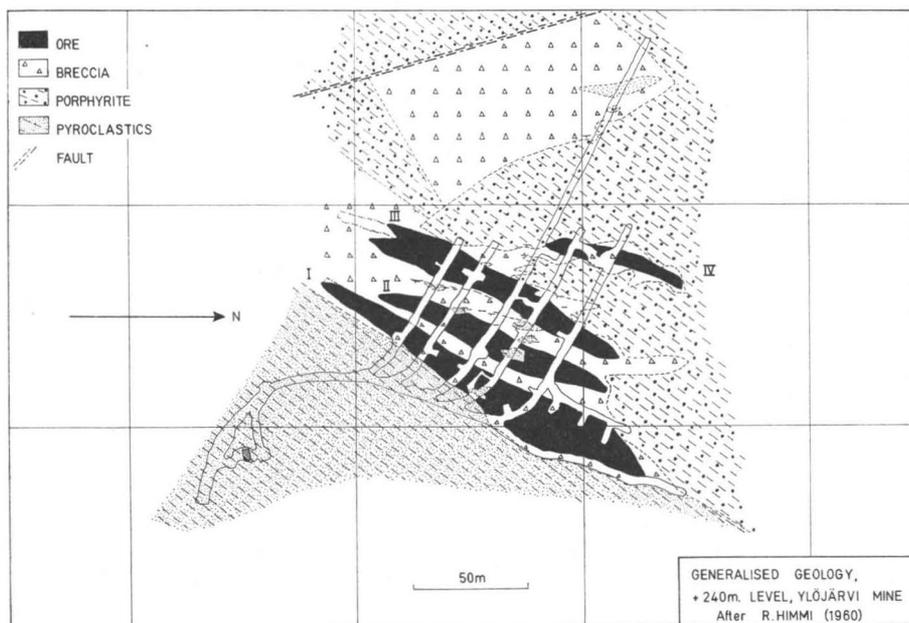


Fig. 6.

The major concentration of arsenopyrite is in orebody IV, especially below the 240 m level; in this zone, which averages 0.6—0.8 per cent As, chalcopyrite, elsewhere the dominant sulphide, is exceeded by arsenopyrite. Arsenopyrite is a common constituent of orebody I, but is generally present in only minor amounts in orebodies II and III.

It has been possible to collect representative samples of arsenopyrite in almost all underground exposures of the mineralized zones, but drill cores have been relied upon for the zones from surface to the 60 m level, and from the bottom level (465 m) to below 560 m.

Although the cause of the brecciation is unknown — Himmi (1960) suggests that it may have been the result of gaseous explosion, and certainly a simple tectonic fracturing appears to be very unlikely — the mineralization at the present level of exposure is undoubtedly epigenetic with respect to the volcanic country rocks. In many respects the mineralogy and structure of the deposit are closely comparable to those of the tourmaline-copper breccia pipes of the Andean province (e.g., the Braden deposit: Howell and Molloy, 1960). It has been assumed that the transport of the ore and gangue minerals was effected by means of hypogene solutions rising through the shattered zone, but the source of these solutions is not defined. This factor does not, however, affect the interpretation of the compositional data presented below.

PARAGENETIC RELATIONS OF ARSENOPYRITE

The relations between arsenopyrite and the other sulphides in the Ylöjärvi ores are similar to those described by many authors from other comparable deposits. Arsenopyrite either forms euhedral, wedge-shaped crystals disseminated in the metasomatized wall-rocks, and breccia fragments and matrix, (Fig. 7), or occurs as massive aggregates of coarse, subhedral-anhedral grains cementing the breccias. The euhedral crystals are generally short and stumpy, but highly elongate needles with length:breadth ratios of up to 40:1 have been observed (Fig. 8). The euhedral nature of much of the arsenopyrite hinders the clarification of its paragenetic relations with many associated minerals, but both in underground exposures and microscopically it is evident that tourmaline and the sulphides of the chalcopyrite-pyrrhotite assemblage were introduced later than a period of fracturing affecting the arsenopyrite (Fig. 5). Chalcopyrite, particularly, often occurs as fine veinlets in fractured arsenopyrite, although it is unlikely that any extensive replacement of the earlier sulphide took place. The microscopic textures suggest that arsenopyrite remained, for the most part, chemically stable during the deposition of the later ore minerals, of which only rare tetrahedrite-tennantite and löllingite, which replaced arsenopyrite to a minor degree, contain arsenic.

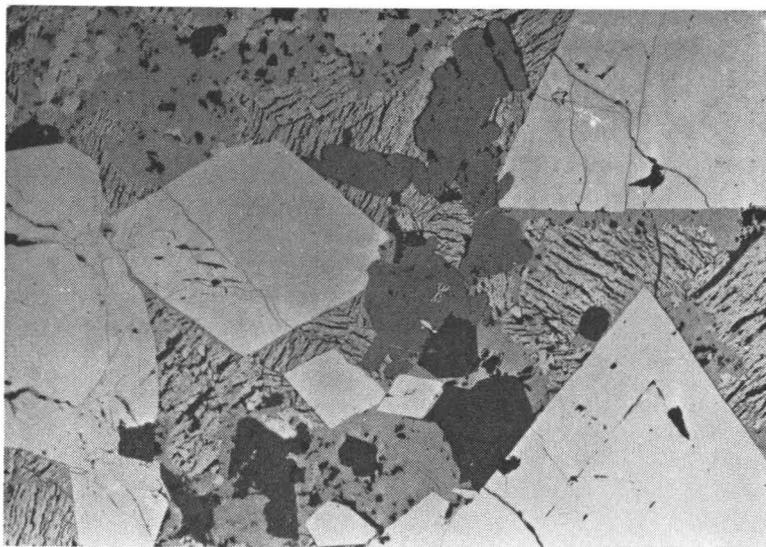


Fig. 7. Euhedral crystals of arsenopyrite ($d_{131} = 1.6330 \pm 0.0003$ Å), enclosed by intergrowths of later ilmenite laths (dark grey), marcasite-pyrite II partial pseudomorphs after pyrrhotite (medium grey), chalcopyrite (pale grey), and tourmaline. Orebody IV, 358 m level. (Reflected light, in air; nicols uncrossed; $\times 65$).

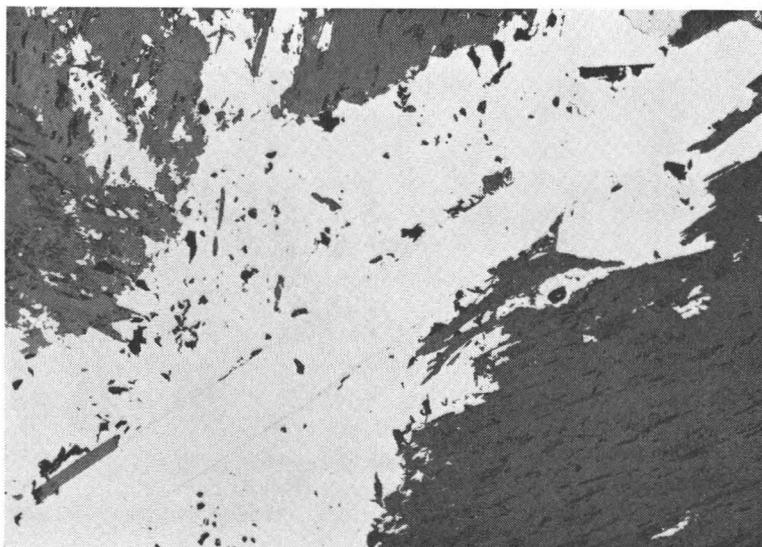


Fig. 8. Highly acicular arsenopyrite crystal, enclosed by anhedral arsenopyrite, chalcopyrite, tourmaline, quartz, and chlorite. Orebody IV, 330 m level. (Reflected light, in air; nicols uncrossed; $\times 60$).

The relations to the ore minerals introduced before the formation of tourmaline are often less clear-cut. In many polished sections magnetite and ilmenite are seen to be definitely later than arsenopyrite, and may replace that mineral to a limited extent (Figs. 9, 10), although it is possible that crystallization of magnetite may have taken place both during the period of initial wall-rock alteration and throughout much of the earlier stages of sulphide mineralization. Ilmenite laths frequently infill fractures in, or contain brecciated fragments of arsenopyrite, and it is probable that all but a small portion of the ilmenite crystallized later than the arsenopyrite. Molybdenite may be strikingly concentrated within arsenopyrite (Fig. 11), particularly where streams of molybdenite and uraninite inclusions in tourmaline intersect earlier arsenopyrite grains. This association probably reflects the preferential replacement of arsenopyrite by molybdenite. There is considerable doubt as to the order of crystallization of scheelite and arsenopyrite. These two minerals are not closely associated, and, since they both show a marked tendency to form euhedral crystals, diagnostic textural relations are lacking. Fractured scheelite is, however, cemented by tourmaline, pyrrhotite, chalcopyrite, and magnetite, and arsenopyrite and scheelite were probably approximately contemporaneous.

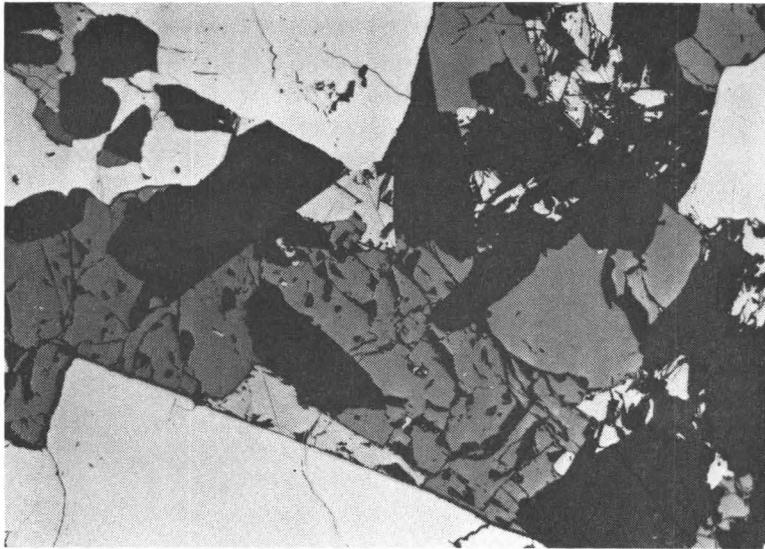


Fig. 9. Anhedral magnetite (medium grey) and chalcopyrite (pale grey), with tourmaline, infilling the interstices between euhedral arsenopyrite grains. Orebody I, 174 m level. (Reflected light, in air; nicols uncrossed; $\times 70$).

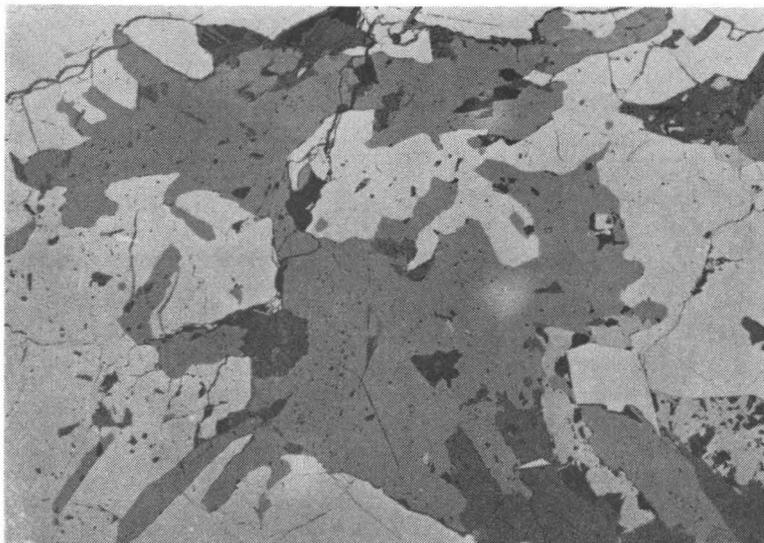


Fig. 10. Anhedral and lath-shaped ilmenite grains (medium grey) and chalcopyrite infilling fractures in- and possibly replacing arsenopyrite. Orebody II, 240 m level; (Reflected light, in air: nicols uncrossed; $\times 70$).

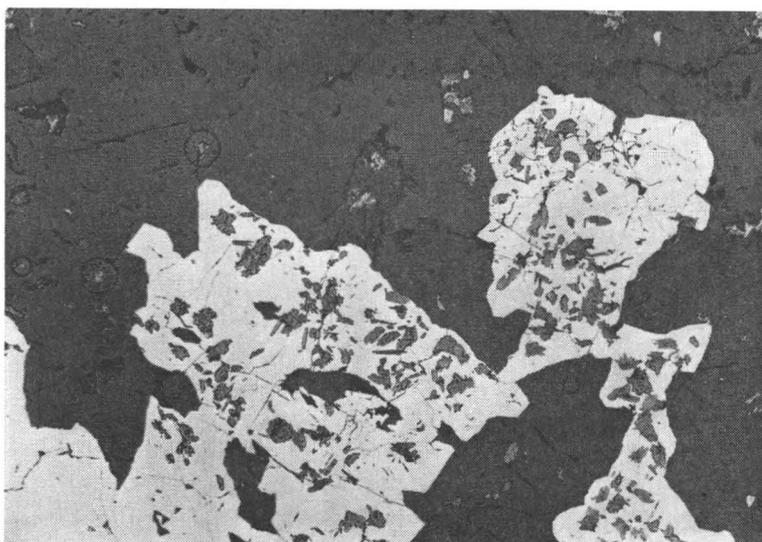


Fig. 11. Arsenopyrite, enclosed and probably replaced by later tourmaline, and containing many subhedral flakes of molybdenite. There is a close spatial relation between the occurrence of the molybdenite and the presence of uraninite and radiogenic galena inclusions in the tourmaline. Orebody IV, 285 m level. (Reflected light, oil immersion; nicols crossed; $\times 63$).

