A review of what is presently known about the nature, distribution and genesis of certain authigenic minerals in the stanniferous alluvial deposits of Southeast Asia

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"This is not the end. It is not even the beginning of the end.
But it is, perhaps, the end of the beginning."
(Winston Churchill)

Abstract This paper aims at bringing together and commenting on the scattered published and other data relating to the topic under review and highlighting that which still remains to be done before a really comprehensive treatment of the subject can be attempted. At the outset it is stressed that many of the problems relating to the geneses of some of the material described have not been solved because, of necessity, a considerable proportion of the samples examined were obtained from secondary sources, such as beneficiation plants.

The following authigenic species are discussed:-

pyrite, marcasite, sphalerite, galena, copper-bearing sulphides, siderite and native copper. Authigenic iron oxides, 'chlorite', calcite, silica and phosphates have been passed over, largely because they have not yet been sufficiently researched, although they are all known to occur in the alluvial deposits in question.

All the sulphides discussed in this paper were generated in swamps, some of which may well have been of the fresh-water type, during early diagenesis. At Lenggang, Belitung, where all the sulphides occur, the paragenesis is pyrite and marcasite, sphalerite, galena, copper-bearing sulphides.

In the Southeast Asian stanniferous alluvials both pyrite and marcasite are very common. Both species occur in organic-rich deposits as individual crystals of a variety of habits, but pyrite crystals are by far the more abundant. Marcasite, however, is usually the dominant species replacing and/or occupying cells in fossil plant material, and then pyrite framboids are often included in it. At Lenggang, galena rims voids in marcasite replaced wood.

Slabs of pyrite and of marcasite, both with included framboids, have been found on the bedrock of some opencast mines, as have sandstones and conglomerates cemented by one or both of the sulphides.

Not surprisingly, framboids and polyframboids are commonly found in organic-rich deposits but, in addition, framboids have been located in voids of blocks of primary ore lying on the bedrock, in a supergene colloform chalcopyrite coating of a lode, in siderite dripstone, and as a late component within the hard-rock ore of Sungai Goh where, possibly, it is of hypogene origin. In the mill at Ayer Hitam Tin Dredging Property, Malaysia, an ornamented polyframboid was found whose ornamentation may have developed in the mill.

In addition to the modes of occurrence of marcasite, noted above, spherulites of the species have been recovered from Perak, but they are probably of rare occurrence.

Siderite, a rather common mineral in the alluvials, occurs, as noted above, as dripstone, and also as deposits on pebbles, and within sandy deposits. However, siderite is most commonly found as spher-

ulites, either as isolated bodies or as aggregates. These display radial crystallisation and concentric colour zones, some of which are due to incipient oxidation during development. They may be locally slightly replaced peripherally and/or along fractures, by pyrite. They developed in sandy clays and similar deposits, essentially by replacement, in an environment which was somewhat less reducing than that in which the sulphides developed, and so, not surprisingly, in Perak, siderite-rich dredging areas have been, on occasion, observed to give way laterally to sulphide-rich ones.

Sandy inclusions not uncommonly occur in the sulphides and siderite. These inclusions are often fragmented. The fragments are but little displaced and are cemented by the authigenic host. These facts suggest that the fragmentation was probably largely or entirely due to the force of crystallisation of the host, perhaps during its conversion from a gel state. However, on occasion, the pressure of overlying sediments may have been a contributory factor.

Crystals of native copper have been recorded from some of the Perak alluvial deposits. They occurred at a site visited by the writer in a shallow hematite-rich stanniferous deposit. Most of the crystals showed no deformation such as might be expected were they transported in water. Possibly they developed in the placer from copper-bearing solutions seeping down the shallow valley slope: that they were washed out of a hard-rock oxidised copper deposit is much less likely. Native copper is also reputed to have been found in some of the stanniferous placers in Belitung.

INTRODUCTION

Not surprisingly, those who have been concerned with the search for, evaluation and exploitation of the alluvial tin deposits of Southeast Asia have limited their attention, almost entirely, to cassiterite. Commonly they have saved and sold some of the denser resistate species which often occur in considerable concentrations in the crude cassiterite concentrates and which include zircon, ilmenite, monazite and xenotime. On rarer occasions gold, certain Ta/Nb species, and scheelite have also been recovered and sold. Generally speaking much is known about the nature and source of the cassiterite, and quite a lot about the other species noted above.

In addition to the allogenic species already mentioned a number of authigenic minerals have been recovered from the stanniferous alluvials. Some of the latter species have only been recorded from a few of the hundreds of past and present mining operations, and minerals in this category include galena, sphalerite, chalcopyrite and certain other copper-bearing sulphides, and possibly native copper. On the other hand, authigenic pyrite, marcasite and siderite are widespread and commonly occur in marked concentrations in the crude cassiterite concentrates from the dredges and palongs. Particularly during the upgrading of the dredges' concentrates flotation is employed to remove the unwanted sulphides. While there is no doubt that the tin-miners are well aware of the common presence of sulphides and siderite in the alluvial deposits they exploit, it is also true to state that very few concern themselves with the question as to whether the sulphides they encounter are wholly or partly authigenic or where they and siderite occur in the sedimentary sequences they are exploiting. For a long time it has been known that in some localities dredges occasionally recover allogenic sulphides as free grains and/or in pebbles and other water-worn bodies, and in angular pieces of collapsed veins and lodes. The dredging companies have shown considerable interest in such material during the past decade or so as it can indicate, on occasion, the presence of underlying hard-rock tin deposits that might be worth exploiting by opencast methods at a future date.

Until 1968 the authigenic species of the tin-bearing alluvial deposits of Southeast Asia had been largely neglected by mineralogists and geologists, simply, I think, because, in their

view, which was probably a valid one, there were many more important subjects in need of investigation.

When I arrived in Malaysia, in 1968, I began to study the authigenic species of the placers there, I think because I had previously investigated those occurring in some of the Cornish equivalent deposits. Since then I have continued the study, albeit in a desultory manner, sometimes alone, but often with others, and in particular with E.B. Yeap.

This paper is an account of what I presently know about some of the authigenic species occurring in the stanniferous alluvials of Southeast Asia. It has been prepared with a view to assembling those relevant data that are scattered in the literature and presenting certain unpublished information. To anticipate its conclusion it can surely be said that, hopefully, while its content may serve as a foundation on which to build, it will demonstrate that a great deal of research needs to be done before anything approaching a satisfactory account of the nature and genesis of the authigenic species in question can be written.

A NOTE CONCERNING THE NATURE AND ORIGIN OF THE STANNIFEROUS ALLUVIALS OF SOUTHEAST ASIA

The following is necessary as it provides a sketch of the nature and genesis of the alluvials in which the authigenic species occur that are to be discussed later. For a recent comprehensive account of these alluvials the reader should consult Batchelor (1979).

The cassiterite of the alluvials has been derived from a variety of primary deposits which are spatially and probably genetically-related to granitoids of a number of different ages. The dense resistate species, of some economic importance (zircon, ilmenite, monazite and xenotime) which accompany the cassiterite in the alluvials, have been largely derived from the granitoids as they weathered. Oxidation of some types of primary deposit locally enabled certain heavy metals (Cu, Pb, and Zn) and sulphur (as sulphate) to become mobilised and to report in the sediments of the drainage system where, on occasion, they were deposited.

The granitoids, noted above, were emplaced in a variety of metasediments, both calcareous and non-calcareous, with which were locally associated volcanics of varying composition. The calcareous members, the so-called 'Limestones', are important to what follows later. They are much in evidence in the tin-fields of Kinta, Selangor and, locally, in South Thailand.

From the early part of the Tertiary, at least, the orogenic zone containing the tin deposits was a mountainous belt that constituted a part of the continental mass known as Sundaland. Prolonged denudation up to Pleistocene time resulted in planation to base level of the marginal areas of the northern portions of the Tin Belt and the virtually complete peneplanation of that part of it which is largely occupied by the islands of Singkep, Bangka, and Belitung.

It is not known when the destruction of the primary tin deposits commenced. Indeed, there is still much uncertainty concerning the development of the stanniferous alluvials of Southeast Asia as a whole. These alluvials are often structurally complex, and not infrequently their profiles display a number of stanniferous horizons. It seems difficult to escape

from the conclusion that the major fluctuations in sea-level during Pleistocene times, due to the removal of seawater as ice and the subsequent return of water to the oceans as the ice melted, played a major part in the genesis of the tin-bearing alluvials by inducing rejuvenation of the rivers and rapid valley erosion, followed by transgression of the land by the sea which resulted locally in reworking of alluvial deposits that were previously developed on land. Possibly the position of the coastline may also have been modified to some extent during Quaternary time by isostatic adjustments and local tilting.

During the period occupied by the development of the stanniferous alluvial deposits, which might reasonably be regarded as extending to the present time, swampy areas, which are ephemeral features, developed within the drainage systems, often only to be eliminated by burial beneath sediments. Some of the swamps were undoubtedly of the freshwater type, while others near the sea contained salt-water or brackish-water. In all of them organic matter accumulated and reducing conditions were generated. Variations in the Eh and pH of such environments sometimes favoured the generation of sulphides and on others the development of siderite. The not uncommon occurrence of a number of different authigenic species in a small volume of sediment indicates that locally the chemical environment was capable of rapid change. That much larger lateral changes in the chemical environment may also occur has been demonstrated, for example, in Perak, where the ground being dredged changed laterally from one containing much pyrite to one in which siderite was dominant.

THE NATURE AND GENESIS OF SELECTED AUTHIGENIC SPECIES

At the outset it is pertinent to note that much of what appears in the following pages stems from the examination of samples from beneficiation plants of one sort or another. This means that often the precise original locations in the alluvial deposits of the material examined are unknown. Obviously this constitutes a serious drawback when the question of genesis arises. On occasion, also, the same problem has arisen as a result of the material examined having been provided by a mining company, who had obtained it by drilling, but who was not prepared to reveal much about the location of the bore nor of the nature of the sediments encountered. Still other material examined was derived from old and inadequately labelled collections in the offices of Inspectors of Mines. Only on a few occasions was it possible to collect the material from the undisturbed host and, as will be apparent later, such samples have provided data on which some of the most important findings are based.

Having noted some of the fundamental weaknesses of the study, the nature and genesis of the selected authigenic species are dealt with under the following headings:-

A.   The sulphides (pyrite, marcasite, galena, sphalerite and copper-bearing species).
    Ai.   Generalisations
    Aii.   Pyrite and marcasite.
    Aiii. Views concerning the chemistry of the genesis of authigenic pyrite and marcasite.
    Aiv.   Galena, sphalerite and copper-bearing sulphides.

B. Siderite
    Bi.   Views concerning the chemistry of the genesis of authigenic siderite.

    C. Native copper
        Ci.   Views concerning the chemistry of the genesis of native copper.

A. The Sulphides

Ai. Generalisations

The Eh/pH stability fields of pyrite and marcasite (and siderite, which is discussed later) are such that the species are capable of development in freshwater, brackish-water and salt-water environments. Probably this also applies to the lead, zinc and copper-bearing sulphides. Certainly early diagenetic chalcopyrite and bornite occur in the superficial sediments of the Fal Estuary (Cornwall) (Thorne, 1983).

In Southeast Asia all the authigenic sulphides noted above have been most commonly found in situations characterised by an abundance of organic debris although, on occasion, there is some evidence that some of them, having been generated in an organic-rich environment, were transported by running water to another situation in which organic debris was not much in evidence but where the Eh/pH conditions were such as to permit the sulphides' survival. On the other hand the sulphides, as a result, perhaps, of the removal of overlying sediments, were subjected to oxidation and, as one result of this, iron oxide pseudomorphs after pyrite locally developed: indeed, such pseudomorphs are not particularly rare in the alluvials.