The relations between arsenopyrite and pyrite, of importance in the interpretation of the compositional data, have been studied in some detail. X-ray fluorescence analysis of minor elements in 20 pyrites has lent support to the conclusion, based on textural evidence, that deposition of this mineral both preceded and followed the introduction of the pyrrhotite-chalcopyrite paragenesis. The early generation, pyrite I, is subordinate in most zones to pyrites II and III (Fig. 5), and forms euhedral cubes which are occasionally observed to be veined by chalcopyrite, pyrrhotite, or tourmaline. The early pyrite contains slightly higher cobalt and nickel contents than pyrites II and III. Significantly, tin is present in pyrite I in concentrations of up to 0.60₅ weight per cent, but does not exceed 0.1 per cent in later generations. Although both cassiterite and stannite occur in the deposit, neither has been detected in association with grains of pyrite I in polished sections, and it is probable that this element is present in isomorphous substitution in the pyrite structure. These observations help to clarify the relations between arsenopyrite and early pyrite, but actual contact between grains of these minerals is rarely observed, and zones in which pyrite I occurs are generally poor in arsenopyrite. Contacts of the minerals are almost invariably highly fractured, possibly due to mutual abrasion of the brittle crystals during later cataclasis. In two instances only have small grains of probable pyrite I been observed infilling fractures in arsenopyrite.

Although the evidence is inconclusive, it is considered that arsenopyrite crystallized before pyrite I, and that surface equilibrium between these minerals was only rarely attained. Arsenopyrite may well have commenced crystallization above 491°C, and there is no indication that the formation of later pyrite induced compositional change in the arsenopyrite.

Minute grains (~ 0.001 mm in diameter) of native gold have been detected in two polished sections, from the 285 m and 358 m levels in orebody IV. In each case the gold forms irregular, subvermicular inclusions in arsenopyrite in the vicinity of narrow fractures partially infilled by chalcopyrite. The preferential association of native gold with arsenopyrite has been described and discussed by several authors (e.g., Schwartz, 1944; Coleman, 1957; earlier studies summarized by Clark, 1960a). Clark has shown that gold diffuses rapidly through synthetic arsenopyrite at 660°C and at higher temperatures, although it remains to be shown that true solid solution between these minerals is attained at elevated temperatures. It is possible that much of the gold in arsenopyrite-bearing deposits was initially introduced in solid solution in that mineral, migrating at lower temperatures to fractured zones.

The distribution of gold in the Ylöjärvi paragenesis is unclear. The chalcopyrite concentrates contain between 0.7 and 4.4 g/t Au (unpublished mine reports), while the mineralized zones of the deposit contain approxi-

mately 0.05—0.2 g/t Au, but there is no simple relation between the Cu and Au (or Ag) contents. No data are available on the concentration of Au in other minerals, or in the arsenopyrite concentrates. The greater portion of the gold is evidently present as submicroscopic inclusions or in solid solution in the sulphide minerals, perhaps predominantly in arsenopyrite and chalcopyrite.

Under high magnification, the arsenopyrite is generally optically homogeneous, and well-defined zoning is only occasionally visible in etched and unetched sections. (The lack of variation of the optical properties of this mineral with varying composition (As:S ratio) would hinder the detection of concordant zoning.) Discordantly zoned grains consist either of euhedral cores mantled by euhedral or subhedral outer zones (Fig. 12), or of one phase irregularly »veined» by another. It is not known whether such zoned crystals always consist of components of differing composition; the 131α reflections of aggregates of such grains may be sharp; broad and diffuse; or, rarely, split into two peaks of varying relative intensity. (It is probable that a more precise determination of the degree and scale of the compositional zoning could be obtained by examination of higher angle X-ray reflections, but the composite nature of most of the high-angle diffraction peaks given by this mineral

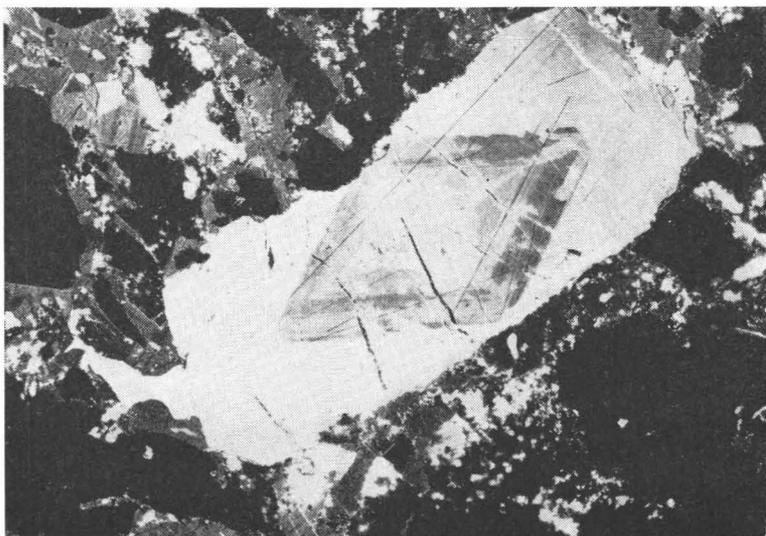


Fig. 12. Discordant zoning in arsenopyrite. X-ray powder diffraction traces of arsenopyrite from this polished section show split or diffuse $131\alpha_1$ reflections; arsenic-rich core zones with $d_{131} = 1.6357 \text{ \AA}$ are apparently mantled by sulphur-rich outer zones with $d_{131} = 1.6322 \text{ \AA}$. Matrix of tourmaline and pyrite III. Orebody I, 285 m level. (Reflected light; oil immersion; nicols crossed; x 170).

(Morimoto and Clark, 1961) would cause difficulties. Within the deposit as a whole there is a partial correlation between peak sharpness and the local range in arsenic:sulphur ratio.)

The rare development of veinlets or patches of possibly later arsenopyrite, if indicating the actual replacement of an earlier phase and not (isochemical) recrystallization along micro-fractures, suggests that a very small proportion of the arsenopyrite was subject to compositional change in response to falling temperatures and/or increasing sulphur fugacity. Most arsenopyrite, however, presumably remained stable after deposition.

Examination with oil immersion shows that the arsenopyrite almost invariably exhibits both simple (large-scale) and fine polysynthetic twinning. Morimoto and Clark (1961) have discussed the development of twinning in natural arsenopyrite, and suggest that the coarse («type I») twinning is due to the pseudo-orthorhombic, and the fine («type II») twinning to the pseudo-monoclinic symmetry of the mineral. Single crystal X-ray studies indicate that, with increasing arsenic content, the triclinic cell geometry of arsenopyrite approaches monoclinic, and, metrically, the cell approaches orthorhombic geometry. Thus, type I twinning should be more commonly developed in arsenic-rich specimens. Careful examination of the frequency of coarse and fine twinning in analysed Ylöjärvi arsenopyrites, however, does not confirm this relation. There is also no apparent relation between the content of Co, Ni, or Sb and the nature of the twinning in arsenopyrites of approximately identical arsenic:sulphur ratios (c.f. Morimoto and Clark, 1961). Some concentration of polysynthetic twin lamellae has been observed in the vicinity of grain boundaries and late-stage, gangue-filled fractures, perhaps reflecting the influence of stress on the symmetry and twinning of this mineral. Veinlets of one arsenopyrite «cutting» another are also bordered by a relatively intense development of fine twin lamellae.

A number of polished sections have been etched with dilute and saturated FeCl_3 solution in order to study the distribution and paragenetic relations of löllingite, which was originally detected in the routine X-ray examination of the arsenopyrites. Löllingite has been identified with certainty in only two parts of the deposit to date, the 174 m and 285 m levels of orebody I, where it apparently replaces earlier arsenopyrite along fracture zones but is not associated with the zoning of that mineral. The löllingite forms irregular, elongated anhedral grains showing no internal zoning. Its development in the Ylöjärvi deposit is referred to the low-temperature period of deposition of minor tetrahedrite, gudmundite, bournonite, boulangerite, and bismuth- and silver-bearing minerals, (Fig. 5), and is probably related to the local breakdown of arsenic-rich arsenopyrite. The composition and conditions of formation of the löllingite will be discussed in a later section of this paper.

DETERMINATION OF ARSENIC:SULPHUR RATIOS OF ARSENOPYRITE

The arsenic: sulphur ratios of the arsenopyrites were determined by measurement of their 131 spacings, using the relationship:

$$d_{131} = 1.6006 + 0.00098x$$

where d_{131} is in Ångström units, and x is the atomic per cent of arsenic (Morimoto and Clark, 1961; the equation is misprinted in the original paper). No attempt has yet been made to analyse the arsenopyrites by wet chemical methods, although, in view of the rarity of löllingite and the ease of separation of the arsenopyrite from other minerals, this would be feasible, and would provide a check on the diffraction measurements. Morimoto and Clark (*op. cit.*) suggest that measurement of the d_{131} value to ± 0.0003 Å will give the arsenic content to approximately one atomic per cent. The phase relations which are significant in the estimation of the P-T conditions of deposition are based directly on d_{131} values (Clark, 1960a, b), and it is considered that minor variations in the composition of this mineral may be reliably detected by accurate determination of this spacing.

All measurements were carried out on a Philips X-ray diffractometer, using nickel-filtered Cu-K α radiation ($\lambda = 1.5418$ Å). The angular positions of the 131 a_1 reflections were measured relative to the 311 a_1 reflection of CaF $_2$; natural fluorite was found to be a satisfactory internal standard. Repeated calibration against silicon showed that the position of the 311 a_1 reflection of the fluorite, at $\theta_{Cu} = 27.882^\circ$, was constant within the limits of precision of the method. Both the arsenopyrite and the fluorite standard were finely ground (to approximately -300 mesh), and pressed into a simple glass cavity mount, the same mount being used for almost all measurements to ensure internal consistency. Smear mounts, if carefully prepared, were found to give comparable results, but rather better resolution of the 131 a_1 reflection was obtained with the cavity. An oscillation technique was used, the final 131 spacing values being the mean of at least five (5–10) complete oscillations about the diffraction peak. There appeared to be no valid reason for accepting only the peak separations given by scans from lower to higher angles (Chayes and MacKenzie, 1957). Rate meter and time constant settings varied, but the following setting gave satisfactory results for most samples:

rate meter — 2: time constant (secs) — 4: multiplier — 1. Other instrumental settings were as follows:

- Divergence and scatter slits, 4° ;
- Receiving slit, 0.2 mm;
- Scan speed, $1/4^\circ$ — $1/8^\circ 2\theta$ per minute;
- Chart speed, 400 mm per hour.

The charts were measured using a vernier scale reading to $0.001^\circ 2\theta$, and the centres of the peaks at approximately $3/4$ peak height were estimated visually. The measurements were precise to 0.0002 — 0.0003 Å in cases where the a_1 , a_2 doublet of the 131 reflection was well-resolved, but the precision of measurement of some specimens was about ± 0.0005 Å.

To ensure comparability with the d_{131} values obtained by Clark (1960a, b), a specimen of arsenopyrite¹, associated with löllingite, from the New Consols mine, Cornwall (Embrey, 1953), and which had previously been studied by Clark (*op. cit.*)

¹) This specimen, B. M. 1958, 403, was kindly provided by Mr. P. G. Embrey, Department of Mineralogy, British Museum (Nat. History).

and by Morimoto and Clark (1961), was examined repeatedly during the course of the present study. The mean of 12 determinations of the 131 spacing of this specimen (70 complete oscillations) was found to be 1.6343 Å, while Clark (1960a) and Morimoto and Clark (1961) record values of 1.6347 Å and 1.6350 Å, respectively. It thus appears that the results obtained in the present study are rather closely comparable to those of the earlier authors.

ARSENIC:SULPHUR RATIOS OF ARSENOPYRITE IN THE YLÖJÄRVI DEPOSIT

Accurate determinations have been made of the d_{131} values of 214 arsenopyrites from the Ylöjärvi deposit. In several samples the combined content of minor constituents (mainly cobalt, nickel, and antimony) was found to exceed one per cent by weight (Table 1), sufficient to cause minor errors in the estimation of the arsenic:sulphur ratios (Clark, 1960a). However, although the minor element concentrations have been determined in only 56 of the samples, the writer feels confident that the observed variations in d_{131} values reflect significant changes in the arsenic contents, and are not seriously affected by fluctuations in minor elements. The distribution of elements other than arsenic and sulphur will be discussed in a later section of the paper.

Arsenopyrite sample locations have been recorded accurately on large scale plans of the mine levels, but for the purposes of this paper it has been considered preferable to present the analytical data in the form of frequency histograms rather than sample location plots. Since no consistent gradients in composition can be demonstrated, this mode of presentation does not detract from the usefulness of the data.

At the outset of this work it became evident that arsenopyrite has a highly variable composition within the deposit. The determined compositions, ranging from approximately 30 to 36.6 atomic per cent (d_{131} values; 1.6302—1.6365 \pm 0.0003 Å), probably cover the greater part of the total range of solid solution shown by natural or synthetic arsenopyrite (Morimoto and Clark, 1961).¹ This observation in itself demonstrates that arsenic-rich arsenopyrites may crystallize in sulphur-rich environments if the P-T conditions are suitable.

It had been hoped that a gradation in arsenic:sulphur ratios would be found over the +550 metre depth interval covered by the analysed samples. Such a consistent variation could be caused by a combined decrease in confining pressure and temperature of deposition as the ore solutions rose

¹ Petruk (personal communication) and the present writer have recently found sulphur-rich arsenopyrites having d_{131} values in the range 1.626—1.630 Å in the Mount Pleasant Sn-Zn deposit, New Brunswick.

Table 1. Minor element contents and 131 spacings of arsenopyrites from the Ylöjärvi deposit

(a) Orebody I:

Specimen no. and level	d_{131} ($\pm 0.0003 \text{ \AA}$)	Concentrations (weight per cent)					Remarks
		Co	Ni	Sb	Bi	Sn	
As 105(7)	1.6319	0.72 ₂	0.14 ₆	0.00 ₆	n.d.	n.d.	
As 150(2)	1.6334	0.71 ₂	0.14 ₉	0.07 ₆	n.d.	n.d.	
As 174(3)	1.6329	0.40 ₂	0.13 ₅	0.01 ₄	0.09 ₀	0.01 ₂	
As 174(6)	1.6360	1.18 ₆	0.19 ₆	0.01 ₉	n.d.	0.02 ₃	
As 174(7)	1.6332	1.62 ₁	0.51 ₅	0.00 ₀	tr.	n.d.	
As 195(3)	1.6359	0.19 ₂	0.09 ₀	0.02 ₉	tr.	n.d.	V, Cr, tr. *
As 195(10)	1.6331	1.01 ₁	0.17 ₈	0.01 ₆	0.12 ₀	n.d.	V, Cr, tr.
As 195(11)	1.6328	0.23 ₇	0.11 ₂	0.03 ₂	n.d.	n.d.	
As 240(3)	1.6329	0.68 ₀	0.13 ₆	0.00 ₉	.d.	n.d.	
As 240(4)	1.6335	0.74 ₀	0.14 ₈	0.02 ₁	n.d.	n.d.	
As 253(1)	1.6331	0.29 ₁	0.12 ₆	0.02 ₇	0.15 ₂	0.04	Ti, tr.
As 253(6)	1.6337	0.33 ₁	0.13 ₇	0.01 ₆	0.09 ₂	n.d.	
As 253(19)	1.6332	0.96 ₀	0.15 ₈	0.02 ₅	0.15 ₅	n.d.	Ti, tr.
As 285(1)	1.6339	0.19 ₂	0.10 ₆	0.02 ₉	n.d.	n.d.	
As 285(3)	1.6327	0.17 ₆	0.08 ₃	0.03 ₂	0.05 ₈	n.d.	
As 285(7)	1.6342	0.69 ₄	0.15 ₁	0.01 ₇	n.d.	n.d.	
As 285(8)	1.6333	1.52 ₇	0.27 ₅	0.03 ₃	0.07 ₁	n.d.	
As 330(6)	1.6340	1.22 ₁	0.19 ₅	0.09 ₂	0.06 ₅	n.d.	
As 330(9)	1.6350	0.93 ₄	0.16 ₀	0.07 ₀	0.06 ₃	n.d.	

(b) Orebodies II and III:

As 140(3)	1.6306	0.9 ₆	0.02 ₁	0.00 ₉	n.d.	n.d.	
As 140(4)	1.6308	0.12 ₁	0.01 ₆	0.03 ₄	n.d.	n.d.	
As 240(9)	1.6316	0.41 ₉	0.19 ₁	0.02 ₆	n.d.	n.d.	
As 240(10)	1.6330	0.13 ₂	0.14 ₀	0.01 ₀	0.05 ₁	n.d.	
As 253(10)	1.6333	0.11 ₀	0.00 ₉	0.05 ₂	n.d.	0.01 ₅	
As 285(11)	1.6342	0.07 ₀	0.01 ₆	0.00 ₇	n.d.	n.d.	
As 420(1)	1.6325	0.17 ₄	0.10 ₂	0.02 ₆	0.07 ₀	n.d.	
As 420(2)	1.6309	0.16 ₃	0.01 ₃	0.00 ₉	n.d.	n.d.	
As 465(2)	1.6316	0.09 ₉	0.00 ₆	0.01 ₇	n.d.	n.d.	Ti, tr.
As 465(3)	1.6303	0.00 ₇	0.00 ₅	0.01 ₆	n.d.	n.d.	

(c) Orebody IV:

As 88(1)	1.6320	0.16 ₅	0.10 ₂	0.04 ₇	n.d.	n.d.	V, Cr, Ti, tr
As 91(1)	1.6323	0.29 ₃	.09 ₅	.03 ₆	n.d.	n.d.	
As 95(1)	1.6319	0.10 ₂	0.03 ₀	0.03 ₀	n.d.	n.d.	
As 95(6)	1.6332	0.09 ₆	0.06 ₅	0.03 ₃	n.d.	n.d.	
As 105(1)	1.6318	0.44 ₅	0.17 ₇	0.02 ₇	n.d.	n.d.	
As 105(2)	1.6326	0.52 ₅	0.14 ₆	0.02 ₉	0.04 ₉	n.d.	
As 105(2 a)	1.6325	0.59 ₀	0.07 ₃	0.02 ₆	n.d.	n.d.	
As 105(6)	1.6320	0.49 ₃	0.05 ₁	—	n.d.	n.d.	
As 130(4)	1.6339	0.09 ₆	0.01 ₁	0.02 ₅	n.d.	n.d.	
As 130(5)	1.6330	0.06 ₁	0.01 ₈	0.02 ₂	0.04 ₄	n.d.	
As 130(9)	1.6326	0.13 ₆	0.01 ₃	0.02 ₃	n.d.	n.d.	
As 150(11)	1.6331	0.16 ₈	0.02 ₆	0.02 ₉	n.d.	n.d.	
As 150(12)	1.6333	0.26 ₄	0.04 ₈	0.01 ₉	n.d.	n.d.	

* ~ 0.05 — 0.10 weight per cent.

Table 1. — Continued

Specimen no. and level	d_{131}	Concentrations (weight per cent)					Remarks
		Co	Ni	Sb	Bi	Sn	
(c) Orebody IV							
As 150(17)	1.6329	0.05 ₃	0.05 ₀	0.02 ₅	n.d.	0.00 ₉	
As 240(5)	1.6332	0.72 ₁	0.04 ₅	0.02 ₆	n.d.	n.d.	
As 240(6)	1.6316	0.80 ₄	0.11 ₅	0.02 ₈	n.d.	n.d.	
As 285(17)	1.6328	0.10 ₅	0.10 ₅	0.02 ₄	0.05 ₈	n.d.	
As 307(3)	1.6320	0.02 ₀	0.00 ₅	0.02 ₉	n.d.	n.d.	
As 307(4)	1.6325	0.09 ₀	0.17 ₂	0.03 ₂	n.d.	n.d.	
As 307(5)	1.6316	0.50 ₃	0.11 ₀	—	0.07 ₂	n.d.	
As 330(1)	1.6329	0.49 ₉	0.07 ₆	0.03 ₀	n.d.	n.d.	
As 349(1)	1.6336	0.68 ₈	0.08 ₇	0.02 ₆	n.d.	n.d.	
As 349(5)	1.6330	0.12 ₈	0.01 ₄	0.02 ₅	n.d.	n.d.	Ti, tr.
As 349(5 a)	1.6320	—	—	0.02 ₉	tr.	n.d.	Ti, tr.
As 358(3)	1.6333	0.09 ₁	0.08 ₈	0.02 ₃	n.d.	n.d.	
As 358(4)	1.6332	0.11 ₄	0.05 ₃	0.01 ₅	0.08 ₄	n.d.	
As 375(4)	1.6325	0.13 ₂	0.13 ₇	0.00 ₉	0.05 ₄	n.d.	
As 375(8)	1.6320	0.08 ₆	0.04 ₆	0.01 ₅	n.d.	n.d.	

through the brecciated zone. The difference in hydrostatic pressure between the exposed top and bottom of the deposit, equivalent to approximately 130 bars, would not in itself be sufficient to have an appreciable effect on the arsenopyrite phase equilibria, but slight changes in temperature would be expected to be reflected in the composition of this mineral. No consistent composition gradation, however, is observed. Examination of the compositions of the sphalerite and pyrrhotite which were introduced shortly after the arsenopyrite suggests that deposition of these sulphides took place at almost constant temperature throughout the deposit.

Figures 13 a-d are histograms illustrating the range and frequency of d_{131} values and arsenic contents of the arsenopyrite in the deposit as a whole and in individual orebodies. Comparatively few samples were examined from orebodies II and III, and these zones, which are geochemically similar in many respects, will be treated as a unit in this discussion.

The lattice spacings show a well-defined bimodal distribution with a primary maximum in the range ~ 1.6317 — 1.6333 Å (~ 31.7 — 33.4 atomic per cent arsenic), and a subsidiary maximum in the range ~ 1.6348 — 1.6355 (~ 34.9 — 35.6 atomic per cent arsenic). Only in orebodies II and III does a considerable proportion of the d_{131} values fall outside these ranges. The data show that, although a particular As:S ratio is not indicative of location within the deposit, each of the three main sample zones is characterized by a differing composition distribution. These differences are paralleled by other mineralogical and geochemical factors, and are believed to be of importance in the interpretation of the conditions of deposition of the arsenopyrite.

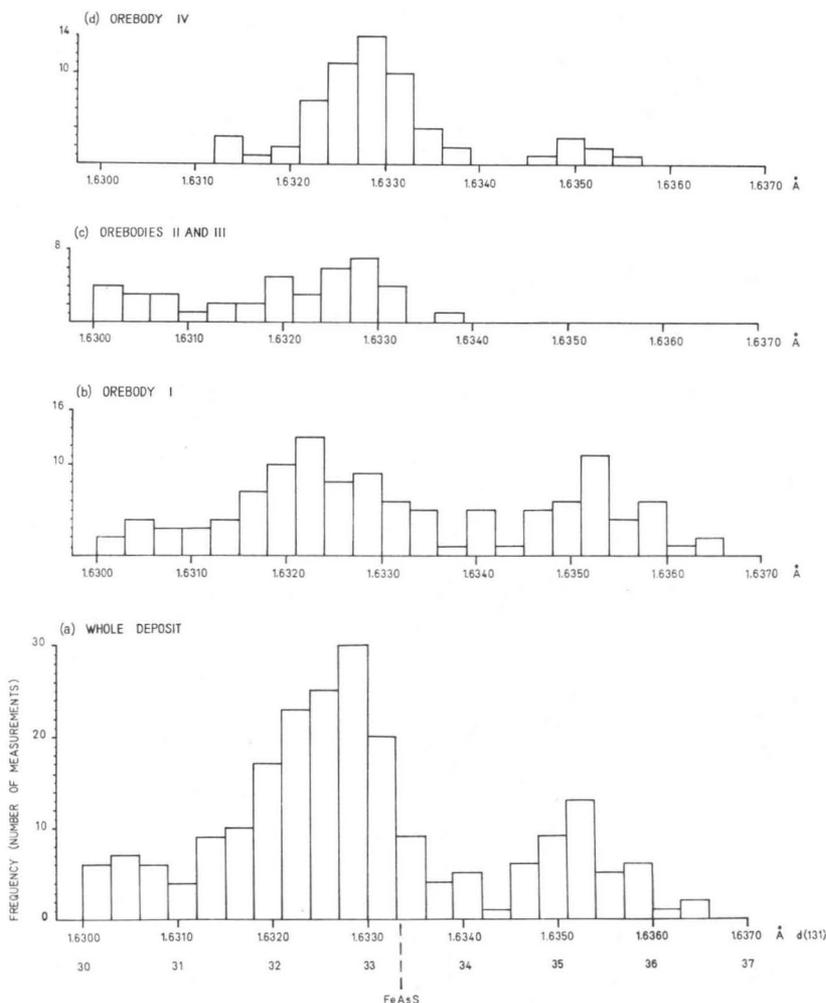


Fig. 13. Histograms showing the arsenic content of 214 arsenopyrites, Ylöjärvi mine.

In orebody IV over 60 per cent of the d_{131} values coincide closely with the primary maximum (Fig. 13d). No sample from this zone had a spacing less than $1.6314 \pm 0.0003 \text{ \AA}$, and the arsenic-rich secondary maximum is poorly represented. Most samples with more than 34 atomic per cent arsenic occurred above the 240 m level, but this trend may not be significant. Compositional zoning on a small scale is almost absent in this orebody, and most specimens yielded sharp, well-resolved 131 reflections. Within the limits of precision of the analytical method, compositions were often found to be constant over exposures of several square metres.

In contrast, the arsenopyrite in orebody I shows a highly variable arsenic content, and the bimodal composition distribution is well displayed (Fig. 13b). A significant proportion of the samples examined from this zone have arsenic contents exceeding that of ideal FeAsS, although very sulphur-rich compositions are also represented. Detailed sampling of the 174 m, 253 m, and 285 m levels shows that this mineral may vary in composition even within a single hand specimen, but is more homogeneous in other zones. Examination of several exposures has indicated that the variations are generally random on a megascopic scale. Rarely, however, veins of arsenopyrite were found to have discontinuous arsenic-rich wall zones flanking sulphur-rich cores, and wall-rock fragments are occasionally surrounded by irregular zones of arsenic-rich arsenopyrite. Disseminated euhedral crystals of this mineral in silicified wall-rocks generally have essentially the same composition as the adjacent massive material, but in two exposures were found to be richer in arsenic. The variable composition of arsenopyrite in orebody I is reflected in a frequent broadening, or, occasionally, in a definite splitting of the 131 diffraction peak. The d_{131} values of the split peaks coincide closely with the two frequency maxima (Fig. 13b). Measurement of broadened peaks should give a rough indication of the mean composition of the samples, but measurements of such peaks have been omitted from the consideration of the results. The most arsenic-rich specimens in the deposit have been found in the 150—195 m section of this orebody, but there is no evidence of any consistent gradation in average composition with depth.

A large proportion of the arsenopyrites from orebodies II and III are richer in sulphur than the composition maxima of the two outer orebodies (Fig. 13c), while very arsenic-rich samples are not present. The range of compositions represented in restricted zones is intermediate between those in orebodies I and IV.

It should be stressed that, in view of the considerable tonnage of arsenopyrite occurring in orebody IV below the 240 m level, the analytical data given in Fig. 13a do not reflect the true distribution of As:S ratios in the deposit as a whole. Allowance for the actual quantities of this mineral in the individual mineralized zones would strongly accentuate the primary maximum, but would probably have little effect on the frequency distribution of other compositions.

THE SIGNIFICANCE OF THE ARSENIC:SULPHUR RATIOS

The accumulated data on the As:S ratios of arsenopyrite in the Ylöjärvi deposit provide evidence of the range of P-T conditions prevailing during the earlier stages of mineralization, although precise estimation of the

temperatures and pressures is not possible. In addition, the range of composition represented in the specimens examined is of some significance in the broader study of arsenopyrite geochemistry.

On the basis of published chemical analyses, Morimoto and Clark (1961) suggested that most (»probably over 70 per cent») natural arsenopyrite is more sulphur-rich than ideal FeAsS , reflecting the predominance of sulphide-bearing over arsenide-bearing environments. In support of this, Clark (written communication) has determined the 131 spacings of a number of arsenopyrites from various localities, finding a range from 1.6300—1.6352 Å, with most values falling between 1.6300 and 1.6330 Å. No detailed studies, however, have been made of the composition of this mineral in arsenide-bearing deposits. Preliminary studies by the writer on the Pihtipudas arsenopyrite-löllingite-galena-gold deposit, Ritovuori,¹ central Finland (Kouvo and Kulp, 1961), and on arsenopyrite-löllingite bearing veins in the Penlee quarry Newlyn, Cornwall, have demonstrated a fairly consistent positive correlation between the arsenic content of arsenopyrite and the presence of löllingite. Arsenopyrites with d_{131} spacings greater than 1.6365 Å have not, however, been detected in these occurrences. Study of this aspect of arsenopyrite geochemistry is hindered by the difficulty of demonstrating equilibrium in complex arsenopyrite-löllingite parageneses, but in most assemblages arsenopyrite replaces löllingite and may have attained »arsenic saturation» during deposition.

The present study shows that very arsenic-rich arsenopyrite may crystallize in deposits in which arsenide minerals are rare or absent, and in which this mineral must be assumed to have been deposited at or near to the sulphur-rich limit for the prevailing P-T conditions. Comparably arsenic-rich compositions have been found in several other normal sulphide-bearing deposits, including the Panasqueira tin-tungsten deposit, Portugal (A. H. Clark, 1964b).