Because much has yet to be discovered about the development of the alluvial deposits of Southeast Asia, generally one cannot be sure of the precise nature of the situation in which a given sample of sulphides were developed. In particular, we are often not sure if the host sediments were accumulating in a salt, brackish-, or fresh-water environment. With the fluctuations in the land to sea relationship which were known to occur there is no doubt that the alluvials, as a whole, contain sulphides which were formed in all the environments noted above. It is of no small importance to the topic under review to note that Sivam (1971) has demonstrated, beyond reasonable doubt, that the stanniferous alluvial deposits of the North Kinta Valley (Perak, Malaysia) are of non-marine origin. From these North Kinta deposits authigenic pyrite and marcasite (and siderite) have been recovered and in considerable amount locally. This fact is of interest in that some find it difficult to believe that authigenic sulphides can develop, in appreciable quantity, in a fresh-water environment. Thus, for example, Degans (1965, p. 155) writes " .... *sulphate reduction is the major phenomenon in the geochemistry of sulphur at the early stages of diagenesis. All sediments contain more sulphur than could possibly be attributed to the sulphate ions in the interstitial waters. Organic sulphur can also be excluded as a major source, in as much as organic matter contains only about 1 per cent sulphur per dry weight of sample. Instead the result of Kaplan et al. (1963) indicates that most of the sulphides originated at the sediment/water interface by utilising seawater sulphate*". In spite of Degans' remarks there is support, other than that from the work at North Kinta, noted above, that sulphides can be generated in a fresh-water environment. Thus Deans (see Eager, 1952) who originally suggested that pyrite framboids were only developed in a marine environment, later revised his views (see Love, 1958, p. 437) and declared that *"in considering the origin of these tiny pyrite bodies, it should be realized that they could be found in a very wide range of sediments of all ages, from Cambrian to the present day, mostly marine, but also freshwater"*. Deans further remarks (op. cit., p. 437) that

pyrite framboids are also to be found *"in foul-smelling muds from shallow ponds in some London parks"*.

In view of Degans' remarks that are noted above it might be inferred that the general low sulphur content of freshwater sediments would militate against the generation of sulphides in anything approaching the concentrations that might be expected in some marine sediments. Certain studies indicate that this assumption is a valid one. Thus Williams and Keith (1963) having made a geochemical study of the Pennsylvanian coal beds, concluded that the coal beds which were covered by freshwater sediments were lower in sulphur content than those underlying marine beds. The same workers also noted that Spackman, having worked on certain peat bogs in Florida, concluded that the marine peats contain, on an average, about six times more sulphur than the corresponding freshwater peats. Unfortunately no work of a similar nature has been carried out in Southeast Asia.

To return to Degans' observations, which are noted above, it is relevent to remember that in a freshwater environment the sulphur requirements for the generation may be derived not only from the breakdown of sulphur-containing organic compounds. In ore-fields containing primary sulphide-bearing deposits, active oxidation of the latter may release sulphate ions which, on migrating into the local drainage systems, may result in high but restricted concentrations of sulphur. It is not suggested that this source of sulphur has played anything but a very minor role in the genesis of freshwater sulphides in Southeast Asia except possibly in the very close vicinity of certain primary deposits. Perhaps the authigenic copper and other sulphides at Sungai Way and at Lenggang (Belitung), which are described later, contain sulphur, which wholly, or in part, has been derived from oxidising primary deposits.

In Southeast Asia hepatic springs, which are known to exist there, may have made small local contributions to the sulphur used in the generation of the authigenic sulphide. The best local but indirect support for this suggestion is the occurrence of late pyrite framboids in the stanniferous skarn of Sungai Goh (Pahang). Scrivenor (1928, p.p. 113-114), who was unaware of the presence of framboids in the ore in question, having described the genesis of all but the latest components, remarks that *"much later, perhaps in recent times, a siliceous hot spring attacked part of the deposit where it was particularly calcareous, dissolved away much of the calcite, formed the cave (in which ore can still be found), deposited onyx and green chalcedony ...."*. As the framboids occur in chalcedony perhaps they were deposited as a result of hot spring activity but one which was not only siliceous but also hepatic (Footnote).

Finally it is relevant to note that there is ample evidence in support of the view that in the sediments in which the authigenic sulphides (and siderite) developed, the chemical environment commonly varied considerably over very small distances. Only by invoking such a view can one explain, for example, the occurrence of pyrite framboids and single pyrite crystals in a very small sediment sample, the wide variety of habit displayed by crystals of pyrite extracted from a handful of peat collected at Sungai Besi (Selangor) and textural variations exhibited by botryoidal sulphides which developed side-by-side at Lenggang, Belitung.

Footnote: I discovered the presence of framboids in ore from Sungai Goh some years ago but I have yet to write
a note about the discovery.

Aii. Pyrite and marcasite

Authigenic pyrite occurs in the alluvials as individual crystals (as in the peat of Sungai Besi, noted above), as more-or-less randomly organized crystal aggregates in the form, on occasion, of slabs and also as cements of sandstones and conglomerates and as inclusions in other sulphides. In addition, pyrite framboids are not uncommon and polyframboids have been recorded. Examples of framboids included in other sulphides and in siderite are known. Examples of these various types of occurrence will be dealt with below.

Although from appearance one cannot tell whether an individual pyrite crystal had developed within the alluvial deposit in which it had been found or whether it had become detached from, say, a lode in the bedrock, often precisely how and where it is disposed enables the problem to be resolved. There is no doubt, for example, that the pyrite crystals in the Sungai Besi peat, which are noted earlier, are authigenic, as is the black coating of hydrotroilite which invests some of the peat components (Footnote). A further example of pyrite crystals which are authigenic occurred in Sungai Besi Number 2 opencast mine where one side of the originally alluvial-filled valley is granite while the other side is limestone. As will be understood from what is written later, the pyrite crystals under discussion, in spite of their unusual disposition, owed their development to the nature of the alluvials which originally covered the site where they were discovered. In the granite there were a number of replacement bodies, which have since been exploited, and which contained cassiterite, sulphides and the oxidized products of the latter. In the upper superficial parts of one of these bodies, known as the Lee Gossan, scorodite occurred in which were set projecting pyrite crystals. The pyrite crystals were commonly so orientated that each rested on a cube edge rather than on a face (Figure 1). Satellite pyrite crystals had grown on the anchored ones. These observations are difficult to explain. I suppose that the river cut down rapidly, having been rejuvenated, in Pleistocene time, when a low sea-level was established. Then rapid oxidation of the Lee Gossan, and somewhat similar neighbouring deposits, occurred. Later, as the sea-level rose, the Sungai Besi valley became infilled with sediments, the drainage became sluggish and the oxidised in situ ore bodies were in part covered by sediments which were locally rich in organic debris and so provided a reducing environment. At this stage the pyrite crystals investing the scorodite were deposited. But it is not known why they were so deposited in that they rested on edges rather than faces? Hosking and Yeap (1975a, pp. 90-91) discuss the general problem of the deposition of the pyrite at some length and conclude that the best explanation "*postulates that at some time after the scorodite had (virtually) completed its development, the environment, as noted above, changed to a reducing one. Biogenically derived sulphide ions and native sulphur entered the system and reacted initially with some of the ferric ions (that would need to be converted at the outset to ferrous ones) of the scorodite, thus initiating the development to pyrite by replacement. What happened to the released arsenate ions is unknown..........*". The further development of the pyrite crystals beyond the scorodite surface may have been effected by all the ingredients necessary for the development of the pyrite being transported down concentration gradients to the sites of pyrite deposition but in such concentrations that the solubility product of the sulphide was not exceeded except at the surfaces of the already established pyrite centres. This is a good example of a continuum which is sometimes seen to exist between the gene-

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Footnote: The sulphide component of melnikovite may be confirmed by applying the simple and rapid sodium azide/iodine test, for details of which see Feigl (1954, p.p. 280-282).
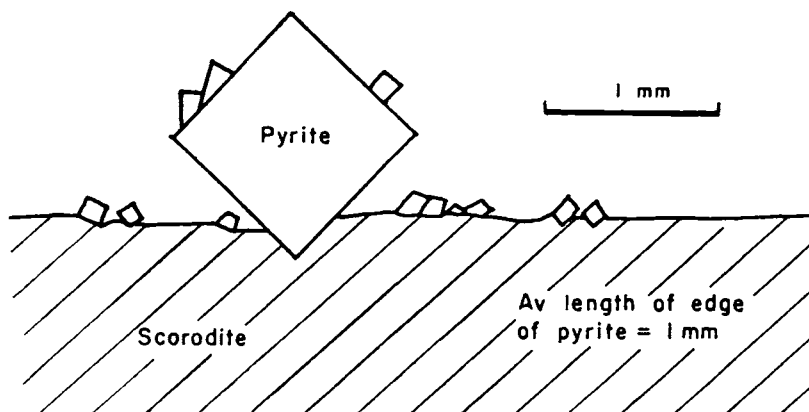
Fig. 1.   Diagramatic section through a scorodic crystal from the Lee Gossan No. 2 Opencast, Sungei Besi
Mines, showing the common orientation of the larger pyrite crystals and the distribution of the minor ones (After
Hosking & E.B. Yeap, 1975).

sis of authigenic species in alluvial deposits and mineralogic modifications which, on
occasion, can occur during the changes of the more superficial portions of a hard-rock ore-
deposit by oxidation and/or reduction processes. Another example will be described later.

In the piles of iron sulphide from the 'tin sheds' beneficiation plants, particularly those
of the dredging companies that use flotation to remove this unwanted commodity, isolated
framboids are not uncommon. Each framboid varies in size, in most instances, from about 7
μm to 35 μm, and is generally approximately spheroidal in shape. In addition, but much less
frequently, one encounters polyframboids, as noted earlier. The individual crystals of the
framboids and polyframboids are never more than a few microns in length and in such
Southeast Asian examples as I have examined the individual crystals are octahedra, on
occasion, somewhat modified. However, without resorting to the S.E.M. the habit of any
individual crystal is often difficult to establish with certainty. The crystals within a given
framboid may be highly ordered, moderately ordered or poorly ordered.

In polished section framboids which developed in rather close proximity to each other
may show a considerable variety of textural patterns which, in part, is due to the different
planes along which similarly or identically ordered framboids have been cut and in part due
to fundamental differences in the ordering of the crystals of the framboids. One framboid that
I examined in polished section (Hosking, 1972b, p. 186) displayed what was, in my
experience, a new textural pattern and one that I have not seen subsequently. The lines of
crystals in one half of the body were orientated at right-angles to those in the other half. I think
this texture may indicate that the nature of the immediate environment in which a framboid
develops determines the degree and mode of ordering of its pyrite crystals. The peculiar
ordering of the framboid described above is, in my view, best explained by assuming that the
developing framboid was "sitting" at an interphase between two different chemical environ-

ments with one half subject to one environment and the other half to the other during the period of its formation.

Sometimes, as in the material from South Thailand, I have seen framboids which have developed so close together that mutual interference has occurred so that in thin section each framboid is polygonal in shape. Skripchemko and Berber'yan (1975) not only claim that mutual interference of growing framboids tends towards the development of polygonal forms, but that at the same time, internal adjustment of the pyrite crystals of which they are composed tends to make the framboids highly ordered. My observations of Southeast Asian polygonal framboids support this claim to some measure in that they have invariably been highly ordered. However, it is well to remember that polyhedral framboids may not always be due to mutual interference. Morrissey (1972, B35-36) describes syn-sedimentary, quasi-framboidal aggregates from the Lower Carboniferous limestones at Tynagh, County Galway, Ireland, which are similar to ones described earlier by Love and Amstutz (1966). These aggregates, from 5-10 μm in size, and consisting of microcrystallites from 0.5-1 μm, fall within the ranges established for syn-sedimentary framboids at Tynagh. The outlines of all the aggregates noted are either hexagonal or pentagonal. Morrissey rejects the view that these aggregates are framboids that were originally normal but have become distorted or that they originated by pseudomorphous replacement of single crystal of some earlier substance. He suggests that probably "the polyhedral aggregates resulted from an exceptionally systematic build-up of pyrite microcrystallites, probably under the influence of van der Waals forces, on a single individual or on a nucleus of several that presented an orderly arrangement of crystal faces to a medium containing pyrite microcrystallites of the same size and shape in suspension".

Curious aggregates of small polygonal masses of pyrite have been seen by me in polished sections of 'grains' of authigenic sulphides from Lenggang (Belitung) (Figures 2 and 3). Beyond reasonable doubt these aggregates, which have been observed in pyrite and in galena matrices, are the pyrite-infilled lumina of wood cells, the walls of which having been completely obliterated during the development of the sulphide matrix.

Finally, Love (1967, p. 337) when discussing the early diagenetic iron sulphide in recent sediments in the Wash (England) notes that in the material investigated *"there appears to be transition ... between single (pyrite) crystals and some framboidal spherules which show a tendency to polygonal outline"*. I have not found a parallel to this in the Southeast Asian pyritic material that I have examined but the Southeast Asian siderites do show such a tendency.