Arsenopyrites with 131 spacings of 1.6350 and 1.6360 Å, crystallizing in a sulphur-rich environment, would be stable only at temperatures above ~ 580° and ~ 625—630°C, respectively (Clark, 1960b; Fig. 2). Even if deposited in equilibrium with arsenic-rich fluids these compositions would be unstable below ~ 460° and ~ 560°C. The influence of the »arsenic:sulphur ratio» of the environment of deposition on the composition of arsenopyrite decreases with increasing temperature and/or pressure, as reflected in the convergence of the sulphur- and arsenic-rich solvus curves (Fig. 1).

Thus, the composition of arsenic-rich arsenopyrites may be used in the estimation of the minimum temperatures of ore deposition, even where no independent means of temperature determination is available. Arsenopyrites

¹) Specimens generously provided by Aatto Laitakari, Geologinen Tutkimuslaitos.

with d_{131} values greater than 1.6340 Å are, however, correspondingly less precise as indicators of confining pressure. For the purposes of the present discussion it will be assumed that the arsenopyrite was deposited at or near its sulphur-rich limit, and that no supersaturation with respect to arsenic occurred during deposition. L. A. Clark (written communication) has suggested that arsenopyrite crystallizing above $\sim 400^\circ\text{C}$ may be assumed to have formed in equilibrium with its environment.

UPPER TEMPERATURE LIMITS

The maximum temperature at which the arsenopyrite may have been deposited is necessarily $702 \pm 3^\circ\text{C}$, the upper stability limit of this mineral. This limit is closely approached by the minimum temperature at which arsenopyrite with $d_{131} = 1.6365$ Å would be stable in a sulphur-rich environment at < 1 bar confining pressure, i.e., $640\text{--}645^\circ\text{C}$. At confining pressures in the range 1 000—2 000 bars, which it is probably reasonable to assume in the present context, this composition would be stable at approximately $680\text{--}700^\circ\text{C}$. It is considered that deposition of arsenopyrite in the Ylöjärvi deposit may have commenced at approximately 700°C , effectively at the upper stability limit. Although such an elevated temperature would at first sight seem improbable, there are no mineralogical features in the environment of crystallization which would necessitate postulating a more moderate temperature. Since, in the deposit as a whole, the arsenic-rich compositions are subordinate, and are largely restricted to orebody I, it is probable that they reflect a minor, early pulse of deposition occurring at high temperatures shortly after the initial brecciation of the mineralized zone. There is no satisfactory evidence of the rate of cooling of the ore solutions and of the deposit as a whole, but the structurally open nature of the fractured zones and the restricted extent of the severe wall-rock alteration suggest that the very high temperatures were not long maintained.

Several other parageneses in the deposit place restrictions on the probable maximum temperatures attained during the earlier stages of ore deposition, but these are not directly applicable to the period of arsenopyrite deposition. The presence of pyrite (pyrite I) indicates temperatures below about 743°C (Kullerud and Yoder, 1959), but deposition of pyrite I followed that of arsenopyrite (see above). Magnetite (< 0.5 weight per cent Ti), pyrrhotite, and pyrite I occur in contact in many parts of the deposit, and it is possible that magnetite and pyrrhotite crystallized for a short period in equilibrium with pyrite (Fig. 5). Barnes and Kullerud (1961), in a study of the Fe-S-O system, have shown that the assemblage pyrrhotite + pyrite + magnetite + vapour is stable only below about 675°C ; above that temperature pyrrhotite coexists with hematite. The absence of hematite in the Ylöjärvi

breccia zones and the apparent stability of the pyrite I-magnetite assemblage suggest that these coexisting minerals crystallized at some temperature below 675°C. Pyrite I and molybdenite are closely associated in several zones of the deposit, and may have crystallized in equilibrium. Kullerud and Buseck (1962), in a recent study of the Fe-Mo-S system, have demonstrated that these two minerals may coexist in the presence of vapour only below $762 \pm 3^\circ\text{C}$. None of these relations contradicts the postulated temperature of $\sim 700^\circ\text{C}$ for the initial deposition of arsenopyrite. Since there is no close association between arsenopyrite and pyrite I, and these minerals rarely occur in contact, it is considered that they did not attain equilibrium during deposition. Locally pyrite may have crystallized in surface equilibrium with earlier arsenopyrite, and must then have formed at some temperature below $491 \pm 12^\circ\text{C}$ (Clark, 1960a). There is no apparent relation between the composition of arsenopyrite and the presence of pyrite I.

The parageneses formed during wall-rock alteration (hornblende — spessartine-almandine — biotite — plagioclase (An_{5-20}) — titanomagnetite — ilmenite) are comparable to those of the amphibolite grade of regional metamorphism, but are not diagnostic of a narrow range of P-T conditions. There is as yet no good agreement as to the P-T conditions prevailing during (almandine) amphibolite facies metamorphism, and temperature ranges of 500—700°C (Fyfe, Turner and Verhoogen, 1958), and 400—500°C (Ramberg, 1952) have been recently postulated. The high spessartine content of the garnet, although in part reflecting metasomatic introduction of Mn into the mineralized zones, perhaps suggests that wall-rock alteration took place at temperatures not exceeding about 500°C. It is probable that the initial deposition of sulphides in the altered and fractured country rocks immediately followed a local rise in temperature of at least 200°C. However, since wall-rock alteration itself certainly occurred at temperatures exceeding those prevailing during the preceding retrograde alteration period, a further rise in temperature in the vicinity of the deposit would not be improbable.

Temperatures of sulphide deposition in the range 600—700°C have been proposed for several deposits on the basis of sphalerite-pyrrhotite relations (e.g., Sims and Barton, 1961; Kalliokoski, 1961; Rose, 1961), and there is no *a priori* objection to such elevated temperatures.¹ The source of the ore solutions responsible for the formation of the Ylöjärvi deposit, whether of magmatic or metamorphic origin, cannot, however, have been far removed from the site of ore deposition. It is considered unlikely that the metamorphosed volcanic country rocks in the immediate vicinity of the deposit, at the present level of exposure, could have contributed significantly to the processes of ore deposition and concentration, but nothing is known of the

¹) The recent re-examination of phase relations in the Fe-Zn-S system (Barton and Toulmin, 1964), however, casts doubt on the validity of these temperatures.

metamorphic state of these rocks at greater depths. A detailed geochemical study of the environment of the deposit might reveal consistent minor element trends relative to the mineralized zone. The »tuffites» and »porphyrites» in the mine area are richer in zinc than in copper, however, and the copper contents show no significant variations for distances of up to 750 metres from the orebodies.

The considerable concentration of boron in the breccia zone makes it unlikely that the ores were derived from extensive diffusion of material from the volcanics towards the walls of the Hämeenkyrö quartz-diorite during its intrusion, unless the ore solutions were polygenetic. The volcanic schists are considerably poorer in boron than the metasedimentary phyllites to the south of the mine area, but economic tourmaline-rich mineralization has not been found in the quartz-diorite — phyllite contact zones. It is considered that the elevated temperature of arsenopyrite deposition suggests a hydrothermal, magmatogene origin for the ore solutions, and the quartz-diorite immediately recommends itself as the source of the solutions.

THE RANGE OF P-T CONDITIONS DURING ARSENOPYRITE DEPOSITION

Examination of the compositions of hexagonal pyrrhotite, monoclinic pyrrhotite, and sphalerite has suggested that these sulphides were probably deposited in the temperature range $\sim 565^{\circ}$ — 470° C. On the assumption that temperatures decreased, albeit irregularly, during mineralization, the crystallization of arsenopyrite therefore probably terminated at some temperature above about 570° C. Since the depositions of arsenopyrite and the pyrrhotite-chalcopyrite-sphalerite assemblage were separated by at least two periods of fracturing, and by the introduction of pyrite I, molybdenite, ilmenite, magnetite, and tourmaline, the main constituent of the ores (Fig. 5), it is considered unlikely that deposition of arsenopyrite continued below ~ 600 — 580° C. Such extrapolation of P-T conditions in a paragenetic sequence is obviously susceptible to serious error, but is unavoidable in all applications of experimental data to natural assemblages where contemporaneity of the significant minerals cannot be inferred. In most deposits arsenopyrite preceded sphalerite and pyrrhotite, the main »geothermometers», and its temperature of deposition may be only roughly estimated.

The more important factors affecting the composition of the crystallizing arsenopyrite were probably the sulphur and arsenic fugacities of the ore solutions, and the confining pressure and temperature. There is at present no way in which the sulphur fugacity at the time of arsenopyrite deposition may be reliably evaluated,¹ but it is probable that the fugacity of arsenic

¹) The sulphur fugacity during the initial deposition of pyrrhotite in equilibrium with pyrite I, at 565° C, was probably approximately 10^{-3} atm. (Toulmin and Barton, 1964).

in the environment of deposition decreased rapidly during the deposition of arsenopyrite. Very little arsenic apparently remained in the ore solutions after the formation of arsenopyrite, and this element does not occur in amounts greater than 30 p.p.m. in the later sulphides. In deposits where two distinct generations of arsenopyrite may be distinguished, the later generation would be expected to be richer in sulphur than the earlier. Thus, at Panasqueira, Portugal (A. H. Clark, 1964b), early arsenopyrite with $d_{131} = 1.6347 - 1.6355 \text{ \AA}$, preceded a minor second generation with $d_{131} = 1.6322 - 1.6330 \text{ \AA}$. It is considered that the wide range in arsenic:sulphur ratio of the arsenopyrite in the Ylöjärvi deposit was caused primarily by a decrease in temperature of deposition from $\sim 700^\circ$ to $\sim 580^\circ\text{C}$. Deposition of the entire range of compositions is considered to have been essentially continuous, the two composition maxima (Figs. 13a b) presumably representing pulses of relatively intense deposition.

The range of composition in a particular zone may be regarded as a rough indication of the duration of arsenopyrite crystallization and, in a broad sense, the composition of this mineral in the individual orebodies may reflect the progressive penetration of the ore solutions into the brecciated zones during this earliest stage of mineralization. It is assumed that the nature of the country rocks, which contain only trace amounts of arsenic, and had not been subject to extensive introduction of sulphides prior to the deposition of arsenopyrite, had little effect on the arsenic:sulphur ratios of that mineral. On this basis it is inferred that deposition of arsenopyrite commenced in orebody I, the ore solutions later penetrating, at somewhat lower temperatures, into orebody IV, and, finally, into orebodies II and III. Arsenopyrite deposition continued for a comparatively extended period in orebody I, but was rapidly terminated in IV, where, however, a considerable tonnage soon accumulated. It is significant that the other major pre-tourmaline ore mineral, scheelite, is abundant in orebody I, is present in minor amounts in IV, but is rare in most zones of II and III. The master fracture system of the breccia zone forms the southeastern wall of orebody I, and movement continued along this plane throughout the mineralization. It is probable that the ore solutions initially rose in the vicinity of this major fracture, and spread northwards into the breccia zone at higher levels.

Although the wide range of arsenic:sulphur ratios is considered to yield significant data on the probable temperatures of deposition of the arsenopyrite, it seriously complicates estimation of the confining pressures prevailing during mineralization. Arsenopyrites with d_{131} values greater than 1.634 \AA cannot provide sensitive estimates of confining pressures (Fig. 2). Since probably over 70 per cent of the arsenopyrite in the deposit has a 131 spacing in the range $1.6315 - 1.6333 \text{ \AA}$, or $1.6324 \pm 0.0009 \text{ \AA}$ (Fig. 13), this average composition will be used in the tentative estimation of pressure. Arsenopyrite

with $d_{131} = 1.6324 \text{ \AA}$ was probably deposited at approximately $600 \pm 20^\circ\text{C}$, and application of the data in Fig. 2 leads to an estimate of confining pressure of between 2000 and 2500 bars, or possibly as high as 3000 bars. The effect of pressures of over 2000 bars on the sulphur-rich arsenopyrite solvus curves is unknown, but it is considered unlikely that the slope of the 131 spacing contours (Fig. 2) will change abruptly in the 2000—3000 bars range. If arsenopyrite with $d_{131} = 1.6324 \text{ \AA}$ was deposited at somewhat higher temperatures, the estimated confining pressure would be correspondingly higher. Similarly, if the very sulphur-rich arsenopyrite ($d_{131} = 1.6302 \text{ \AA}$) was deposited at temperatures in excess of ca. 580°C in equilibrium with its environment, confining pressures may have been above 3000 bars at the time of crystallization. There is evidently no way in which a valid choice may be made between the several possible pressure-temperature estimates in the absence of a second reliable geobarometer, but the structurally »open» nature of the breccia bodies suggests that confining pressures were not extremely high, and were probably not in excess of approximately 3000 bars. Because nothing is known of the rate of movement of the hydrothermal solutions in the brecciated conduit; of the nature and distribution of possible »chokes» in the conduit (Smith, 1963, p. 454—456); or even whether the breccia pipe was open to the surface at the time of sulphide mineralization, the true significance of the pressure estimate cannot at present be evaluated. Smith (*op. cit.*, p. 455) has suggested that »If the solution is moving in a conduit, the pressure may vary positively and negatively from the rock-load pressure depending on the degree of choking and position of chokes from source to surface. . . . Since many veins are formed by deposition in dilated faults, and the hydraulic pressure for dilation must be at least as great as the rock-load pressure, it is suggested that a reasonable approximation is made by converting pressure to depth by the rock-load relation». By analogy with the high-level, tourmaline-bearing breccia pipes of the Andean region, the upward-flaring Ylöjärvi breccia masses may have been open to the surface at the time of arsenopyrite deposition, and confining pressures significantly in excess of the rock-load pressure would probably not have occurred. If it is assumed that confining pressures were approximately equivalent to the rock-load pressure during mineralization, it appears that arsenopyrite deposition took place at a depth of about 7—11 km.