Spheres composed of an aggregate of pyrite framboids have been known for a considerable time and were termed 'Rogenpyrite' by Fabricius (1961). More recently such bodies have been named 'polyframboids' by Love (1971). I first found such bodies in a pile of pyrite reject from the tin-shed of Tronoh Mines in 1956 (see Hosking, 1969, p. 57). Since then I have often found polyframboids in samples of pyrite from the opencast tin mines of Southeast Asia. However, in my experience they are extremely rare there by comparison with the frequency of occurrence of single framboids. Of the polyframboids which I have examined, by far the most interesting one was obtained from the pyrite flotation product of the Ayer Hitam (Selangor) tin-shed and this has been described by me earlier (Hosking,
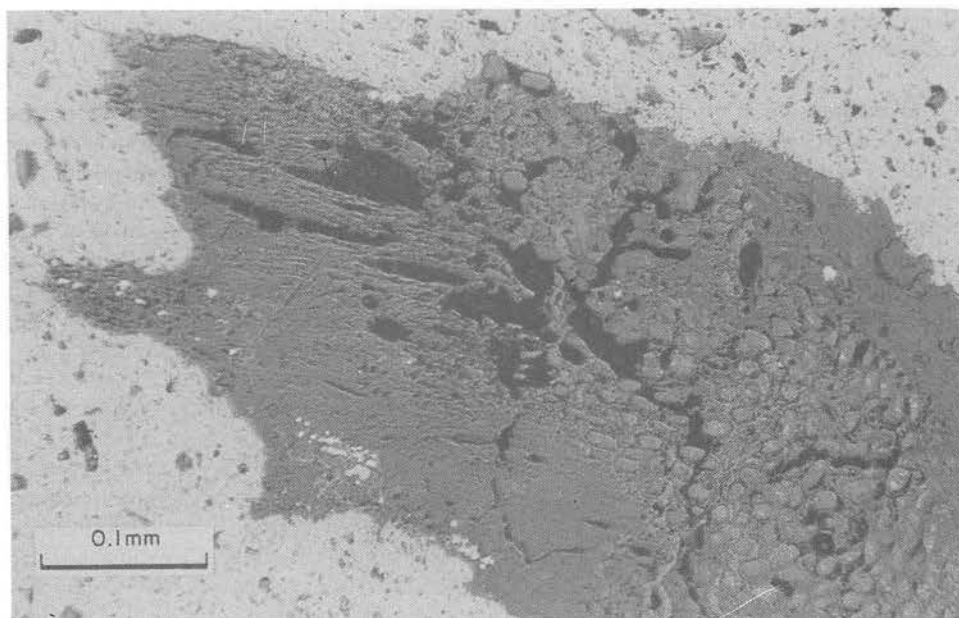
Fig. 2.   A photomicrograph of a polished section of a fragment of wood in a galena nodule. Locality: Lenggang, Belitung, Indonesia.
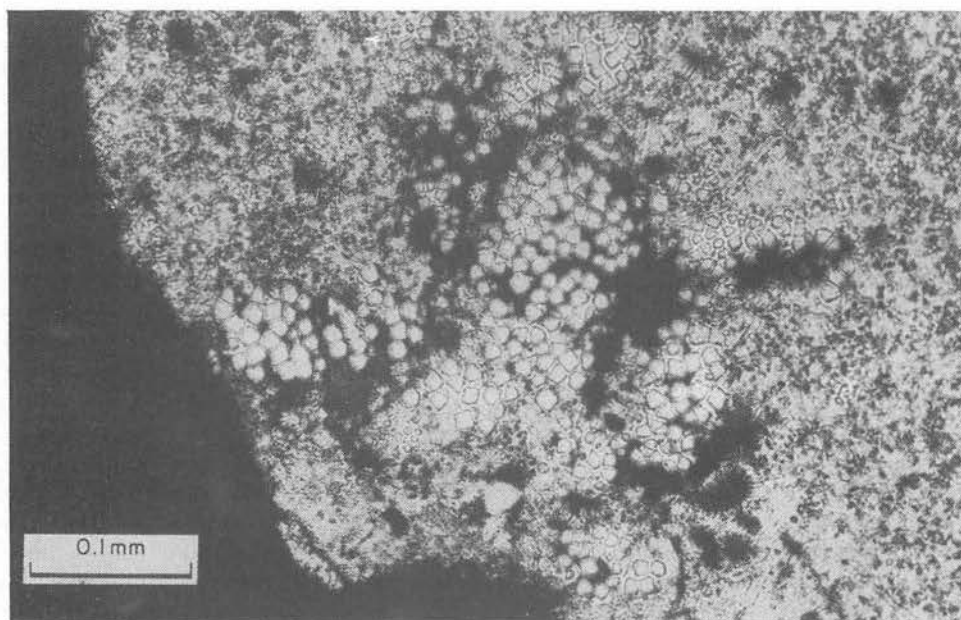

Fig. 3.   A photomicrograph of a polished section of a galena nodule containing polygonal (near white) masses of pyrite. The pyrite was deposited in the lumina of wood cells and after the event galena was deposited which completely oblitered the cell walls. Locality: Lenggang, Belitung, Indonesia.
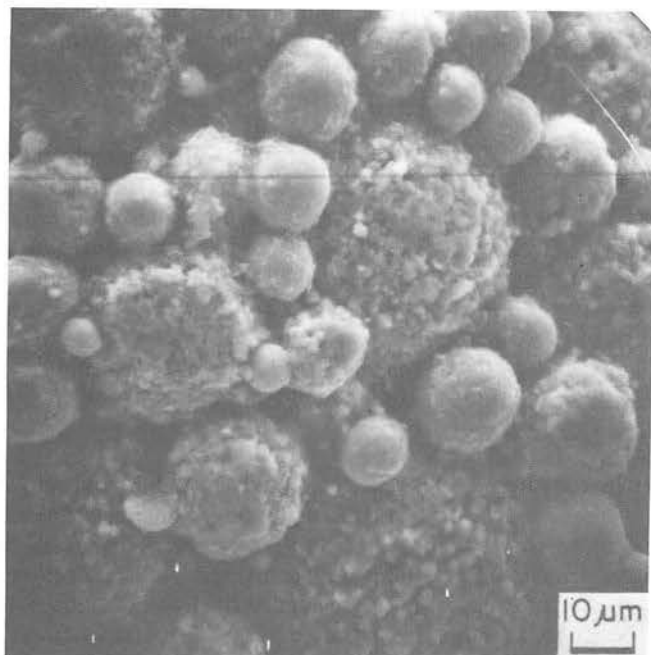
Fig. 4   A scanning electron photomicrograph of a portion of the ornamented Ayer Hitam polyframboid.

1980). The specimen in question, which was examined under the S.E.M., (Figure 4) consisted of a mass of framboids, each from c. 25-40 µm in diameter, and composed of poorly ordered octahedra, each about 8 µm in length. Within the 'gutters' between the framboids were smaller spheres, from c. 4 to 10 µm in diameter, which were of iron sulphide, but "*were not made up of an aggregate of pyrite crystals, indeed*" under the highest magnification obtainable each displayed a cumulus cloud effect''(Hosking, op. cit., p. 125).

Whilst the question of the generation of framboids and polyframboids is discussed at some length later, it is convenient to provide some observations about the development of the ornamented Ayer Hitam polyframboid at this point. I suppose that the polyframboid was generated in an organic-rich environment and, like single framboids is a product of early diagenesis. Possibly, in an unornamented state, it was subsequently transported by moving water to a point where cassiterite-rich deposits were accumulating, there to be buried rapidly in a situation where reducing conditions prevailed. Alternatively, it may have been mixed with the cassiterite grains during dredging operations. The major question to be answered is '*why is the ornamented polyframboid composed of "normal" framboids together with smaller spheres that lack a framboidal texture?*'. I believe that the smaller spheres are much younger than the framboid components and that they may have developed in the pyrite stockpile of the mill where xanthate flotation reagent films were present which are capable of yielding sulphide ions and sulphur on degradation, and where, within the pile, the Eh/pH

conditions were such that migrating ferric ions liberated during the surface oxidation of the pile would be reduced. These ions would combine with the sulphur and sulphide ions to form pyrite. The gutters between the framboids of the polyframboids would provide ideal supports for the spherical masses of sulphide which possibly were initially in a gel state and later consolidated by dehydration.

Some support is given to the view that the spherulites in the gutters of the polyframboid are of very recent origin is provided by the following remarks of Trudinger (1969, p. 16):- *"For some time we've been looking at material which is generated in biological systems which are normally just a culture of sulphate-reducing bacteria containing 300 to 500 ppm ferrous iron. And for many months we've examined these by X-ray diffraction, and in every case they just appeared to be an amorphous form of iron sulphide. We've now looked at these growths in the electron microscrope and this has revealed that a good proportion, in fact, in some of our systems, the bulk, of the iron phase present is in the form of pyrite, but it is pyrite which is so microcrystalline, that one cannot see any structure on the elctron microscope and it is amorphous to X-rays"*.

In addition to the occurrence of isolated framboids in organic- rich and other sediments, the bodies have also been encountered in slabs of pyrite and of marcasite. For instance, during Banka drilling of the deposits in a limestone sink-hole, in Perak, irregularly shaped slabs of pyrite, each weighing in the order of 100 g, were recovered. Polished sections of the material showed that it consisted of isolated and aggregated pyrite framboids in a matrix of the same mineral. *"The lobate character of the pyrite matrix, together with what were considered to be marked syneresis cracks, suggested that it was formed originally as a gel whose consequent crystallisation resulted in a complex mosaic of pyrite crystals with which were associated; numerous voids. Locally the pyrite masses were bounded by crystals displaying growth zones suggesting that they did not pass through a gel stage"* (Hosking, 1972b, pp. 184-5). The presence of these bounding crystals gives reason for wondering if any of the pyrite matrix passed through a gel stage, in spite of the observations in support of it that are noted above.

Somewhat similar sulphidic slabs to those just described were recovered from an organic-rich horizon in an opencast mine in Selangor. However, these consisted of erratically disposed pyrite framboids in a marcasite matrix which was patterned by what I thought were syneresis cracks (Hosking, 1972, p. 185).

As noted elsewhere, iron sulphides may act as the cement of conglomerates and sandstones and I found an example of the first near Kuala Lumpur and of the second in Belitung (Indonesia): these occurrences are now described and discussed.

A decade or so ago I found a sizeable specimen containing iron sulphides in the Seng Mines, near Kuala Lumpur, which I subsequently described (Hosking, 1972, p. 185). This specimen, which rested on a schistose bedrock and may have been moved to the place where it was discovered during mining operations, consisted essentially of pebbles and fragments of quartz in an iron sulphide cement. Examination of polished sections established that the cement consisted of marcasite in which there were some sparsely distributed pyrite framboids. Some of the smaller pebbles, etc., had been fractured and the resulting, little displaced fragments, had been cemented by marcasite. In addition, the marcasite binding the detrital fragments together had also been fractured. The preferential fracturing of the smaller

components and the cement (doubtless a product of early diagenesis) suggests that the cause was the increasing weight of rapidly accumulating overburden. Apropos of this it is well-known that pebbles in the Older Alluvium of Peninsular Malaysia of which the specimen under review is, doubtless, a sample, are often fractured, while those of the Young Alluvium which often covers the Older, are not.

At Gumba, Belitung, within the shallow alluvial deposit there is locally a horizon consisting essentially of quartz grains cemented by iron sulphides. Pyrite is the minor component of the cement, being limited to sparsely distributed and erratically disposed framboids. The major component is marcasite which whilst occurring locally as a crystal mosaic is much more commonly present as aggregates of small spherulites. Occasionally, also, isolated spherulites are in evidence. While some polished sections of the material reveal the cement more-or-less completely filling the original voids between the sand grains, others reveal a form of cementation that is reminiscent of spot-welding (Figure 5).

Within the organic-rich horizons of the alluvial deposits it is not uncommon to find woody material that has been partly or entirely sulphidised. Excepting on very occasions the sulphides present are marcasite and/or pyrite and the latter may be represented partly or entirely by framboids. An exception was found at Lenggang (Belitung) where voids, in fragments of originally woody tissue which had been replaced by iron sulphides, were lined with galena.

Polished sections of woody tissue that has been sulphidised show great variation. They vary in the degree of the replacement, the extent to which the woody texture has been modified and the relative percentages of marcasite and pyrite and of pyrite framboids that are present. On occasion, individual cells or voids may be packed with framboids (Figure 6), but commonly polished sections reveal cells in which one or more framboids occur in a marcasite matrix (Figure 7). Generally, within my experience, marcasitisation dominates during the sulphidisation of plant tissue, but on occasion, a marcasitised stem or root, containing, perhaps, included framboids, is invested by a cylinder of radiating pyrite crystals.

The common phenomenon of pyrite framboids being deposited within plant cells followed by the deposition of cementing marcasite within the cells may, perhaps, be due to the framboids being deposited before the destruction of the plant material is far advanced, a state of affairs which might be expected during the early stages of diagenesis. Then, with progressive destruction of the cell walls, etc., of the plant its internal environment would become more acidic as a result of the generation of carbonic acid and other organic acids, and so congenial to the deposition of marcasite. (It is generally agreed that marcasite is generated in a more acid environment than pyrite). It is relevant to note that, on occasion, pyrite may dominate the scene within plant fragments and when this happens pyrite framboids may be found embedded in a pyrite cement. This is often the case when the plant fragment had an original hollow centre such as characterises the stems of many aquatic plants. Then the centre may contain an abundance of framboids perhaps in a pyrite cement. The cells surrounding such a 'core' may contain either pyrite or marcasite and in them framboids may or may not be present (Figure 6).

The degree of cell wall changes also provides great variation. On occasion the original internal architecture of the plant fragment may be perfectly preserved and in such a
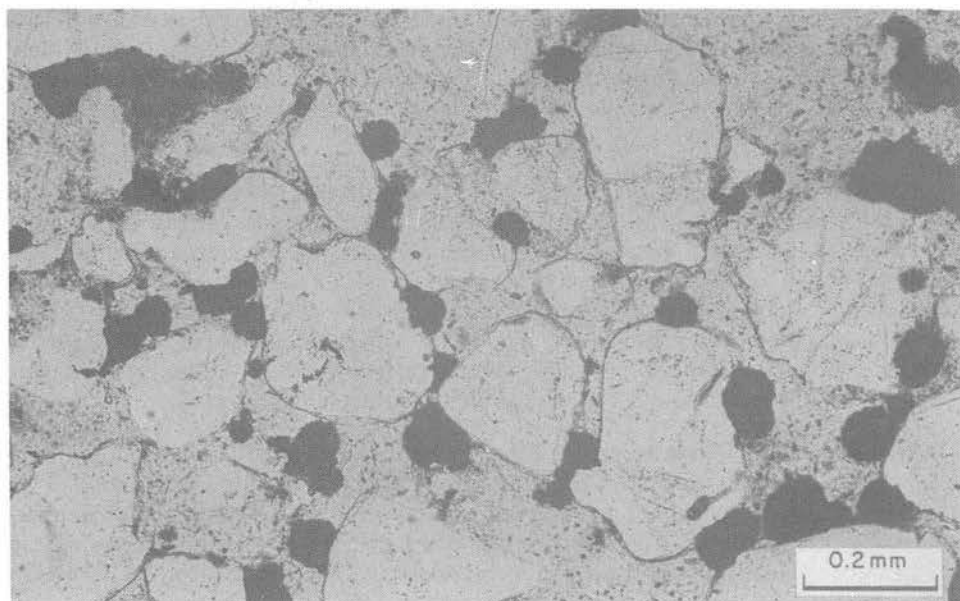
Fig. 5.   A photomicrograph of a thin section from a sandy horizon of the shallow stanniferous alluvials at Gumba, Belitung, showing essentially quartz grains 'spot-welded' by marcasite in which the occasional pyrite framboid is to be found.
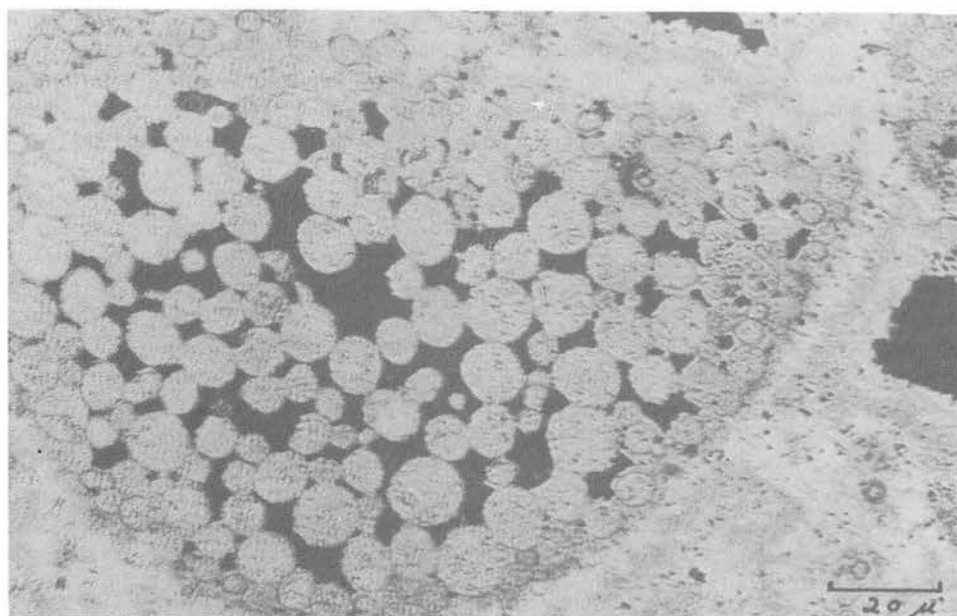

Fig. 6.   A photomicrograph of a polished section of a pyritised stem whose originally hollow centre is now packed with pyrite framboids. Locality: Ayer Hitam, Selangor.
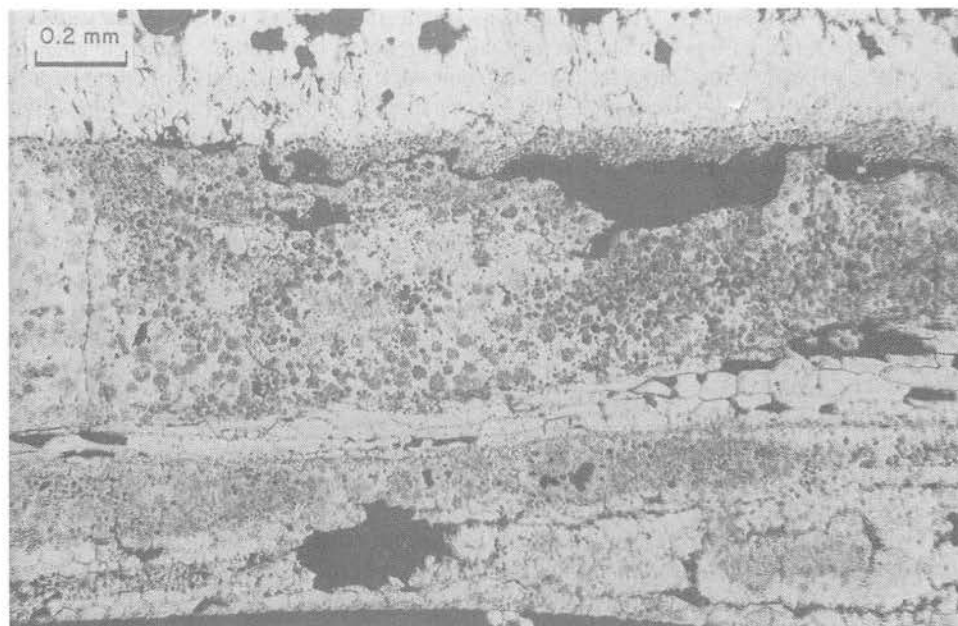
Fig. 7   A photomicrograph of a polished longitudinal section of a sulphidised stem, the centre of which consists of myriads of pyrite framboids in a marcasite matrix. Marcasite has also completely filled the lumina of cells sheathing the core. The near-white layer of palisade crystals bordering one side of the specimen are also marcasite. Locality: Berjuntai, Selangor.

circumstance the cell walls may either be carbonized or sulphidised. Specimens of plant material, when examined in polished section, may show evidence of local cell wall distortion or destruction while, in the extreme case, virtually all evidence of the original cell organisation may be obliterated by a mosaic of sulphide crystals (Figures 8, 9 and 10).

Although how and where pyrite framboids occur in the stanniferous alluvials of Southeast Asia has occupied a considerable proportion of this paper up to this point, the subject has not yet been exhausted. These bodies are sometimes found in close association with sulphides other than pyrite and marcasite, and with siderite, but it is convenient to delay dealing with these topics until later. However, it is relevant to return to marcasite at this stage.

The occurrence of authigenic marcasite in the stanniferous placers of Southeast Asia has already been referred to on a number of occasions in this paper so that only a little more needs to be said about it.

It needs to be mentioned that isolated marcasite spherulites do occur in the stanniferous alluvials of Southeast Asia albeit, my experience suggests that they are rare. In any event I have only encountered them once and that was in a polished briquette of a crude tin concentrate from the Bang Seng Lee opencast tin mine in the Tronoh area of Perak. These spherulites, which have been described by Hosking and Yeap, (1973, pp. 1-4) range in size from c. 400 μm to c. 1,000 μm. Although some are crudely circular in section, others depart

considerably from this shape. Their outlines are dentate, due to the fact that the outer surfaces consist of the terminations of marcasite crystals, which generally radiate. Like the siderite spherulites, to be described later, the marcasite ones lack nuclei, but, in section, their bodies display a number of textural variations that suggest that the chemical environment in which they were generated probably varied appreciably over very short distances and with time. Some of the variations of the textural theme have been described by Hosking and Yeap, (op. cit., p. 2) as follows:-

"In one example the spherulite consists of radiating crystals that originated from a point source and continued to grow in a 'uniform' manner throughout the development of the body.

In a second example a core of 'acicular' radiating crystals is fringed by distinctly coarser radiating ones.

In a third example a marcasite body of imperfect shape consists essentially of a fine granular marcasite mosaic with an imperfectly developed and discontinuous band of crudely radially orientated crystals that locally constitute the peripheral parts of the 'spherulites'.

Finally, the spherulite may contain sand inclusions. One, ... (Figure 11) contains a grain of quartz that, in the section, is wholly within the spherulite, and a grain of maghemite (?) that in part protrudes from the sulphide body.

The centre of origin of the spherulite lies between these two inclusions and the body's development was initiated by the deposition of radiating marcasite needles. These were then invested by an outer palisade of coarser radiating crystals.
During the crystallisation of the marcasite the inclusions were subject to tension of sufficient magnitude to cause them to fracture. The fractures so produced are now infilled with marcasite (Figures 11a and 11b) *and perhaps their present widths are in part due to 'push apart' effected by the force of crystallisation of the marcasite upon the fissure walls."*

Finally, I think it is necessary to emphasise the fact that marcasite is in some respects a neglected species in that, as far as I am aware, it is not known with any degree of precision why, on occasion, marcasite develops in preference to pyrite. To simply say what has already been said in this paper, and what has been said by virtually all who have concerned themselves with the subject, namely, that marcasite develops in a somewhat more acid environment than pyrite, is surely to admit a gross lack of knowledge of its genesis of the species in question. Of course, some, such as Love and Rickard aired similar views fifteen years ago. Love (1969, p. 41) remarked that *"in experimental precipitation work a degree of acidity appears to encourage the yield of marcasite with or without pyrite, but marcasite has been precipitated where acid has not been used .... None (of the syntheses made to date) is convincingly comparable with situations in the natural environment, and neither makes it clear whether pH is the exclusive factor controlling whether pyrite and/or marcasite should be yielded, as has often been suggested by the study of rocks in which they are found."*

Rickard (1969, p. 58) commenting on Love's paper, noted above, states that *"there is no question of pH, in itself, affecting whether pyrite or marcasite is formed although the pH may affect the type of metastable or stable sulphur species present in the solution. At more acid pH values elemental sulphur is stable, and we found that warming sulphur with mackinawite or greigite gave marcasite."*
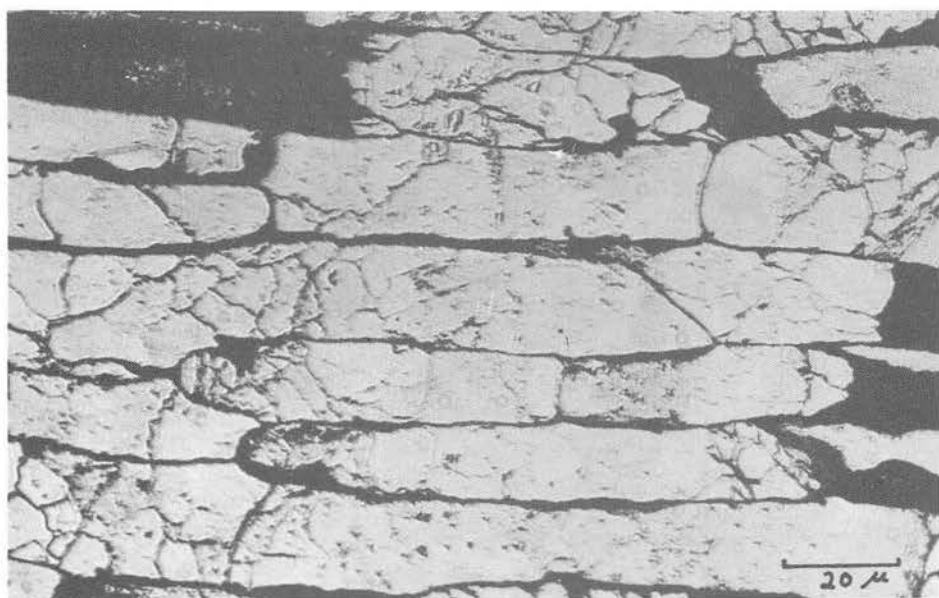
Fig. 8   A photomicrograph of a polished section of wood from South Johore, showing cells, whose walls are hardly distorted, infilled with marcasite.