PART II
THE DISTRIBUTION OF MINOR ELEMENTS
IN THE ARSENOPYRITE

INTRODUCTION

The cobalt, nickel, and antimony contents of 56 arsenopyrites from the Ylöjärvi deposit have been determined by X-ray fluorescence analysis in order to study the distribution of these minor elements, and to investigate their possible relation to the As:S ratios of the host arsenopyrites and to the conditions of deposition. It was further necessary to ascertain whether the minor elements (particularly Co) are present in concentrations sufficient to affect the X-ray diffraction measurements of the As:S ratios (1.0 weight per cent). In addition, bismuth and tin were detected and determined in a number of specimens, while traces of V, Cr, and Ti occurred in several samples. Cu, Zn, and Mo were present in some specimens, but probably represented mechanical impurities of chalcopyrite, sphalerite, and molybdenite, respectively. Selenium, not detectable with the X-ray fluorescence equipment available, was determined by wet chemical methods in 10 arsenopyrites by J. Kinnunen, Outokumpu Oy. It is considered probable that Co, Ni (and Mn) occur in isomorphous substitution for Fe, Sb and Bi for As, and Se for S in the arsenopyrites.

PREVIOUS STUDIES

Although it is known that Co, and, to a lesser extent, Ni, Mn, Sb, Bi, and Se frequently occur as minor constituents in natural arsenopyrite, few authors have carried out quantitative determinations of the minor elements in this mineral. Little is known of the variations in concentration of these elements in arsenopyrite in individual deposits, or, on a larger scale, in mineralized areas. Fleischer summarized the available data on minor elements in arsenopyrite in 1955, and little work has apparently been carried out since that date. Arsenopyrite has been neglected in comparison with other common sulphides.

Gavelin and Gabrielson (1947), in a spectrochemical examination of sulphides from the Skellefte district, northern Sweden, have contributed the most extensive study of minor elements in arsenopyrite. These authors

examined 39 arsenopyrites from a number of deposits, and discussed the factors influencing the distribution of Co, Ni, and Mn in arsenopyrite, pyrite, pyrrhotite, and chalcopyrite. Several of the arsenopyrite-rich Skellefte deposits, and particularly that of Boliden (Ödman, 1491), are mineralogically very similar to the Ylöjärvi tourmaline breccia, and might be expected to show broadly similar minor element assemblages. Eighteen of the arsenopyrites examined by Gavelin and Gabrielson were from the Adak area, and only in the Bjurliden, Adak, and Lindsköld deposits were the small-scale variations in minor element contents studied. Cobalt was found to exceed nickel (and manganese) in all but two specimens, the reverse relationship being found in arsenopyrites from the Ravliden deposit and from a quartz vein at Fäboliden. Manganese is generally subordinate to both cobalt and nickel, but may exceed the latter. Cobalt contents of > 3 and 2.5 per cent, respectively, were recorded in arsenopyrites from the Adak and Karlsson ores, which also show markedly higher Co:Ni ratios than other deposits. On a regional scale, there was found to be no simple relation between cobalt and nickel contents, and no such relation is indicated by the analyses of material from the Adak and Lindsköld deposits. In the area as a whole, however, both cobalt and nickel are preferentially concentrated in arsenopyrite relative to the other sulphides, the order of average content being:

for cobalt: arsenopyrite > pyrite > pyrrhotite > chalcopyrite, and
for nickel: arsenopyrite > pyrrhotite > pyrite > chalcopyrite.

It was considered that the marked differences in the Co:Ni ratios and concentrations in arsenopyrite from the Adak and Karlsson deposits (high Co and Co:No ratio) and the nearby Lindsköld (low Co and Co:Ni ratio) deposit were not, apparently, due to »geological milieu, temperature, and chemical composition» (*op. cit.*, p. 37), but were related to the structural relations of the orebodies. The Adak and Karlsson orebodies are irregular, transgressive breccias, showing many similarities to the Ylöjärvi breccia pipe, whereas the Lindsköld ores occur as conformable plates. In addition to the analyses for Co, Ni, and Mn, Sn was detected qualitatively in 6.5 per cent of the samples studied, and Bi was found to be present in a few of the arsenopyrites.

Quantitative determinations of minor elements in arsenopyrite by other authors are few, and the data are rarely related to the chemistry of the associated assemblages. Many early determinations of Sb and Bi in arsenopyrites were performed on material of doubtful purity (Palache *et al.*, 1944), and Fleischer (1955) does not record quantitative determinations of these elements. Ödman (1942), however, found 1.44 per cent Sb (Bi not detected) in apparently pure arsenopyrite from the Varuträsk pegmatite, Sweden, in association with native antimony, allemontite, and stibnite, the antimony-rich paragenesis probably resulting from the replacement of earlier

stibiotantalite. The same author (1941) found 0.18 per cent Sb in arsenopyrite from the Boliden deposit, Skellefteå. Morimoto and Clark (1961) have doubted the purity of the Boliden sample, which was associated with sulphosalt minerals. The writer has, however, found 0.28 ± 0.04 per cent Sb, 0.22 ± 0.03 per cent Co, and 0.009 ± 0.003 per cent Ni (Pb, Zn, and Cu not detected) by X-ray fluorescence analysis of extremely fine-grained arsenopyrite from the 130 m level, Boliden mine.¹ Arsenopyrite, free from gudmundite or other antimony-rich minerals, from the Ortano sulphide deposit, Elba (Gottardi, 1962), has been found to contain 0.57 ± 0.04 per cent Sb, ~ 0.07 per cent Bi, and traces of Cu and Zn (probably as chalcopyrite and sphalerite); Co and Ni were not detected (A. H. Clark, 1963). High concentrations of Bi have been reported in arsenopyrites from the O'Brien mine, Cobalt, Ontario (0.79 per cent), and from Llalagua, Bolivia (0.88 per cent; Sb not recorded), by Ellsworth (1916) and Morimoto and Clark (1961), respectively. These contents are apparently exceptional, and Sb may exceed Bi in most arsenopyrites.

These scattered data suggest that natural arsenopyrite may contain up to at least 1.5 per cent antimony, and, possibly, 1.0 per cent Bi in solid solution. L. A. Clark (1960a) concluded that the limits of solid solution of Sb and Bi in natural arsenopyrite were approximately 0.2 and 1.0 per cent, respectively. It is probable that analysis of carefully separated samples from deposits rich in antimony will confirm the extension of the limit of natural solid solution of this element.

The only reliable published data on the selenium content of arsenopyrite are those of Edwards and Carlos (1954), who found 0.0042, 0.0047, and 0.0057 per cent Se in three samples from Australian deposits. Williams and Byers (1934) recorded the presence of this element in a single arsenopyrite. Bergenfelt's (1953) analyses of arsenopyrite-rich ores from the Skellefte area were unfortunately carried out on only partially separated material (confirmed in written communication, 1964).

ANALYTICAL METHOD

Co, Ni, Sb, Bi and Sn were determined by comparison with synthetic mixes made up of »Specpure» iron sponge, »Specpure» arsenious oxide, and Analar grade sulphur, with variable amounts of »Specpure» Co_3O_4 , NiO, Sb_2O_4 , BiO, and SnO_2 . Mo, Cu, and Zn were estimated semi-quantitatively, providing an indication of the presence of molybdenite, chalcopyrite, and sphalerite. Variations in the relative proportions of As_2O_3 and S in the mixes were found to have no measurable effect on the minor element determinations, but the Fe content was constant at 34.30 weight per cent. Fully analysed natural arsenopyrites would have provided more reliable standards for this

¹) University of Manchester Collections.

work, but were not available. No internal standard was used, but standards and unknowns were run alternately, and a number of determinations were checked by an additive method (Campbell and Carl, 1954). Errors due to the non-correspondence of the natural and synthetic matrices are thought to have been minor.

All analyses were made with a Philips total vacuum X-ray spectrograph attachment, operated at 44–50 kV, 20 mA, and using a high purity tungsten X-ray tube (PG 1559), a LiF analysing crystal, and a scintillation counter. 1.5 g portions of arsenopyrites and standards were ground to minus 300 mesh in agate mortars, mixed with 0.2 g of borax binder, and pressed into smooth-surfaced, homogeneous discs in a hydraulic press at 15 000 p.s.i. for 1.5 minutes. In cases where it was not possible to separate as much as 1.5 g of pure arsenopyrite, 0.8 g of the mineral was evenly pressed directly onto Mylar film. All determinations were carried out with the sample chamber evacuated. Standard curves of integrated counts above background against concentration were linear in the range studied (0–2 weight per cent) for both sample preparation methods.

Bismuth was determined, where detected, by measurement of the $L\alpha$ and $L\beta$ (first order) lines, while for the other elements the $K\alpha$ (first order) lines were used. The peak positions were located by counting at 0.01° 20 intervals, and remained constant throughout the duration of the project (6 months). The lower limits of detection for Co, Ni, Sb, and Bi were 0.007, 0.005, 0.005, and 0.025 weight per cent, respectively (using the borax dilution method). The precision and accuracy of the Co, Ni and Sb determinations in the concentration range 0.01–2.0 per cent were better than 10 per cent of the amount present, as shown by the repeated analysis of several standards and arsenopyrites. For concentrations of less than 0.01 per cent (in the case of Bi less than 0.05 per cent) the accuracy was approximately 20 per cent of the amount present.

THE NEW DATA

COBALT, NICKEL, ANTIMONY, AND BISMUTH

The quantitative determinations of Co, Ni, Sb, Bi, and Sn are listed in Tables 1 a-c, together with the d_{131} values of the arsenopyrite. Qualitative values for other elements (Ti, Cr, and V) are given for some specimens (see below). The more frequent contaminating minerals were chalcopyrite, which often invades arsenopyrite along networks of fine, hair-like fractures, and molybdenite. These sulphides contain small or negligible amounts of Co, Ni, Sb, and Bi, and cannot have caused serious error in the determination of the significant minor elements in the arsenopyrite. Copper and molybdenum contents were invariably less than 0.2 per cent, and neither element was detected in pure arsenopyrite. Both magnetite and monoclinic pyrrhotite could be easily separated magnetically from the arsenopyrite.

The X-ray fluorescence method used in this work is not suitable for the determination of minor amounts of manganese in arsenic-rich minerals, owing to the close proximity of the As $K\beta$ (2nd order) and Mn $K\alpha$ (1st order) lines. The absence of the Mn $K\beta$ (1st order) peak in all samples, however, indicates that the manganese contents do not exceed approximately 0.1 per

cent, as shown by examination of synthetic standards. With the possible exception of sphalerite, the main sulphides of the deposit (pyrrhotite, chalcopyrite, and pyrite) are all comparatively poor in manganese, and this element may in fact show a slight preferential concentration in early arsenopyrite.

Although only a few arsenopyrites from orebodies II and III were analysed, the samples provide a reasonable coverage of orebodies I and IV and the ensuing discussion will be largely restricted to these two zones.

The cobalt and nickel contents and the Co:Ni ratios of arsenopyrite in the Ylöjärvi deposit are of the same order as those found by previous workers on this mineral (Tanaka, 1943; Gavelin and Gabrielson, 1947; Fleischer, 1955). In the majority of specimens, cobalt exceeds nickel, the Co:Ni ratios varying from 0.52 to 16.0, but falling predominantly in the range 1—8. The cobalt contents range from ~ 0.007 to 1.62_1 weight per cent, and nickel from ~ 0.005 — 0.49_3 per cent. More comprehensive sampling might reveal sporadically higher Co and Ni contents, but the determined values probably cover much of the actual ranges. Routine sampling (unpublished mine reports) has shown that the average cobalt and nickel contents of the mineralized zones are 0.005—0.02 per cent, and 0.003—0.008 per cent, respectively, the highest concentrations of these elements occurring in the arsenopyrite-rich orebody IV. The order of preferential concentration of these elements in the main sulphides has been found to be¹:

for Co: arsenopyrite \gg pyrite I and pyrrhotite $>$ pyrites II and III, marcasite and chalcopyrite,

and for Ni: arsenopyrite \gg pyrrhotite $>$ pyrite I $>$ pyrites II and III and marcasite $>$ chalcopyrite.

In the majority of specimens, pyrrhotite, pyrites I, II and III, and marcasite showed very similar Co and Ni contents, intermediate between those in arsenopyrite and chalcopyrite. If it is assumed that arsenopyrite, pyrrhotite, chalcopyrite, and pyrite are present in the approximate proportions 0.8:0.4:1.0:0.2 in the deposit as a whole, it is apparent that over ~ 80 per cent of the cobalt and ~ 70 per cent of the nickel in the deposit are present in the arsenopyrite. The early crystallization of this mineral exerted a fundamental control over the amounts of these elements which were available for incorporation in the later sulphides.

No discrete cobalt or nickel minerals have been detected in polished sections of the ores, or in routine study of X-ray diffraction charts of the arsenopyrites. Cobaltite, glaucodot, and gersdorffite have been recorded

¹) The distribution of minor elements throughout the ores will be discussed in a more comprehensive description of the mineralogy of the deposit (in preparation).

from the mineralogically similar Haveri deposit, a short distance to the northwest of Paroinen (Stigzelius, 1944; Paarma, 1947), and Saksela (1947) has observed ullmannite in the antimony-rich Järvenpää deposit to the northeast of Paroinen. Arsenopyrite from Järvenpää contains 0.9 per cent Co (Ni?) (Saksela, *op. cit.*).

It is not known whether cobalt and nickel are zonally or irregularly distributed within individual arsenopyrite grains. Careful sampling in selected zones of orebodies I and IV suggests, however, that the concentrations of these elements vary widely on a small scale in orebody I, but are comparatively constant over exposures of several square metres in IV. Thus, the variability of cobalt and nickel contents in these orebodies broadly parallels the variability of the arsenic:sulphur ratios of the host arsenopyrites (see above), although the data are insufficient for a detailed examination of this relation. The analysed specimens from orebody I probably consist of grains having relatively widely varying minor element contents, and the quoted values for Co, Ni, and other elements should be regarded as mean values for the sampled zones.

Apart from the local variability there are apparently no relations between the cobalt and nickel contents and the arsenic:sulphur ratios of the arsenopyrites in any single orebody. Arsenopyrites from orebody IV with very similar d_{131} values, and which were probably deposited under almost identical temperature-pressure conditions, have very different cobalt and nickel contents and cobalt:nickel ratios. The relations between the cobalt and nickel contents in orebodies I and IV are illustrated in Figs. 14a and b. In orebody I, the available data suggest that there is a fairly well-defined positive correlation between the concentrations of these two elements, such as has been demonstrated, for instance, for Co and Ni in pyrrhotite from the Hardy mine, Sudbury, Ontario by Naldrett (1961). At very high and low cobalt contents the Co:Ni ratios show marked changes, but the positive correlation is preserved. In contrast, the Co:Ni ratios for arsenopyrites in orebody IV, and, probably, in II and III, are apparently random. The range of cobalt and nickel contents in orebody I is greater than that in the other orebodies, and the average concentrations of both elements are significantly higher (all samples with more than 1.0 per cent Co are from orebody I). There is, on the other hand, no systematic variation in the contents of either cobalt or nickel with depth in orebodies I and IV, or, on the available data, in II and III. Within each orebody the more important factors in the composition of the arsenopyrite — the arsenic:sulphur ratios, and the cobalt and nickel contents — are apparently randomly variable.