Fig. 9   A photomicrograph of a polished section of wood from Pengerang, South Johore, whose cell-walls have been locally distorted and even obliterated during the process of marcasitisation.
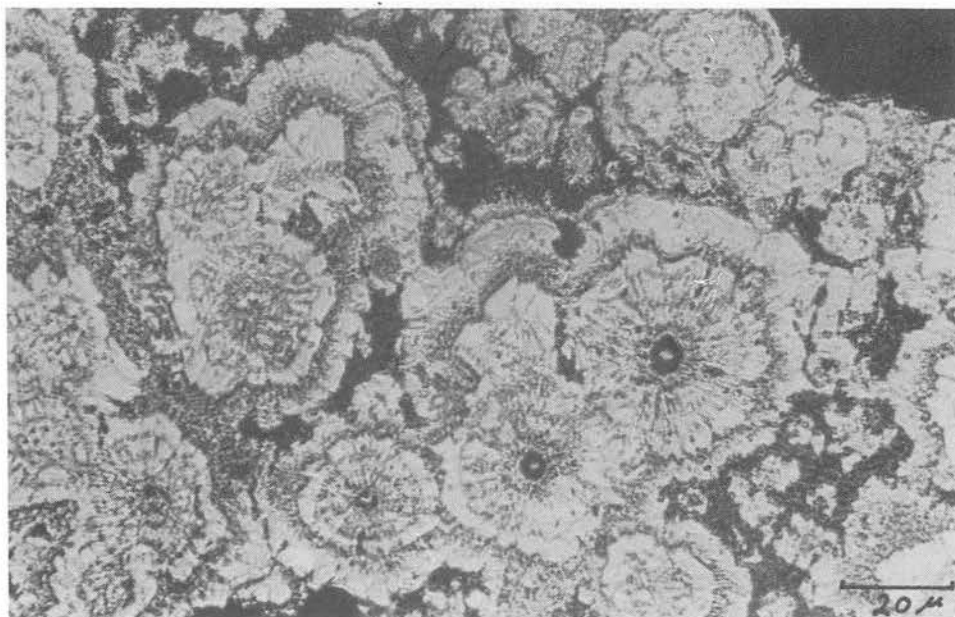
Fig. 10. A photomicrograph of a polished specimen of what was originally wood but which was intensely marcasitised with the generation of a mosaic of rosettes of radiating crystals and the concomitant complete destruction of the cellular structure. Locality: Lenggang, Belitung.

Aiii. Views concerning the chemistry of the genesis of authigenic pyrite and marcasite.

The production of pyrite in aqueous solution, at low temperatures and pressures has been the subject of extensive study, unlike that of marcasite, but it cannot be dealt with in anything approaching a comprehensive manner here. For details of much of the work one should consult Rickard (1975). However, I cannot do better at this stage than to provide Rickard's summary (1975, p. 636) of what he believes to be the view of many workers regarding pyrite genesis. He writes *"Generally, the reaction between an iron salt (commonly goethite in sediments) and dissolved sulphide species results in the formation of one or more of a variety of metastable ferrous or ferroso-ferric sulphides. These sulphides, which commonly consist mainly of a mixture of X-ray amorphous and crystalline compounds with the general formula, FeS, react with aqueous sulphide and sulphur to form FeS_4. ... Marcasite tends to be formed in acid conditions and pyrite in alkaline environments ..."*

There is some evidence, from a number of sources (see Rickard, 1975, p. 637) to suggest that the conversion of FeS to FeS_2 was via the following path:-

FeS → kansite (mackinawite, tetragonal) → melnikovite (greigite, cubic F_3S_4) → pyrite (The black, finely-divided iron sulphide, hydrotroilite, is probably one or more of the internal sulphides noted in the reaction chain.)

Rickard's own work (1975, p. 636) suggests to him that the mechanism of pyrite formation at low temperatures and pressures involves the dissolving of elemental sulphur in sulphide solutions with the production of polysulphide ions, whilst ferrous sulphide dissolves to form aqueous ferrous ions and sulphide species. Pyrite is formed directly through the reaction between aqueous ferrous ions and polysulphide ions of unknown origin. According to Rickard (1975, p. 636) *"the pyrite produced through this reaction is not framboidal"*.

Dimroth (1976, p. 228) also emphasised the complexities of the collective reactions leading to the development of iron sulphides in sedimentary environments. He stated that *"pH, Eh and pS^{2-} of the diagenetic pore solutions are not independent variables. The acidity is buffered by dissolved carbonate species and is a function of the concentration of weak acids (CH$_2$, organic acids) in the pore solutions. Eh and pS^{2-}* are determined by dynamic equilibria. *Eh and pS^{2-} are functions of the rates of organic decay and of bacterial sulphate reduction, and of the rates at which oxygen diffuses into the sediment and by which dissolved reducing substances diffuse out of the sediment. Therefore the concentration of organic matter in the sediment, and the relation between diffusion rates and other sediment properties require discussion in order to understand iron-mineral diagenesis"* (and, also, in the present writer's view, in order to establish the chemistry associated with the diagenesis of the lead-, zinc- and copper-bearing sulphides found in certain Southeast Asian stanniferous alluvials and de-scribed later in this paper).

The genesis of framboidal pyrite presents further problems. About twenty-five years ago Love (1958) proposed that framboids were large anaerobic sulphate-reducing bacteria that had invested themselves with pyrite, but this view was soon demonstrated to be erroneous. Earlier, Barringer (1954) had succeeded in producing bodies similar to the framboids that occurred in the Rio Tinto sulphide ore by pouring colloidal pyrite in finely-powdered Rio Tinto slate, thus indicating that perhaps colloidal chemistry played a role in the genesis of framboids. For about fifteen years there has been a widely held view that framboids developed in a reducing and slightly acid environment from spheres of iron sulphide gel during early diagenesis. The sulphide component of the gel having been generated by sulphate-reducing bacteria. Love and Amstutz (1969, p. 106), for example, demonstrated their belief in the gel stage when they wrote *"the pyrite spherules of the Chattanooga Shale are also regarded by the authors (i.e., Love and Amstutz) as exhibiting evidence of their origin in blebs of gel sulphide"*.

That the genesis of framboidal pyrite is considerably more complex than was originally thought is indicated, for example, by the work of Berner (1970), Sweency and Kaplan (1973), and Kribek (1975).

Berner's experimental work (op. cit., p. 1) suggested that framboidal pyrite can probably be generated in natural sediments by the reaction between FeS and elemental sulphur but it is likely to take several years for its completion. For this reaction to take place sulphate must be reduced by bacteria to H$_2$S and so, in his view, the major factors limiting pyrite formation in *marine* sediments are *"the availability of organic matter that can be metabolized by sulphate-reducing bacteria, the diffusion of sulphates into sediments, the total concentration and reactivity of iron minerals, and the production of elemental sulphur"*. Elemental sulphur may be derived from the breakdown of thiosulphate (S$_2$O$_3$) (see Berner, op. cit.,p. 3).
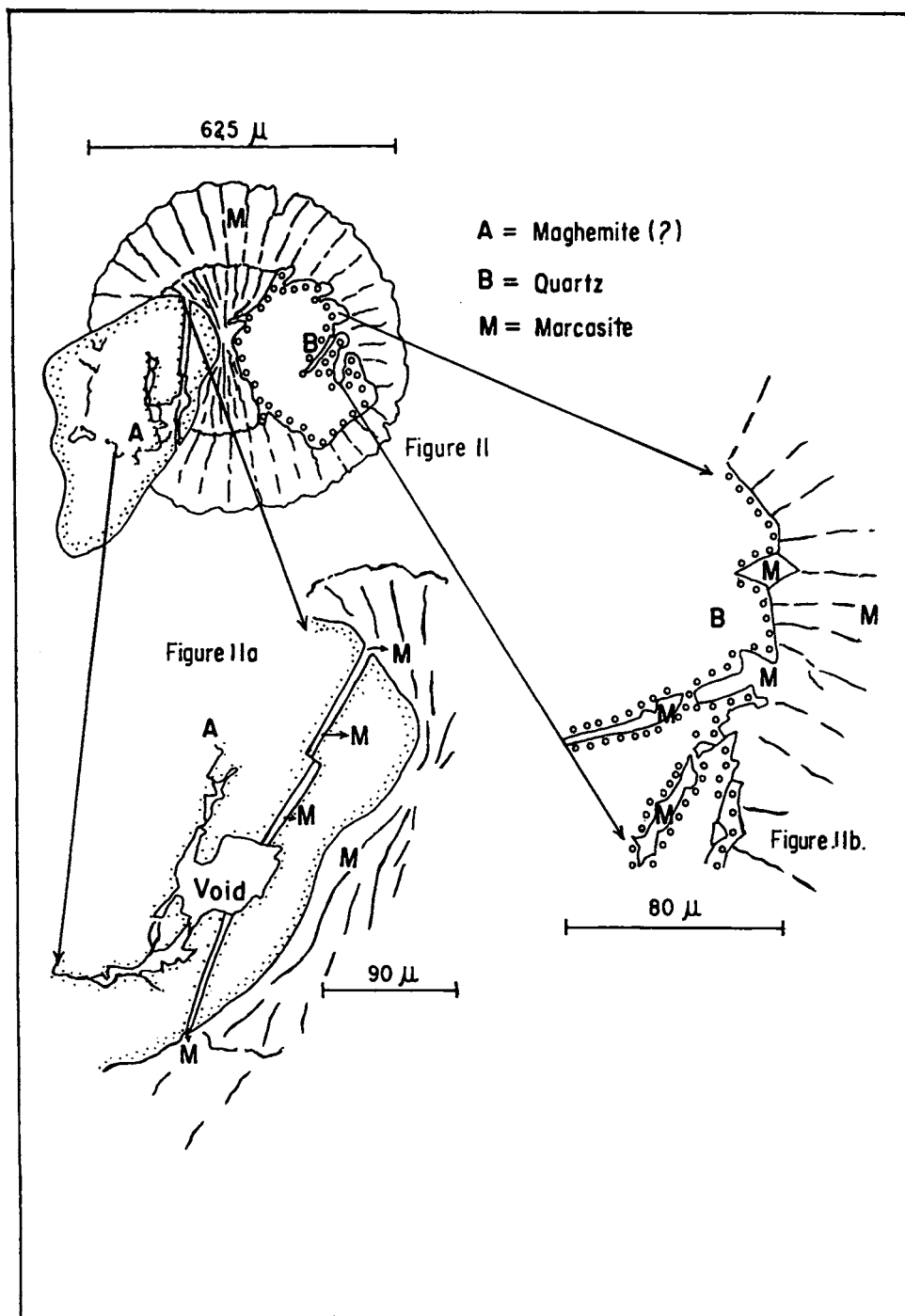
Fig. 11. Marcasite spherulite, with inclusions, from Ban Seng Lee Mine, near Tronoh, Perak.
Figs. 11a & 11b. Enlargements of the fractured portions of the inclusions.

Sweeney and Kaplan (1973) confirmed Berner's findings (noted above) that framboids could be formed by reaction between elemental sulphur and freshly precipitated suspensions of iron sulphide, FeS. They also demonstrated that one route was via mackinawite to greigite and from there to framboidal pyrite.

Kribek (1975) demonstrated that framboids can be prepared *"by precipitation of oxyhydroxides of iron, peptized by humic acids using .... hydrogen sulphide, spherical grains of elemental sulphur being present."* This synthesis depends on the development of a monodispersive sulphide sol and the development, by rapid oxidation of H_2S, of sulphur spherulites, then *"particles of the sulphidic sol precipitate on the surface (of the sulphur) and the grains become gradually replaced by sulphides of iron. At the same time, framboids of an average diameter of 14 um are generated"* (op. cit., p. 389). Kribek (op. cit., p. 395) believes that the reactions leading to the development of pyrite from elemental sulphur and iron sulphides are as follows:- The sulphur, being metastable in a reducing environment, slowly reacts with sulphide ions to produce disulphide ions and these react with the iron sulphides present on the surfaces of the sulphur grains yielding pyrite. The relevant equations are as follows:-

$$S^{2-} + S_c \rightarrow S^{2-}_2$$

$$FeS + S^{2-}_2 \leftrightarrow FeS_2 + S^{2-}$$
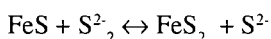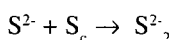
The chemistry of the genesis of polyframboids must be very similar to that of the genesis of framboids. This thought doubtless prompted Love (1969, p. 1043) to suggest that a polyframboid is developed from a globule of iron monosulphide, FeS, that separates into smaller globules which collectively preserve the original spherical shape and volume of the parent. As Love further observes, the major problem, for which he has no satisfactory solution, is to answer the question 'why and under what circumstances do large globules of iron monosulphide form?'. I do not know the answer to this question and can only insert the following comment relating to it that I made in an earlier paper (Hosking, 1980, p. 125):- *"In part, at least it may depend on the ease (and rapidity) with which globule-forming agents can move to the site of globule formation, together with the space available for the globule to develop, or the ease with which a developing globule can make room for itself by pushing aside components of the host."*

Aiv. Galena, sphalerite and copper-bearing sulphides

Almost a decade ago Rabelink and I investigated a most interesting suite of sulphides occurring in the rejects from the beneficiation of the then completely disorganised shallow stanniferous placers of Lenggang, Belitung, Indonesia, and we subsequently described the material in some detail (see Hosking and Rabelink, 1978). Here, it seems sufficient to present the more important details from the abstract of that paper and to support them with some figures.

In the beneficiation rejects, noted above, galena occurs in grains which, as a result of examination of polished sections, may, according to their mineral content, be classified as galena grains, galena/sphalerite grains, galena/copper-bearing sulphide grains, and galena/iron sulphide grains.

The galena grains may consist of primary (detrital) and/or secondary sulphide, and when the latter is present the grains are commonly botryoidal, and in polished section display a banded texture (Figure 12).

The galena/iron sulphide grains are angular fragments of originally woody tissue which has been largely infilled and, on occasion, replaced to some extent by pyrite and/or marcasite which may contain pyrite framboids and voids, some of which are rimmed by galena.

All but the grains of primary galena may contain pyrite framboids (Figure. 13) which are sometimes disrupted, and also woody fragments whose lumina are infilled with iron sulphides, or galena, or sphalerite (Figure 3). In addition, inclusions of organic-rich mud are common, and these, together with small organic particles, are portions of the host material that failed to be eliminated by the developing sulphide spherulites. In the same grains, fragments of resistates, such as quartz are also commonly encountered, and these may be fractured in such a way as to suggest that the fragmentation was due to forces operating during the development of the crystalline sulphide which, perhaps, was preceded by a gel stage (footnote).

The earliest of the authigenic sulphides to be formed were pyrite and marcasite, and these were followed, in the order given, by sphalerite, galena and copper-bearing sulphides (chalcopyrite, bornite, covellite and digenite) (Figures 14 and 15). A wholly satisfactory reason for this paragenesis has not been established.

The evidence suggests that these authigenic sulphides were all the products of early diagenetic processes operating in the oxygen-deficient, organic-rich environment of a swamp that Rabelink and Hosking (op. cit, p. 63) thought was probably a freshwater type, and in the vicinity of fragmented galena that had been shed from a lode or from a collapsed portion thereof. It is thought that the lead, copper and zinc required for the formation of the authigenic sulphides were derived from these parts of an undiscovered but neighbouring hard-rock deposit that were in an oxidizing environment. It is believed that mobilisation of the elements was in part effected by direct oxidation and in part by solution of oxysalts by organic agents. The iron was largely derived from organo-iron complexes and/or from ferrous ions in the swamp waters while the necessary elemental sulphur and sulphide components were produced, if sulphide genesis occurred in a freshwater swamp, by biogenic means, from sulphate ions liberated from the oxidising part of the primary sulphide deposit and from sulphur-containing plant proteins. If, as I think unlikely, further work should establish that the authigenic sulphides were not developed in a freshwater swamp, but one containing brackish- or salt-water, then, of course, the sulphate ions which are normal components of such waters would, in all probability, have been the major progenitors of the sulphide ions and the elemental sulphur.

An interesting example of the sometimes close relationship that exists between the generation of authigenic species in a placer and modifications effected by supergene processes operating on a hard-rock sulphide-bearing deposit was discovered in the Bylco Azira opencast tin mine at Puchong, Selangor, Malaysia and was subsequently described by Hosking and Yeap (1975b). In the mine cassiterite was being recovered from placer material lying largely between limestone pinnacles and also from certain lodes and veins. Examina-

Fig. 12   A photomicrograph of a polished section of a galena nodule which has been etched to emphasise its zoning. Locality: Lenggang, Belitung.
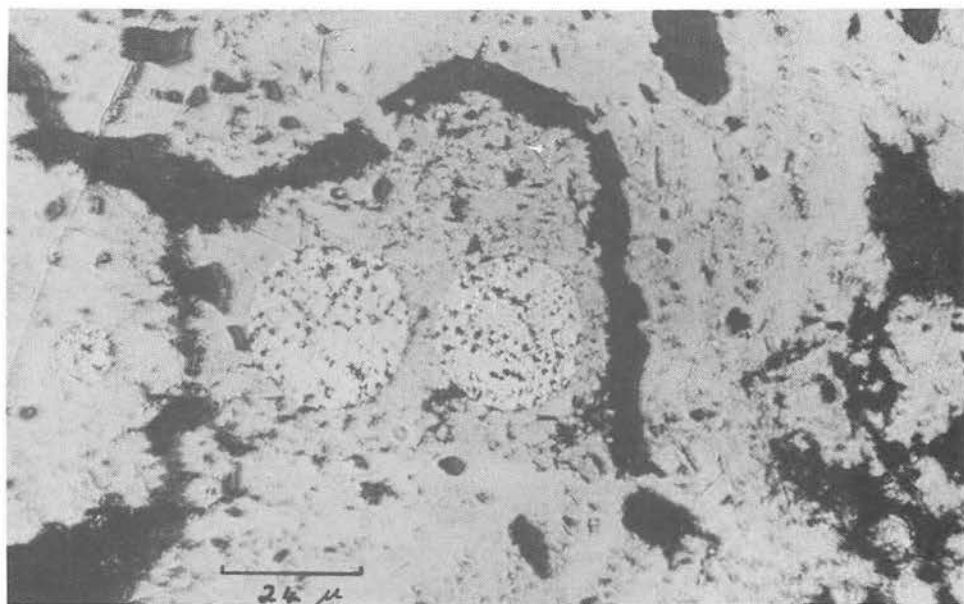

Fig. 13   A photomicrograph of a polished section of a portion of a galena nodule showing three pyrite framboids (two large and one small). Locality: Lenggang, Belitung.
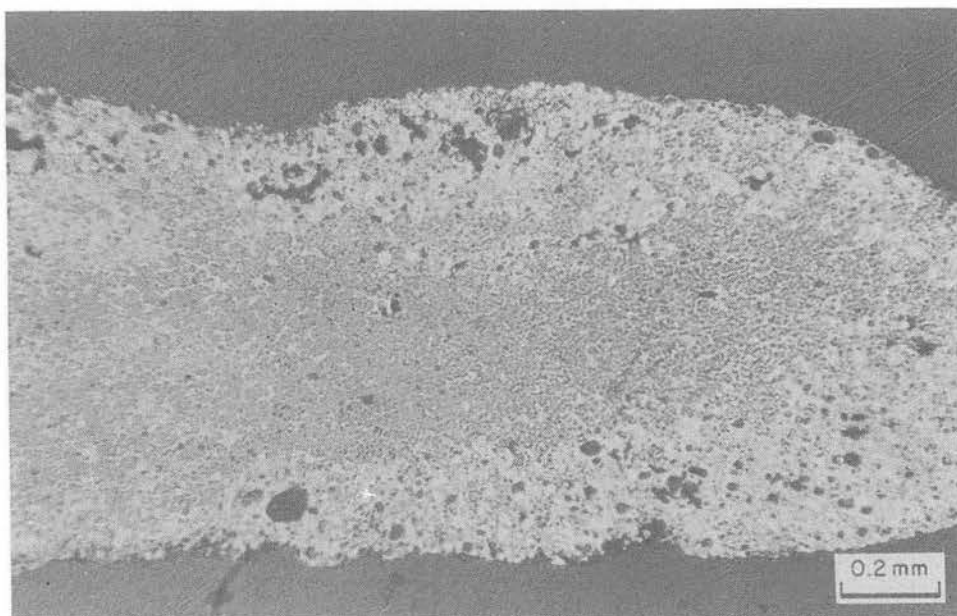
Fig. 14   A photomicrograph of a polished section of a portion of a nodule characterised by a sphalerite-rich ("dark-grey") core and a galena-rich (pale-grey) periphery. Locality: Lenggang, Belitung.
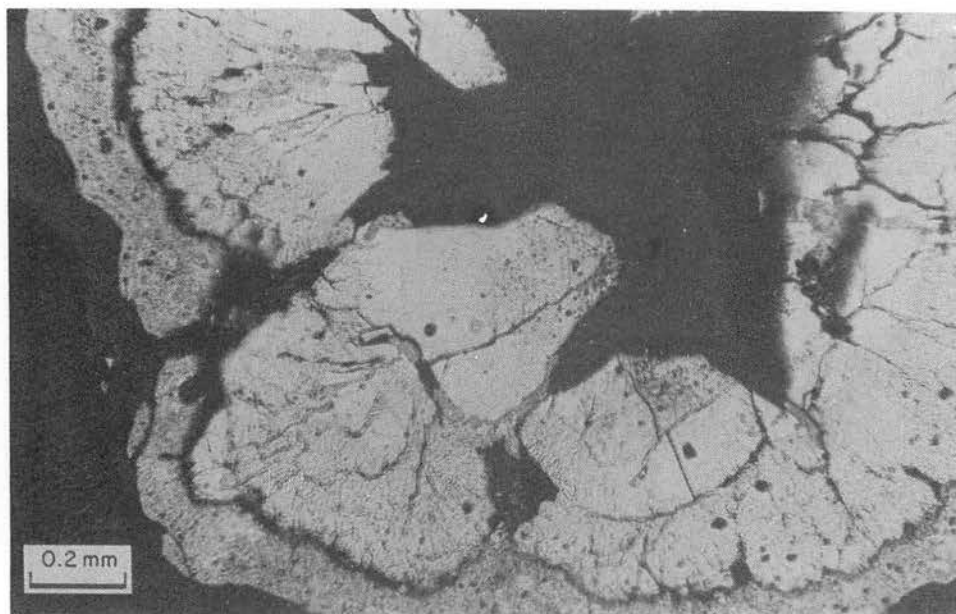

Fig. 15   A photomicrograph of a polished section of a portion of a galena nodule with a hollow centre. The galena is rimmed and veined by copper-bearing sulphides of which digenite is the dominant one. Locality: Lenggang, Belitung.

tion of polished sections of the peripheral parts of a stannite-rich block lying on the floor of the mine and derived, beyond reasonable doubt, from one of the hard-rock tin deposits there, provided the information upon which that which immediately follows is based.