It is evident that the combined minor element content exceeds 1.0 per cent by weight in a small proportion of the arsenopyrites examined, especially in orebody I. These specimens have been omitted from the arsenic:sulphur

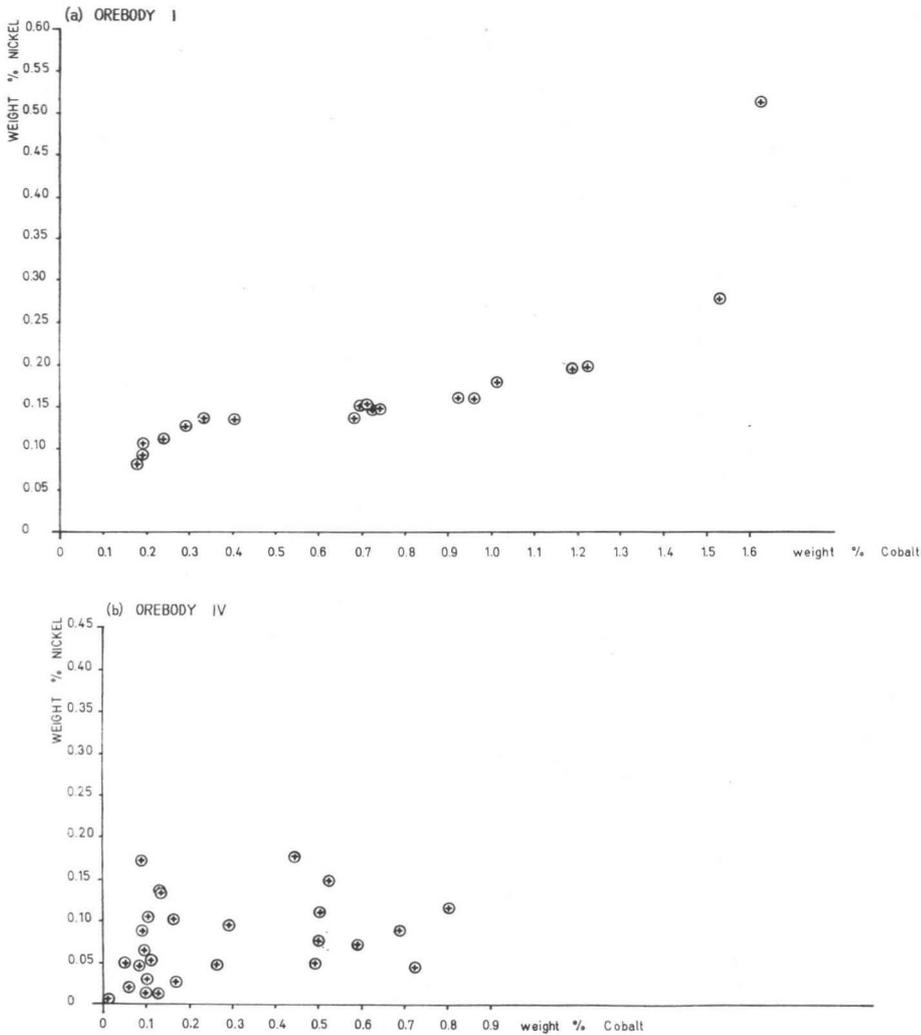


Fig. 14. Relations of cobalt and nickel contents in arsenopyrite, orebodies I and IV, Ylöjärvi mine.

ratio data (see above), but it is likely that a few of the ratios may be in error. However, it is considered that this factor has probably had no serious effect on the composition frequencies.

In comparison with cobalt and nickel, antimony shows a smaller overall variation in the arsenopyrites, from 0.006 to 0.092 weight per cent. The mean concentration of this element in arsenopyrite in orebody I is only slightly higher than that in II, III, or IV. As with cobalt and nickel, the antimony contents are apparently unrelated to the arsenic: sulphur ratios of the host

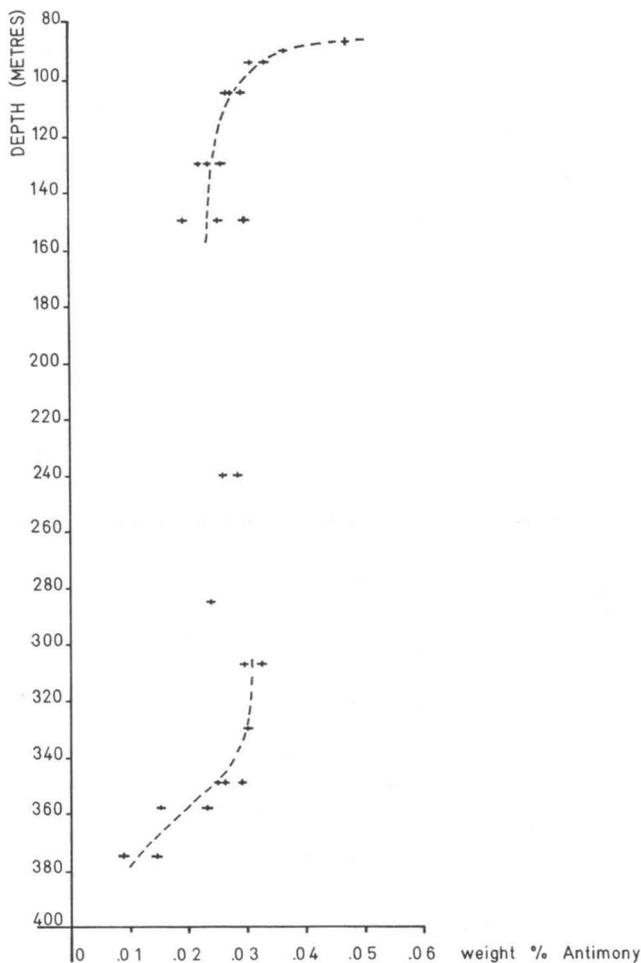


Fig. 15. Variation of antimony content in arsenopyrite with depth, orebody IV, Ylöjärvi mine.

arsenopyrites. Antimony shows no consistent trends in orebody I, but increases irregularly with decreasing depth in the arsenopyrites of orebody IV (Fig. 15). The upward increase in antimony content is clearest between the 375 m and 285 m and the 130 m and 81 m levels and may be of some significance, possibly reflecting the progressive enrichment of the rising ore solutions in this element. As pointed out in a previous section, there is no evidence that a marked temperature gradient existed in the mineralized zone during sulphide deposition, and the other minor and major elements of the arsenopyrite vary irregularly with depth. Probably over 90 per cent of the antimony in the deposit is concentrated in the

arsenopyrite; the late stage formation of minor tetrahedrite and rare gudmundite may have been brought about by the replacement of a small proportion of the arsenopyrite by löllingite (q.v.).

The X-ray fluorescence analysis method used in this study is relatively insensitive for bismuth, and this element was not detected in many of the arsenopyrites. Discrete bismuth-rich minerals (native bismuth, bismuthinite, and matildite) are present in minor amounts in the deposit, but are rarely closely associated with arsenopyrite, and none were observed in the analysed samples. The distribution of bismuth in the Ylöjärvi deposit is of considerable interest, although the problem has been studied in only a preliminary fashion. Apart from the late stage bismuth-rich minerals, the highest concentrations of this element have been found in hydroxyapatite (Fig. 5), which contains up to 0.11₅ weight per cent Bi in the lower parts of orebody IV. Bismuth was evidently available in the ore solutions throughout the main period of mineralization, although its rather variable concentration in arsenopyrite is in contrast to the more consistent antimony contents. A more sensitive analytical method capable of detecting less than 0.025 per cent bismuth would have to be used for the detailed study of the distribution of this element in the arsenopyrite; the present data serve merely to indicate the upper limits of bismuth solid solution in the present instance. As with the other minor elements, there is no simple relation between the bismuth contents and the arsenic:sulphur ratios and locations of the arsenopyrites. This element is apparently present in approximately equal concentrations in all orebodies.

It is not known whether the minor amounts of tin which were detected in several arsenopyrites, especially in orebody I, are due to contamination with cassiterite and/or stannite or reflect actual substitution in the arsenopyrite structure. Gavelin and Gabrielson (1947), similarly, were unable to come to any firm conclusions as to the mode of occurrence of tin in the arsenopyrites from the Skellefte district. Tin, however, apparently occurs as a minor element in pyrite (see above) which crystallized shortly after the arsenopyrite. The occasional minor contents of Ti, V, and Cr (Table 1) may also be due to mechanical impurities. Titanium could be contributed by ilmenite, but none of the major ore or gangue minerals contain appreciable vanadium or chromium.

SELENIUM

At the request of the writer, J. Kinnunen determined the selenium contents of 10 arsenopyrites from the deposit¹, using a modification of Cheng's (1956) spectrophotometric 3,3'-diaminobenzidine method. The analytical

¹) Professor P. Haapala and Dr. A. Häkli, of Outokumpu Oy, kindly arranged for the analyses to be carried out.

Table 2. Selenium contents and d_{131} spacings of arsenopyrites from the Ylöjärvi deposit

Specimen no. and level	Orebody	Selenium content (weight %)	d_{131} ($\pm 0.0003 \text{ \AA}$)
As 58(4)	II/III	0.043	1.6313
As 88(1)	IV	0.014	1.6325
As 125(2)	III	0.013	1.6328
As 150(4)	IV	0.010	1.6322
As 174(1)	I	0.012	1.6319
As 253(3)	I	0.023	1.6342
As 285(6)	IV	0.018	1.6334
As 307(8)	IV	0.015	1.6330
As 358(2)	IV	0.038	1.6327
As 358(12)	IV	0.038	1.6320

Analyst: J. Kinnunen, Outokumpu Oy.

data are presented in Table 2. In addition, three pyrrhotites (containing 0.008, 0.020, and 0.017 weight per cent Se), two chalcopyrites (0.007 and 0.018 per cent Se), and a single pyrite (0.019 per cent Se) were analysed. Selenium is extracted, together with gold and silver, from the Ylöjärvi chalcopyrite concentrates, which contain approximately 0.008—0.013 per cent Se (unpublished mine reports).

These few data are clearly insufficient for any firm conclusions as to the distribution of selenium in the arsenopyrite to be drawn, but indicate that there are probably no significant differences in the Se contents in the individual orebodies, and no consistent changes in the Se content with increasing depth. Furthermore, there is no apparent relation between the Se contents and the arsenic:sulphur ratios of the arsenopyrites, although the overall ranges of the Se and S contents are perhaps insufficient adequately to demonstrate any such relation. The average Se content (0.022₄ per cent) of the 10 arsenopyrites is slightly higher than that of the later sulphides, but the preferential concentration of this element in the early arsenopyrite is less marked than that of Co and Ni. Selenium appears to have been present in the ore solutions throughout the main period of mineralization. It is possible that some late-stage concentration of this element took place during the deposition of galena and the antimony-silver-bismuth-rich paragenesis (Fig. 5), but no analyses of these minerals are yet available.

DISCUSSION

The factors controlling the entry of minor and trace elements into sulphide structures have received considerable attention in recent years, and many quantitative data are available on the variety and extent of minor element substitution in pyrite, chalcopyrite, pyrrhotite, sphalerite, and galena (e.g.,

Fleischer, 1955; Fryklund and Harner, 1955; Fryklund and Fletcher, 1956; Hawley and Nichol, 1959, 1961; Burnham, 1959; Raychaudhuri, 1960, 1961; Sims and Barton, 1961; Arnold *et al.*, 1962; Hawley, 1963). In some instances details of the variation in minor elements within individual deposits or orebodies are given. In the majority of deposits it is evident that the minor element distribution is largely random, and systematic variations in the concentration of minor elements or in their partition between co-existing sulphides are apparently exceptional (e.g., Stoiber, 1962). Few authors, however, have studied post-Precambrian deposits. With few exceptions, such as the correlation of Fe and Mn contents in sphalerite, few simple relations between minor element concentration and major element composition of sulphides showing solid solution have been demonstrated (Raychaudhuri, 1960, 1961, Arnold *et al.*, 1962). The distribution of minor elements in the Ylöjärvi deposit is of considerable interest because the major element variations of two of the principle sulphides, arsenopyrite and pyrrhotite, are known in some detail.

The possibility and extent of substitutional solid solution of minor elements in sulphides are probably influenced by a combination of some or all of the following factors:

(a) The ionic, covalent, or, possibly, the atomic radii of the minor and major elements, and their electronegativities. Whereas some observed substitutions may be explained on the basis of the ionic or covalent radii, as pointed out by Fleischer (1955), knowledge of the exact nature of the bonding in sulphides is a necessary preliminary to the prediction and interpretation of minor element substitution.

(b) The original concentration of the minor element in the ore-forming fluid, the relative concentrations of other elements capable of solid solution in the host sulphide, and the concentration of the minor element at the immediate site of deposition.

(c) The P-T conditions prevailing during deposition, and the mode of transport of the minor and major elements in the ore solutions.

(d) The major element composition of the host sulphide, where variable.

(e) The proximity of other earlier or approximately contemporaneous sulphide or gangue minerals capable of accepting the minor element, and the degree of surface equilibrium between the ore solution and the several phases crystallizing in a particular zone (Sims and Barton, 1961).

(f) Contamination with wall-rock material, especially where the minor elements under consideration are present in equivalent or greater concentrations in the host rocks than in the ore solutions.

(g) The rate of crystallization and the grain size of the host sulphides.

(h) The chemical stability of the host sulphide after deposition, and the possibility of preferential diffusion and migration of minor elements with exsolution, falling temperatures and pressures, during re-equilibration with later minerals, and as a result of deformation.

Minor elements in sulphides may also be present in mechanical inclusions of other minerals, in fluid inclusions, in thin films on grain boundary or fracture surfaces, or within fine-grained exsolution bodies (Auger, 1941; Hawley and Nichol, 1961). These possibilities are not considered to have played a significant role in the concentration of minor elements in Ylöjärvi arsenopyrite, and will not be further discussed. The nature of the major (Fe, As, and S) and minor (Co, Ni, Sb, Bi and Se) elements under consideration suggests that solid solution of the latter in the arsenopyrite was substitutional rather than interstitial or »proxy» (Auger, 1941).

In the face of so many possible factors, few of which are susceptible to quantitative evaluation, the observed minor element distributions may obviously be discussed in only very general terms.

The minor elements for which quantitative data are available are, to a greater or lesser degree, preferentially concentrated in arsenopyrite, the earliest major phase crystallizing in the brecciated zones. If it is assumed that a measure of equilibrium between early-forming crystals and the whole of the ore fluid responsible for mineralization existed in the »magmatic hearth» from which the fluids were derived, and if the mineralizing processes are considered to have been structurally and chemically monoascendent, this concentration may reflect a true partitioning with respect to later pyrite, pyrrhotite, and chalcopyrite. Later sulphides crystallizing in contact with, or in proximity to arsenopyrite may have attained surface equilibrium with the earlier mineral with respect to both major and minor elements, the concentrations of minor elements remaining in the ore fluids permitting. There is no evidence of post-depositional migration of minor elements from arsenopyrite during the formation of the sulphides, with the possible exception of some diffusion during the growth of löllingite (q.v.) and gudmundite.

Arsenopyrite euhedra enclosed by wall-rock silicates, and presumably unaffected by the later movement of the ore solutions, contain the same range and concentrations of minor elements as arsenopyrite in contact with pyrite, pyrrhotite, and chalcopyrite in the breccia matrix. Within the wall-rocks, Co, Ni (and Mn) are concentrated to a very minor degree in titanomagnetite, and in hornblende and biotite which formed during the wall-rock metasomatism immediately preceding the deposition of arsenopyrite. The original concentration and the possible release of these elements during the chloritization and silicification of the altered zones may have slightly influ-

enced the minor element content of the arsenopyrite, but the few available data do not confirm any relation between the composition of arsenopyrite and the wall-rock paragenesis in any zones.

The absence of any direct relation between the minor element contents and the arsenic: sulphur ratios has been stressed. It is possible that the P-T conditions during deposition had no marked influence on the entry of minor elements into the crystallizing minerals or that any such relation was greatly outweighed by other factors. Similarly, Raychaudhuri (1960, 1961) found no correlation between minor element content and temperature of deposition (as indicated by the Fe-deficiency) of pyrrhotite in the Dore Lake deposits, Chibougamau district, Quebec, and no such relation is shown by the pyrrhotite in the Ylöjärvi deposit. The available concentrations of minor elements in the ore solutions, which, especially in orebody I, were apparently subject to wide local variations, may have been the dominant factor controlling the minor element distribution in the mineralized zones. The association of highly variable arsenic: sulphur ratios and minor element contents in orebody I, and the more consistent nature of both factors in orebody IV, may reflect the greater compositional homogeneity of the ore fluids in the latter zone and/or the more extended period of arsenopyrite deposition in orebody I. On the other hand, the relatively rapid crystallization of large tonnages of massive arsenopyrite in orebody IV might have been expected to result in the «trapping» of high concentrations of minor elements. The present study has shown that there is no apparent relation between the minor element contents and average grain size, but the more extensive masses of arsenopyrite in orebody IV are more consistent in composition than the less continuous masses of this mineral in orebody I. Diffusion and homogenization of minor (and major) elements during and following deposition may have been facilitated in the former zone.

Although the minor element contents vary irregularly with depth, they support the geochemically distinct nature of the orebodies (I, II and III, and IV) demonstrated by the arsenic: sulphur ratios of the arsenopyrites.

The cobalt: nickel ratios are of some interest, especially since the sympathetic correlation between these elements is shown by the compositionally heterogeneous arsenopyrite in orebody I. None of the minor elements in the arsenopyrite are essential constituents of minerals crystallizing roughly contemporaneously, although Bi and Sb occur in the quantitatively unimportant late-stage native bismuth, bismuthinite, and matildite, and gudmundite, tetrahedrite, bournonite, and boulangerite, respectively. It is considered unlikely that the activity of these volatile elements during arsenopyrite deposition was appreciably influenced by the (potential) formation of these minerals. In no sense do the observed contents of Co, Ni, Sb, Bi, or Se represent saturation concentrations for the prevailing P-T conditions,

although this does not, perhaps, necessarily preclude the attainment of some degree of equilibrium between the several minor elements. Thus, the concentrations of cobalt and nickel in orebody I may have been sufficient to permit an «equilibrium» partitioning of these elements. In the absence of quantitative data on the cobalt and nickel contents of arsenopyrite co-existing with glaucodot, cobaltite, and gersdorffite, or of arsenopyrite from cobalt- or nickel-rich deposits, comparison of the cobalt and nickel contents of Ylöjärvi arsenopyrite with possible saturation contents is not possible. An arsenopyrite from the Haveri deposit, northwest of Paroinen, was found to contain 0.72 ± 0.005 per cent Co, and 0.475 ± 0.005 per cent Ni, but cobaltite, a common constituent of the ore, was not observed in the specimen examined.¹ Although complete solid solution between arsenopyrite and glaucodot is presumably possible in the synthetic system, few reliable modern analyses of arsenopyrite show more than ~ 5 per cent Co, and little is yet known of the probably extensive degree of solid solution of Fe in natural glaucodot.

There is evidently a need for further studies of the major and minor element contents of arsenopyrites from various environments and parageneses. The present study of minor elements in Ylöjärvi arsenopyrite has yielded no precise indications of the conditions of deposition of this mineral, and serves to illustrate the complexity of minor element relations in natural assemblages.

The selenium contents of the Ylöjärvi arsenopyrites are considerably higher than those of the three specimens of this mineral analysed by Edwards and Carlos (1954), but the Australian deposits sampled by these authors appear to be comparatively poor in selenium in comparison with other areas for which quantitative data are available (Fleischer, 1955). On the basis of the analyses of pyrrhotite, chalcopyrite and pyrite, it is evident that the Ylöjärvi ores show a concentration of selenium similar to that found in a number of Canadian Precambrian deposits (including nickeliferous copper sulphide ores, and massive Cu-Fe-Zn-S ores) by Hawley and Nichol (1959), but higher than that in Palaeozoic banded Cu-Fe-Zn-S ores, in gold-pyrite-quartz veins, and in pyritiferous uranium-bearing banded or bedded deposits. Hawley and Nichol suggest that the introduction of Se into earlier sulphides in a «restricted system» by late vapours may have complicated the original partitioning of this element between pyrite, pyrrhotite, and chalcopyrite. Selenium shows some tendency to be concentrated in late chalcopyrite, and irregularly increases with decreasing depth in the Noranda deposit. It was proposed that the widely differing average Se contents of the massive Precambrian deposits and the mineralogically similar Palaeozoic ores of Quebec

¹) Specimens of Haveri sulphides were kindly provided by Vuoksenniska Oy, Helsinki.

and New Brunswick may reflect the Se contents of their parent magmas. In many of the deposits studied by Hawley and Nichol (1959, 1961), as at Ylöjärvi, selenium, unlike cobalt, silver, and lead, appears to show no well-defined order of concentration in the major sulphides.

Edwards and Carlos (1954) and Hawley and Nichol (1959) have shown that, whereas hydrothermal sulphides show a wide range of selenium contents, sulphides of sedimentary or supergene origin are uniformly poor in this element. The comparatively high selenium content of the Ylöjärvi sulphides supports the proposed hydrothermal, possibly magmatogene, origin of the ores.

Bergenfelt (1953), in a comprehensive study of the distribution of selenium in the ores of the Skellefte region, found that the different deposits and types of ore showed widely variable average Se concentrations. In particular, the Boliden deposit is characterized by an extreme though sporadic Se enrichment, and up to 1.5 per cent Se has been found in galena from these ores. The occurrence of »selenocosalite» and »selenokobellite» at Boliden has been described by Ödman (1941). In the more varied parageneses, the order of decreasing selenium concentration was found to be Pb-Bi-Sb sulphosalts-chalcopyrite (with up to 0.14 per cent Se)-arsenopyrite-sphalerite-pyrrhotite and pyrite. In general, pyritic ores are significantly poorer in Se than the arsenopyrite-chalcopyrite ores showing mineralogical similarities to the Ylöjärvi parageneses. More comprehensive sampling of the Ylöjärvi sulphides might reveal a similar order of preferential concentration. It is evident, however, that little partitioning has taken place between »co-existing» arsenopyrite, pyrrhotite, chalcopyrite, and pyrite. Bergenfelt (1953) demonstrated that Se shows an approximately linear correlation with Bi in the Skellefte ores, but not with Cu, Zn, or As. At Ylöjärvi it is known that Se shows no direct relationship with Cu, Zn, Au, or Ag (unpublished mine reports), but the quantitative relations between Se and As have not been examined. Unfortunately, Bergenfelt does not give Se contents for separated arsenopyrites, and no exact comparison of his values with the Ylöjärvi data is possible.

No analyses are available of arsenopyrite from other deposits in the Svecofennian and Karelian provinces, but the selenium contents of concentrates from the Metsämonttu (southern Finland) and Vihanti (north-western Finland) deposits have been determined, ¹ as follows:

Metsämonttu (a Svecofennian deposit):

Ore.....	0.013 per cent Se
Cu-concentrate	0.054 » » »
Pb-concentrate	0.36 » » »

¹) Unpublished data from Dr. A. Häkli, Outokumpu Oy.

Vihanti (probably Karelian):

Ore (1955)	0.004 per cent Se
Pyrite ore	0.003 » » »
Zn-concentrate.....	0.0008—0.004 per cent Se
Cu-concentrate.....	0.006—0.009 » » »
Pb-concentrate	0.011—0.038 » » »

(Analyst, J. Kinnunen).

It is evident that the Svecofennian province as a whole is enriched in selenium but that the degree of enrichment and preferential concentration varies widely from deposit to deposit. Selenium shows approximately the same order of concentration, with significant exceptions, in the major sulphides in a number of deposits, but the degree of partitioning is very variable, and may be disguised by preferential association with Te (as at Boliden), Bi, Sb, and Pb, where these elements were available in some quantity during ore deposition. On the other hand, the Karelian massive sulphide ores may be consistently poor in selenium.

PART III

LÖLLINGITE: COMPOSITION AND CONDITIONS OF FORMATION

The sulphur and cobalt contents of the rare löllingites in the deposit have been estimated by X-ray diffraction methods. In addition, the arsenic: sulphur ratios and, where possible, the cobalt contents of the coexisting arsenopyrites undergoing replacement by the löllingite have been determined. Six löllingites from the 174 m and 285 m levels of orebody I were examined.

Neumann, Heier and Hartley (1955), Clark (1962), and Roseboom (1963), among other authors, have studied the relations between the composition and cell-dimensions of natural and synthetic löllingites, and Clark (*op. cit.*) has developed a rapid X-ray method for the estimation of the cobalt and sulphur contents (see also Roseboom, *op. cit.*). This method, used in the present study, involves the measurement of the 210, 111, 120, and 101 α reflections, and the results are accurate to about 0.2 weight per cent sulphur and 0.5 per cent cobalt¹. In most assemblages it is to be preferred to chemical analysis owing to the difficulty of separating löllingite from other sulphur- and arsenic-bearing minerals. It is probable that the cation: anion ratio of löllingite approaches 1:2 (Pehrman, 1950; Neuman *et al.*, 1955), but Roseboom (1963) has shown that synthetic löllingite is non-stoichiometric at 800°C, varying in composition from FeAs₂ to FeAs_{1.98}. No systematic changes in the 120, 101, 210, and 111 spacings, however, could be observed in this composition range, confirming the findings of Heyding and Calvert (1960).

Although löllingites with up to ~ 30 per cent NiAs₂ have been described (see Roseboom, *op. cit.*), Ni, Sb, and Bi are probably subordinate to S and Co in most specimens, and the variations in cell dimensions of natural löllingites are generally attributable to variable solid solution of the latter elements.

The results of the present study are presented in Table 3. Material for X-ray diffraction and fluorescence analysis was gouged from etched polished sections; it was not possible to obtain sufficient arsenopyrite for the determination of cobalt in three instances. Using a Philips diffractometer and Ni-filtered Cu-K α radiation, the löllingite reflections were measured relative

¹ X-ray analyses have been made of 22 löllingites from other deposits (mainly pegmatites), in a preliminary survey of the range of composition shown by this mineral in various environments. Several samples were found to give reflections which would not plot on Clark's spacing diagram (1962, fig. 2). This effect may be due to particularly high contents of nickel, or, more probably, antimony, which was detected qualitatively in some specimens.

Table 3. Sulphur and cobalt contents of «coexisting» löllingite and arsenopyrite, Ylöjärvi deposit

Sample no. and level	Arsenopyrite composition		Löllingite composition	
	sulphur ($\pm \sim 1.0$ at %)	cobalt (± 0.1 weight %)	sulphur weight % (± 0.2 %)	cobalt (± 0.5 %)
Asp/Lo 174(12 a)	32.1	0.9 ₃	0.6 ₁	0.5 ₈
Asp/Lo 174(12 a)	31.8	0.4 ₃	0.7 ₃	0.4 ₀
Asp/Lo 174(13)	33.9	0.3 ₇	0.5 ₂	0.2 ₉
Asp/Lo 174(17 a)	33.6	—	0.5 ₀	0.7 ₃
Asp/Lo 285(39)	34.6	—	0.3 ₄	0.6 ₅
Asp/Lo 285(42)	34.0	—	0.9 ₀	0.6 ₈

N. B. The Ni and Sb contents of arsenopyrites Asp/Lo 174 (12 a), (12 b) and (13), as determined by X-ray fluorescence analysis, were 0.05—0.26 and 0.02—0.04 weight per cent, respectively. Neither element was detected in the löllingites (limit of detection, 0.005 per cent).

to the 110 and 102 α reflections of quartz as internal standard (calibrated against silicon). Four complete oscillations were carried out for each smear mount; the peaks were assumed to be unresolved K α reflections. The presence of some arsenopyrite in three samples prevented the precise measurement of the 210 löllingite reflection. The relative values of the sulphur contents of the arsenopyrites, estimated from the 131 spacings, are more significant than the absolute contents.

Clark (1962) has attempted to locate the sulphur-rich löllingite solvus curve experimentally, in the expectation that the sulphur content of natural löllingite coexisting with arsenopyrite might prove to be a useful geothermometer. Reaction rates below $\sim 630^\circ\text{C}$, however, were found to be extremely slow, and the solvus could only be determined in the range $702^\circ\text{—}630^\circ\text{C}$. At 630°C , 2.9 weight per cent sulphur may occur in solid solution in löllingite crystallizing in equilibrium with arsenopyrite, the degree of solid solution presumably decreasing at lower temperatures. The available data do not therefore permit an accurate estimation of the temperature of deposition of the Ylöjärvi löllingites. Further, the effect of minor cobalt on the solvus is not known. However, the observed sulphur contents of 0.3₄—0.9₀ weight per cent suggest temperatures well below 630°C , and, very probably, below 300°C (Clark, written communication). It is probable that the löllingite attained some degree of equilibrium with the arsenopyrite undergoing replacement. Since löllingite was deposited after the introduction of pyrrhotite and sphalerite (at $\sim 565\text{—}475^\circ\text{C}$) and in approximate contemporaneity with the Ag-Bi-Sb paragenesis, such a low temperature of formation would not be unreasonable.