The 'body' of the ore consists, essentially, of cassiterite, quartz, pyrite, arsenopyrite, sphalerite, stannite, tetrahedrite (?) and chalcopyrite, the whole rimmed by colloform chalcopyrite in which pyrite framboids are randomly disposed. The framboids, which range in size from c. 10 µm to c. 100 µm, are composed of cubes which may or may not be well-ordered (Figure 19).

As was stated in the original note on the subject (op. cit., p. 107) *"the marginal disposition of the colloform chalcopyrite and the presence of pyrite framboids within it give strong reason for believing that the copper/iron sulphide is of supergene origin and that it was probably deposited initially as a gel. There is nothing to support the view that it originated by replacement of any of the components of the ore"*.

It is thought that rapid down-cutting by the streams of the area during the Pleistocene phase of low sea-level allowed exposed sulphides in the lodes and veins to be stranded in the zone of oxidation. Subsequently, during a general rise in sea-level, there was a rapid accumulation of sediments in the sluggish drainage system and the concomitant local development of swamps. The organic-rich accumulations in the swamps protected the exposed sulphides from destruction by establishing a reducing environment that also favoured, during early diagenesis, the development of pyrite framboids and isolated pyrite crystals initially by reaction between biogenic sulphide ions, elemental sulphur and iron, occuring perhaps as ferrous ions or as a component of organic-iron complexes.

It is believed that those parts of the lodes and veins which were situated above the swamps were subject to attack by oxidising agents and this resulted in the release of copper and other components which were in part transported to lower horizons via the internal channel-ways of the lodes and veins and in part carried down to the zone of reduction along the exteriors of the in situ tin deposits. The externally-moving copper reacted in the zone of reduction with biogenic sulphide ions and iron ions, which may have been derived solely, or in part, from the oxidising portions of the primary ore, to yield a Cu/Fe sulphide gel which locally invested the lode by displacing the finer components of a framboid-bearing carbonaceous mud. The framboids, because of their size and weight, were not rejected, but simply by-passed by the engulfing gel. Subsequently the gel crystallised and the force of crystallisation caused complete disorganisation of some of the framboids. Figure 20 provides, in pictorial form, the postulated genesis of the colloform chalcopyrite with its disseminated framboids.

Footnote: It is not without interest to note that fractured resistate inclusions are commonly encountered in all the authigenic sulphides and the siderite discussed in this paper. The degree of fracture displayed by the inclusions is very variable. Often fracturing results in the development of but little-displaced fragments which were subsequently cemented by the host. Occasionally fracturing reminiscent of exfoliation has occurred. Included mica books are opened in the form of a fan, whilst included framboids are commonly disrupted. Doubtless all these changes that affected the inclusions occurred during the crystal development of the host (Figures 16, 17 and 18).
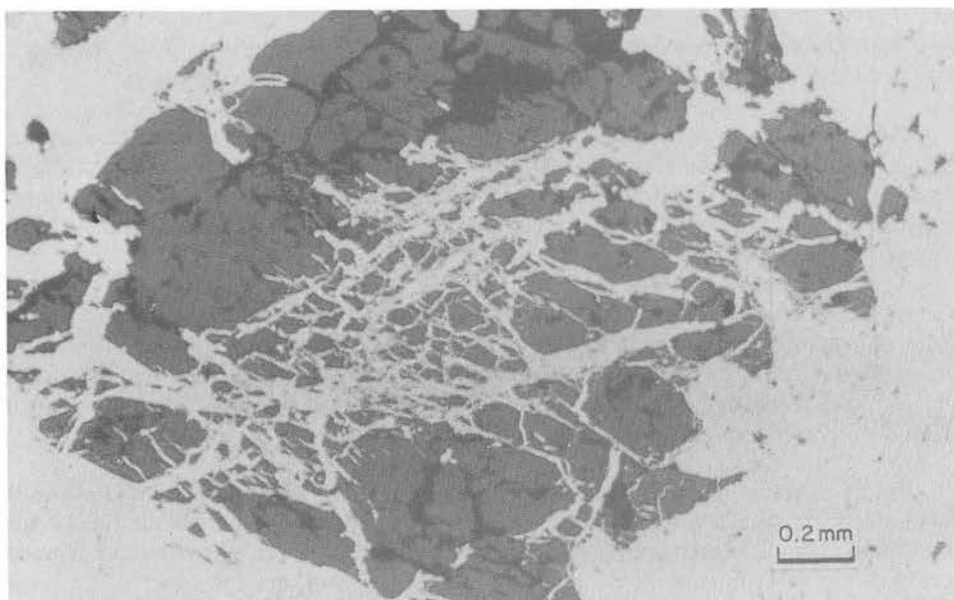
Fig. 16.   A photomicrograph of a polished section of a highly fractured quartz inclusion in a pyrite/marcasite matrix. Locality: Ayer Hitam, Selangor.
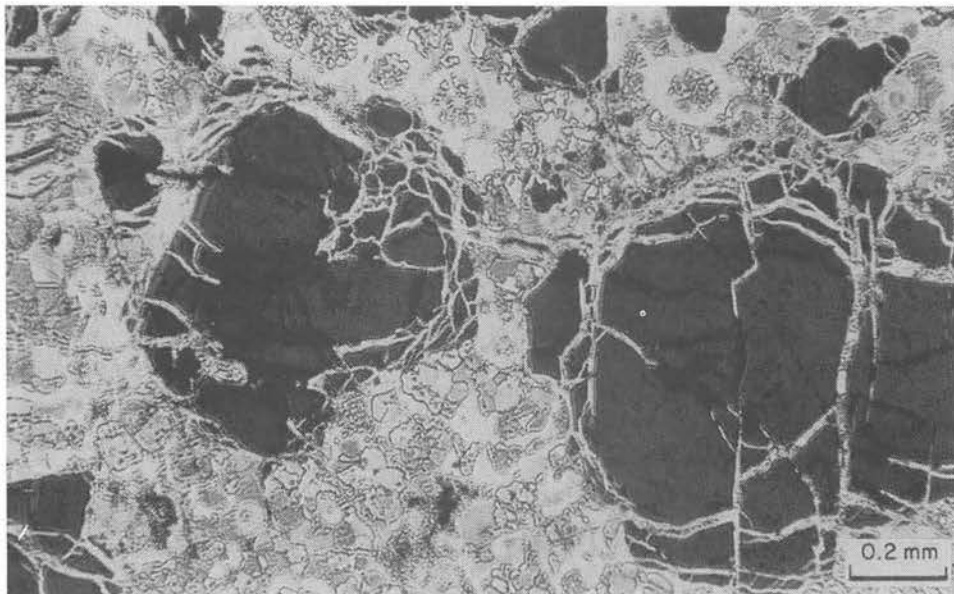

Fig. 17.   A photomicrograph of a polished section of fractured quartz inclusions in a pyrite/marcasite matrix. The texure of the matrix has been revealed by tarnishing. Perhaps an original marcasite cement was partly altered to pyrite. Locality: Sungai Way, Selangor.
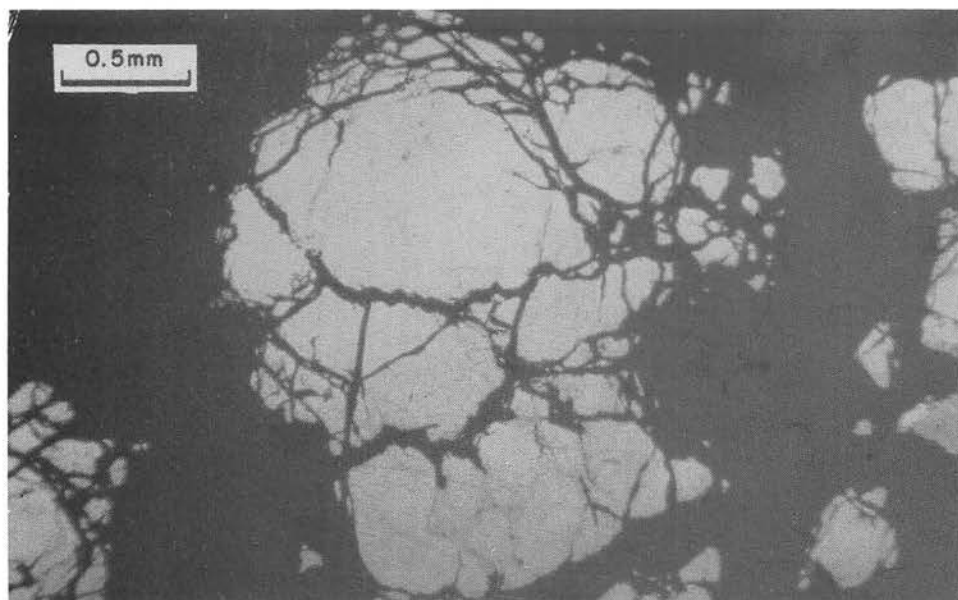
Fig. 18. A photomicrograph of a thin section of fractured quartz grains in a pyrite and/or marcasite matrix. It is to be noted that the fragments resulting from the fracture of the largest grain have been subject only to very slight displacement, and that the fractures have been 'healed' by FeS_2 which may have locally replaced the quartz. Locality: Sungai Way, Selangor.

Collapsed blocks of primary ore are not uncommonly uncovered during opencast mining nor is it particularly rare to recover such blocks when dredging. When such blocks contain fresh sulphides they indicate that they have been preserved in a reducing environment in the alluvium. In such circumstances, that is when there is a close spatial relationship between the blocks and the alluvium, framboids may be deposited in available voids of the former. This was demonstrated by a block of mineralogically complex ore which was recovered by a dredge at Ayer Hitam (Selangor) (Figure 21) (Yeap and Hosking, 1974).

B. Siderite

In spite of the fact that authigenic siderite is relatively common in the stanniferous alluvials of Southeast Asia it has received little or no mention by those who have worked and written about these deposits. Ingham and Bradford (1960, p. 30) note that on the low-lying limestone of the 'cliff' faces between Ipoh and Kampong Kepayang and "*beneath the alluvium, a thin coating of siderite... is often present and in some cases, as at Gopeng, a skin of hematite may cover the limestone surface; these secondary iron minerals have been formed by the action of ferruginous solutions on the limestone.*" One page 291 of the same work Ingham and Bradford mention that the Gopeng hematite, noted above, probably resulted from the alteration of siderite, while their figure 3 of Plate X (P. 35) depicts "*sideritic limestone with marked spherulitic structure from San Hing, Siputeh (Perak) whose partial analysis is:- FeO, 51.43%; MnO, 4.74%; CaO, 3.60%; MgO, trace; insolubles, 1.58%*". I wrote a short
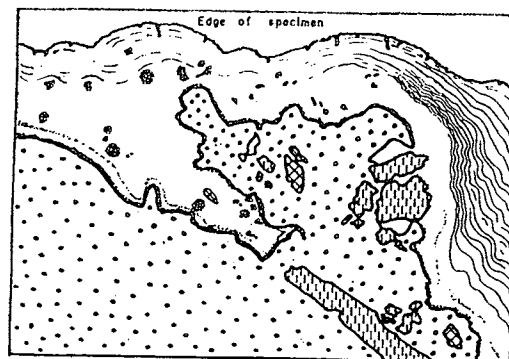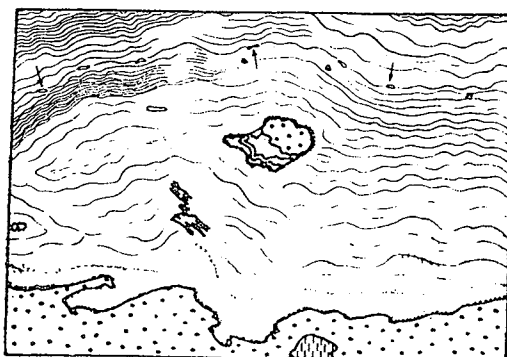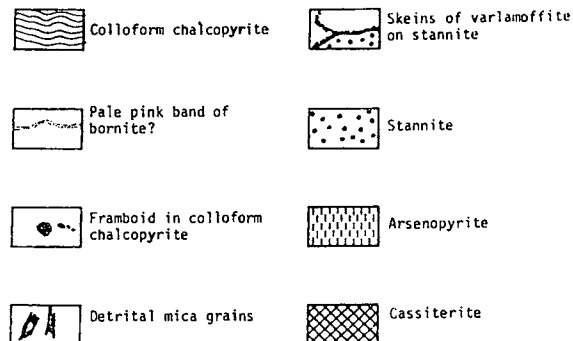
Fig. A

Edge of specimen

600 μ

Fig. B

600 μ

Colloform chalcopyrite

Pale pink band of bornite?