There is no apparent relation between the arsenic: sulphur ratios of the coexisting arsenopyrites and löllingites; thus, samples 285 (39) and (42) contain arsenopyrites with similar arsenic: sulphur ratios in contact with

löllingites showing widely differing sulphur contents. Cobalt shows no marked enrichment or depletion during the replacement process. The formation of gudmundite may have been the direct result of the apparent release of antimony during the replacive growth of löllingite, but no late-stage minerals contain appreciable nickel. Very little is known of the range of composition shown by löllingite in sulphide-rich parageneses, or of the partitioning of sulphur and cobalt between coexisting arsenopyrite and löllingite, so the present data are perhaps worth recording.

The relations between arsenopyrite and löllingite in the Ylöjärvi deposit differ from those described from arsenic-silver-cobalt-rich deposits (e.g., Stillwell and Edwards, 1939; Markham and Lawrence, 1962) in which löllingite is frequently a major constituent, and crystallized at a higher temperature than arsenopyrite. Ramdohr (1960), however, records the replacement of arsenopyrite by löllingite. In a recent review of mineral associations in the Cu-Fe-As-S system, McKinstry (1963) stresses the rarity of the assemblage pyrrhotite-löllingite. At Ylöjärvi löllingite coexists with pyrite II and marcasite (after pyrrhotite), and with intermediate pyrrhotite ($\text{Fe}_{0.912}\text{S}$) and troilite (Fig. 5), but not with high-temperature, very iron-deficient pyrrhotite.

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REFERENCES

- ARNOLD, R. G., COLEMAN, R. G., and FRYKLUND, V. C. (1962) Temperature of crystallization of pyrrhotite and sphalerite from the Highland-Surprise mine, Coeur d'Alene district, Idaho. *Econ. Geol.*, 57, 1163—1174.
- AUGER, P. E. (1941) Zoning and district variations of the minor elements in pyrite of Canadian gold deposits. *Econ. Geol.*, 36, 401—423.
- BARNES, H. L., and KULLERUD, G. (1961) Equilibria in sulfur-containing aqueous solutions in the system Fe-S-O, and their correlation during ore deposition. *Econ. Geol.*, 56, 648—688.
- BARTON, P. B. Jr., and TOULMIN, PRIESTLEY, 3rd. (1964) Sphalerite phase equilibria in the system Fe-Zn-S between 580°C and 850°C (abstract). *Geol. Soc. Amer. Spec. Paper* 76, 8—9.
- BERGENFELT, S. (1953) Om förekomsten av selen i Skelleftefältets sulfidmalmer. *Geol. Fören. i Stockholm Förh.*, 75, 327—359.
- BOYLE, R. W., and JAMBOR, J. L. (1963) The geochemistry and geothermometry of sphalerite in the lead-zinc-silver lodes of the Keno Hill-Galena Hill area, Yukon. *Canad. Min.*, 7, 479—496.
- BURNHAM, C. W. (1959) Metallogenic provinces of the southwestern United States and northern Mexico. *New Mexico Bur. Mines & Min. Res., Bull.* 65.
- CAMPBELL, W. T., and CARL, H. F. (1954) Quantitative analysis of niobium and tantalum in ores by X-ray fluorescent spectroscopy. *Anal. Chem.*, 26, 800—805.
- CHAYES, F., and MACKENZIE, W. S. (1957) Experimental errors in determining certain peak locations and distances between peaks in X-ray (powder) diffractometer patterns. *Amer. Min.*, 42, 534—547.
- CHENG, K. L. (1956) Spectrophotometric determination of selenium in stainless steels and in copper by 3,3'-diaminobenzidine. *Chemist-Analyst*, 45, 67—68.
- CLARK, A. H. (1963) Solfuri e ossidi di ferro del giacimento di Ortano (Isola d'Elba): further data on the composition of the arsenopyrite and pyrrhotite. *Atti Soc. Toscana Sci. Nat.*, 70, ser. A, 312—317.
- »— (1964a) Studies on the mineralogy and geochemistry of the Ylöjärvi copper deposit, south-west Finland. Unpubl. Ph. D. thesis, Univ. of Manchester.
- »— (1964b) Preliminary study of the temperatures and confining pressures of granite emplacement and mineralization, Panasqueira, Portugal. *Trans. Instn. Mining & Metall.*, 73, Pt. 12, 813—824.
- »— (1964c) The composition and conditions of deposition of arsenopyrite in the Ylöjärvi deposit. *Geologi (Helsinki)*, 16, 114—116.
- CLARK, L. A. (1960a) The Fe-As-S system: phase relations and applications. *Econ. Geol.*, 55, 1345—1381, 1631—1652.
- »— (1960b) The Fe-As-S system. Variations of arsenopyrite composition as functions of T and P. *Ann. Rept. Dir. Geophys. Lab., Year Book* 59, 127—130.
- »— (1962) X-ray method for rapid determination of sulfur and cobalt in loellingite. *Canad. Min.*, 7, 306—311.

- COLEMAN, L. C. (1957) Mineralogy of the Giant Yellowknife gold mine, Yellowknife, N. W. T. *Econ. Geol.*, 52, 400—425.
- EDWARDS, A. B., and CARLOS, G. C. (1954) The selenium content of some Australian sulfide deposits. *Proc. Austral. Inst. Mining & Metall.*, 172, 31—64.
- ELLSWORTH, H. V. (1916) A study of certain minerals from Cobalt, Ontario. *Ont. Dept. Mines, Ann. Rept.*, 25, pt. 1, 200—243.
- EMBREY, P. G. (1953) Note on the occurrence of beryl and löllingite at the New Consols mine, Stoke Climsland, Cornwall. *Min. Mag.*, 30, 259—262.
- FLEISCHER, M. (1955) Minor elements in some sulfide minerals. *Econ. Geol.*, 50th Anniv. Vol., 970—1024.
- FRYKLUND, V. C., and FLETCHER, J. D. (1956) Geochemistry of sphalerite from the Star mine, Coeur d'Alene district, Idaho. *Econ. Geol.*, 51, 223—247.
- FRYKLUND, V. C., and HARNER, R. S. (1955) Comments on minor elements in pyrrhotite. *Econ. Geol.*, 50, 339—344.
- FYFE, W. S., TURNER, F. J., and VERHOOGEN, J. (1958) Metamorphic reactions and metamorphic facies. *Mem. Geol. Soc. Amer.*, 73.
- GAVELIN, S. and GABRIELSON, O. (1947) Spectrochemical investigation of sulphide minerals from the ores of the Skellefte district. On the significance of minor constituents for certain practical and theoretical problems in economic geology. *Sver. Geol. Unders.*, ser. C, 491.
- GOTTARDI, G. (1962) Solfuri e ossidi di ferro del giacimento di Ortano (Isola d'Elba). *Atti Soc. Toscana Sci. Nat.*, ser. A, 69, 327—341.
- HAWLEY, J. E. (1963) The Sudbury ores: their mineralogy and genesis. *Min. Assoc. of Canada*.
- HAWLEY, J. E., and NICHOL, I. (1959) Selenium in some Canadian sulphides. *Econ. Geol.*, 54, 608—628.
- »— (1961) Trace elements in pyrite, pyrrhotite, and chalcopyrite of different ores. *Econ. Geol.*, 56, 467—487.
- HIMMI, R. (1954) The copper ore deposit of Parainen. *Geotekn. julk.*, 55, 15—16.
- »— (1960) The Ylöjärvi mine. In »Mining Geology, Finland». Guide to Excursions A, 36 and C, 31, *Int. Geol. Congress*, 24—28. (Also an excursion booklet on the mine).
- HOWELL, F. H., and MOLLOY, J. S. (1960) Geology of the Braden orebody, Chile, South America. *Econ. Geol.*, 55, 863—905.
- KALLIOKOSKI, J. (1961) Temperatures of formation and origin of the Nigadoo and Brunswick Mining and Smelting No. 6 deposits, New Brunswick, Canada. *Econ. Geol.*, 56, 1446—1455.
- KOUVO, O., and KULP, J. L. (1961) Isotopic composition of Finnish galenas. *Ann. New York Acad. Sci.*, 91, 476—491.
- KULLERUD, G. (1953) The FeS-ZnS system; a geological thermometer. *Norsk. Geol. Tidsskr.*, 32, 61—147.
- KULLERUD, G., and BUSECK, P. R. (1962) The Fe-Mo-S system. *Ann. Rept. Dir. Geophys. Lab.*, Year Book 61, 150—151.
- KULLERUD, G., and YODER, H. S. (1959) Pyrite stability relations in the Fe-S system. *Econ. Geol.*, 54, 533—572.
- MARKHAM, N. L. (1961) Mineral composition of sulfide ores from the Peelwood, Cordillera and Mt. Costigan mines, Peelwood district, N. S. W. *Proc. Austral. Inst. Mining & Metall.*, 199, 133—156.

- MARKHAM, N. L., and LAWRENCE, L. J. (1962) Primary ore minerals of the Consols Lode, Broken Hill, New South Wales. *Proc. Austral. Inst. Mining & Metall.*, 201, 43—80.
- MCKINSTRY, H. (1957) Phase assemblages in sulfide ore deposits. *New York Acad. Sci., Trans.*, 20, 15—26.
- »— (1963) Mineral assemblages in sulfide ores: the system Cu-Fe-As-S. *Econ. Geol.*, 58, 483—505.
- MORIMOTO, N., and CLARK, L. A. (1961) Arsenopyrite crystal-chemical relations. *Amer. Min.*, 46, 1448—1469.
- NALDRETT, A. J. (1961) The geochemistry of cobalt in the ores of the Sudbury district. Unpubl. M. Sc. thesis, Queen's Univ. (quoted in Hawley, 1963).
- NEUMANN, H., HEIER, K., and HARTLEY, J. (1955) On loellingite (FeAs₂). *Norsk Geol. Tidsskr.*, 34, 157—165.
- ÖDMAN, O. H. (1941) Geology and ores of the Boliden deposit, Sweden. *Sver. Geol. Unders., årsbok* 25, 1—190.
- »— (1942) Minerals of the Varuträsk pegmatite, XXXIII. Native metals and sulphides. *Geol. Fören. i Stockholm Förh.*, 64, 277—283.
- PAARMA, H. (1947) Haverin kiisumalmin mineraliparageneesi. Pro Gradu, Käsikirjoitus Helsingin Yliopiston geologian laitoksessa.
- PALACHE, C., BERMAN, H., and FRONDEL, C. (1944) Dana's system of mineralogy. Vol. 1. John Wiley & Sons, Inc., New York.
- PEHRMAN, G. (1950) Löllingit von Kuortane (W. Finland). *Acta Acad. Åbo., Math. phys.*, 17, 1—6.
- PRIEM, H. N. A. (1962) Geological, petrological and mineralogical investigations in the Serra do Marão region, northern Portugal. *Doct. thesis, Univ. of Amsterdam.* 160 pp.
- RAMBERG, H. (1952) The origin of metamorphic and metasomatic rocks. Chicago.
- RAMDOHR, P. (1960) Die Erzminerale und ihre Verwachsungen. 3rd. Edn., Akademie-Verlag, Berlin.
- RAYCHAUDHURI, S. (1960) Trace elements in the sulphide deposits of the Chibougamau district, Quebec. Unpubl. Ph. D. thesis, McGill Univ. (Abstr. *Canad. Mining J.*, 82, 1961, 104).
- »— (1961) Glimpses into ore genesis from trace element study. *Science & Culture*, 27, 333—335.
- ROSE, A. W. (1961) The iron content of sphalerite from the Central district, New Mexico and the Bingham district, Utah. *Econ. Geol.*, 56, 1363—1384.
- ROSEBOOM, E. H. (1963) Co-Ni-Fe diarsenides: compositions and cell dimensions. *Amer. Min.*, 48, 271—299.
- ROY, S. (1961) Mineralogy and paragenesis of lead-zinc-copper ores of the Bathurst-Newcastle district, New Brunswick. *Bull. Geol. Surv. Canada*, 72.
- SAKSELA, M. (1947) Über eine antimonreiche Paragenese im Ylöjärvi, SW-Finland. *Bull. Comm. géol. Finlande*, 140, 199—222.
- SCHWARTZ, G. M. (1944) The host minerals of native gold. *Econ. Geol.* 39, 371—411.
- SIMONEN, A. (1952) Suomen geologinen kartta — Geological Map of Finland, 1 : 100 000. Lehti — Sheet 2124. Viljakkala — Teisko.
- SIMS, P. K., and BARTON, P. B. Jr. (1961) Some aspects of the geochemistry of sphalerite, Central City district, Colorado. *Econ. Geol.*, 56, 1211—1237.
- SMITH, F. G. (1963) Physical geochemistry. Addison-Wesley Publ. Co. Inc., Reading, Mass.

- STIGZELIUS, H. (1944) Über die Erzgeologie des Viljakkalagebietes im Südwestlichen Finnland. Bull. Comm. géol. Finlande, 134.
- STILLWELL, F. L., and EDWARDS, A. B. (1939) Notes on loellingite and the occurrence of cobalt and nickel in the Broken Hill Lode. Proc. Austral. Inst. Mining & Metall., 114, 112 et seq.
- STOIBER, R. E. (1962) Minor cobalt in pyrrhotite and chalcopyrite of the Elizabeth mine, South Strafford, Vermont. Geol. Soc. Amer., Prog. 1962 Ann. Meetings, 15 A (abstr.).
- TANAKA, N. (1943) Studies on nickel and cobalt in arsenopyrite. 1. Estimation and determination of cobalt in some arsenopyrites. Bull. Chem. Soc. Japan, 18, 436—446.
- TOULMIN, Priestley, 3rd., and BARTON, P. B. Jr. (1964) A thermodynamic study of pyrite and pyrrhotite. Geochim. Cosmochim. Acta, 28, 641—671.
- WILLIAMS, K. T., and BYERS, H. G. (1934) Occurrence of selenium in pyrites. Ind. Eng. Chem., Anal. Edn., 6, 296—297.