Framboid in colloform chalcopyrite

Detrital mica grains

Skeins of varlamoffite on stannite

Stannite

Arsenopyrite

Cassiterite

Figures A and B, drawn from polished sections, show the relationships of the colloform chalcopyrite rim to the minerals that it is investing. Figure A shows portion of the rim that contains captured framboids while figure B shows islets of stannite. The smaller islets (arrows) are oriented parallel to the local chalcopyrite bands and this orientation may be due to forces acting during the development of the chalcopyrite rim. Note that detrital mica grains are caught in the band also.

Fig. 19   Sketch of polished sections of colloform chalcopyrite rimmed stannite-bearing deposit at Bylco Azira Mine, Puchong, Selangor. (After Hosking and Yeap, E. B., 1975).

paper on the siderite spherulites from Ayer Hitam, Selangor (Hosking, 1972a) the content of which will be referred to later, whilst Aw (1981) noted the nature and occurrence of siderite in stanniferous alluvial material occupying a limestone pot-hole near Pusing, Perak. Aw (op. cit., p. 150) recorded that in the pot-hole *"sphaerosiderite occurs as dark brown globular forms, mainly in the 500-250* µm *size range. It also forms botryoidal masses and concretions on rock fragments and besides acting as a cement, binding clay and sand into various size aggregates. Under the microscope globular siderite can invariably be found on the surface of most gravels."*

Aw's paper, which concludes those known to me in which some prominence is given to Southeast Asian authigenic siderite, is important in that it records most of the ways in which the species in question occurs, namely as spherulites, as a cement and as masses on rock fragments. As noted earlier the mineral may also encrust limestones.

At this point it seems appropriate to record and comment on the Southeast Asian authigenic siderites that I have investigated.

a. Individual spherulitic siderites and closely-related bodies.

Spherulites have a radial texture as is indicated by the black cross that is seen when a thin section of one of them is examined between cross-polars, but commonly the core is composed of a mosaic of siderite crystals. Foreign nuclei are not encountered although inclusions are commonly seen in the spherulites. In a given sample the spherulites may vary considerably in size but often they range between 0.5 and 1.0 mm in diameter.

When two spherulites of unequal size have grown together their common surface, in section may be expressed by a straight line (Figure 22) but much more often the trace is an irregular one. The nature of the common surface depends on how far the sections of the spheroids depart from perfect circular discs and also on the relative sizes of the bodies. When the two sections are more or less perfect circular discs the common surface is concave towards the smaller body. This relationship has been observed in British material by Deans (1934). However, often the Southeast Asian material is, in section, so removed from circular that individuals hardly deserve to be called spherulites (Figure 23). Indeed, they are commonly 4- or 6-sided (Figure 24). Whilst such polyhedral siderite bodies may, on occasion, owe their shape to mutual interference during growth others seem to have developed a polygonal habit when growing in isolation (Figure 24).

Whilst it has been postulated, for example, by Oftedahl (1972, p. 127) that siderite spherulites have passed through a gel stage, I am of the view that this is not generally the case. However, an example of siderite which may have originated from a gel will be noted later. My view is that generally the development of spherulites and similar small bodies of siderite begins with the rapid deposition of a mosaic of small crystals, but I do not know what determines the sites of mosaic development. Having established a mosaic core, radiating crystals grow from it largely by pushing ahead, and/or aside, most, at least, of the finer components of the host (It is possible to demonstrate such accumulations of displaced host material by solution of the carbonate in a thin section, followed by staining the acid-resistant residue.). In an environment in which fine organic material is present some of the latter may remain in the siderite crystals causing discoloration. Larger fragments of the host, for

DIAGRAM INDICATING THE POSTULATED GENESIS OF SUPER-
GENE CHALCOPYRITE IN THE PLACER MATERIAL AT BYLCO
AZIRA MINE, PUCHONG, SELANGOR. (K.F.G. HOSKING, OCT., 1975)

VALLEY

MOBILISED
Cu^{++}, SO_4^{--} ETC.

STANNIFEROUS
PLACERS

ZONE OF OXIDATION

GENERATION OF OXY-SALTS
AND GOSSAN. MOBILISATION OF
Cu^{++}, SO_4^{--} IONS (AND OTHERS)

ZONE OF REDUCTION

CONTAINING:—

(i) PRIMARY SULPHIDES
STRANDED DURING RAPID
DOWN-CUTTING OF RIVER,
THEN PROTECTED BY RAPID
ACCUMULATION OF SEDIMENTS AND
ESTABLISHMENT OF A REDUCING ENVIRONMENT.

(ii) POSSIBLY SUPERGENE SULPHIDES FORMED BY
REPLACEMENT OF PRIMARY ONES.

(iii) POSSIBLY EARLY PRODUCTS OF OXIDATION
OF LODE (NOW STRANDED IN A REDUCING
ENVIRONMENT)

(iv) ACCUMULATIONS OF IRON SULPHIDES
(FRAMBOIDS, SULPHIDISED PLANT MATERIAL)
GENERATED IN THE ORGANIC-
RICH HORIZONS. (BIOGENIC S. AND S^{--}
INVOLVED)

(v) SUPERGENE CHALCOPYRITE DEPOSITED BY
REPLACEMENT OF ORGANIC-RICH, FRAMBOID-
CONTAINING MUD, ADJACENT TO LODE
SULPHIDES PROPER [BIOGENIC S^{--} (AND S?)
INVOLVED]

(vi) DETACHED LODE FRAGMENTS, PERHAPS, IN PART,
EMBEDDED IN CHALCOPYRITE RIM.

PLANE OF
OXIDISING
COPPER-
BEARING
SULPHIDIC LODE

PEAT AND ORGANIC-
RICH MUD HORIZONS
(SITE OF GENERATION OF
BIOGENIC S^{--} AND S, AND OF
IRON SULPHIDES)

DETAILS OF GENESIS OF CHALCO-
PYRITE (Cpy) IN THE PLACERS

ORGANIC-RICH MUD
WITH FRAMBOIDS
(F)

STAGE I

STANNITE,
ETC.

CPY (I)
REPLACING
OTHER
SULPHIDES

STAGE II
Cu^{++} AND BIOGENIC S^{--}

MUD

CPY II

STANNITE
ETC.

CPY (I)

REPLACEMENT OF MUD
BY COLLOFORM CPY. IN WHICH
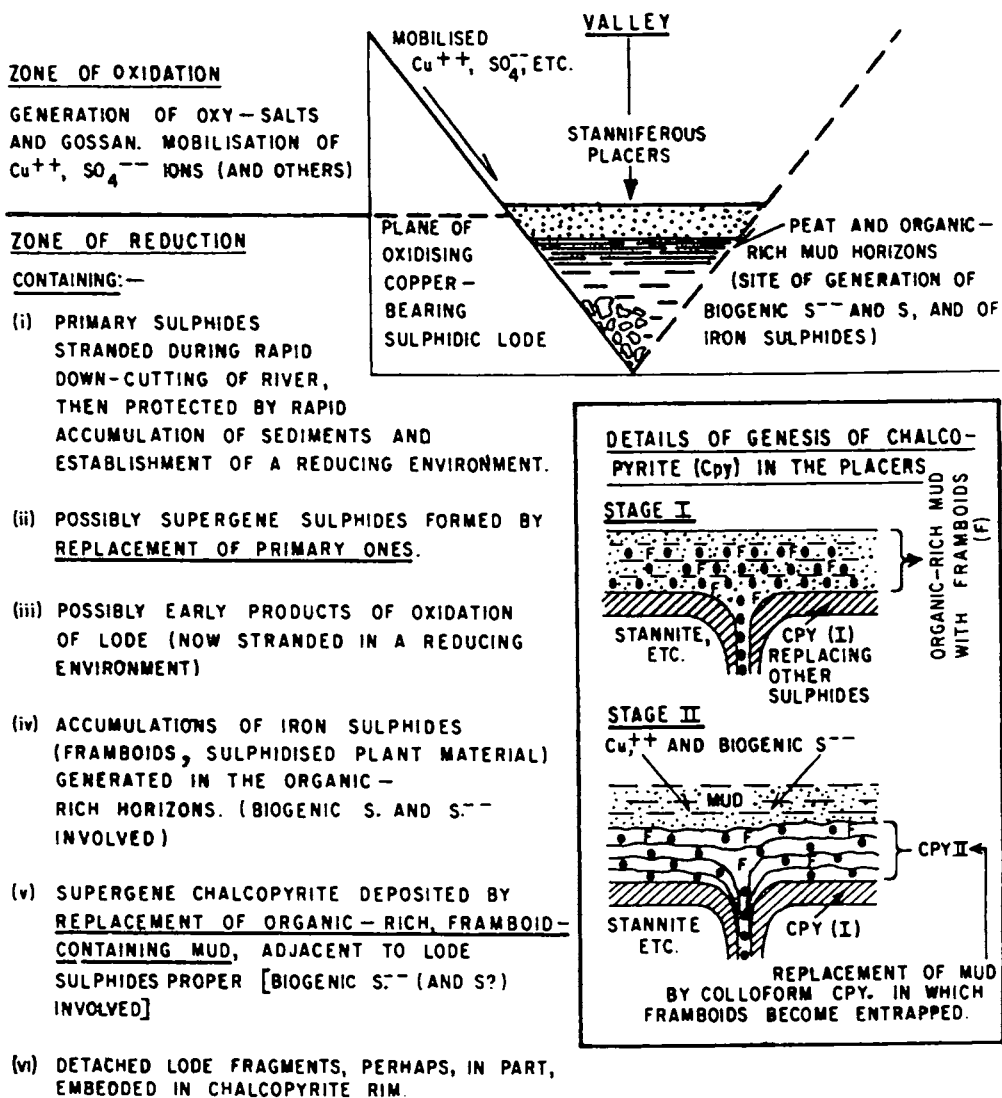FRAMBOIDS BECOME ENTRAPPED.

Fig. 20.   Diagrams indicating the postulated genesis of supergene chalcopyrite in the placer material at Bylco Azira Mine, Puchong, Selangor (After Hosking and Yeap, E.B., 1975).
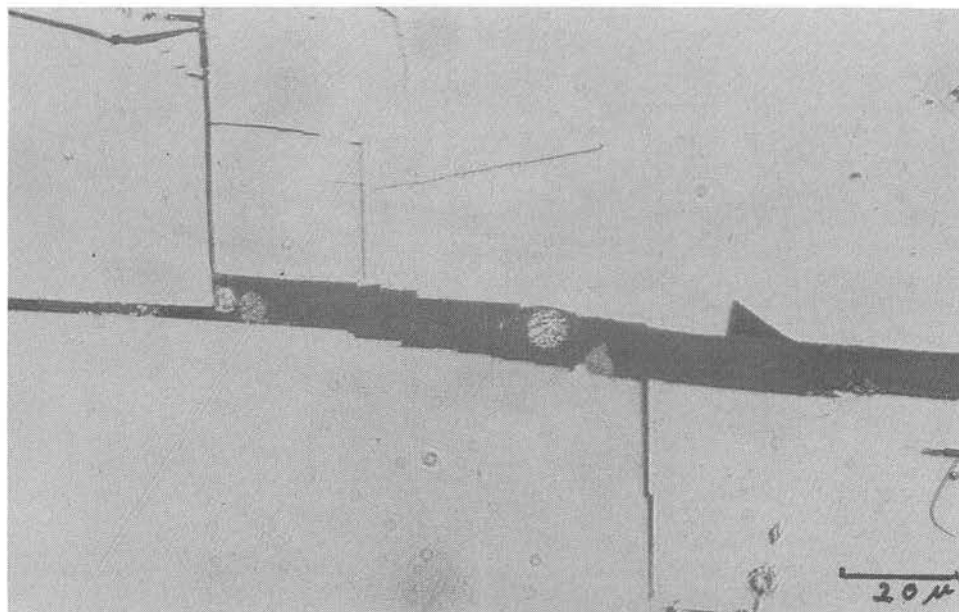
Fig. 21.   A photomicrograph of a polished section of fractured galena with three framboids in the major fracture. The galena is a component of a block of mineralogically complex ore recovered by a dredge at Ayer Hitam, Selangor. The framboids were generated when the block was covered by alluvial deposits.
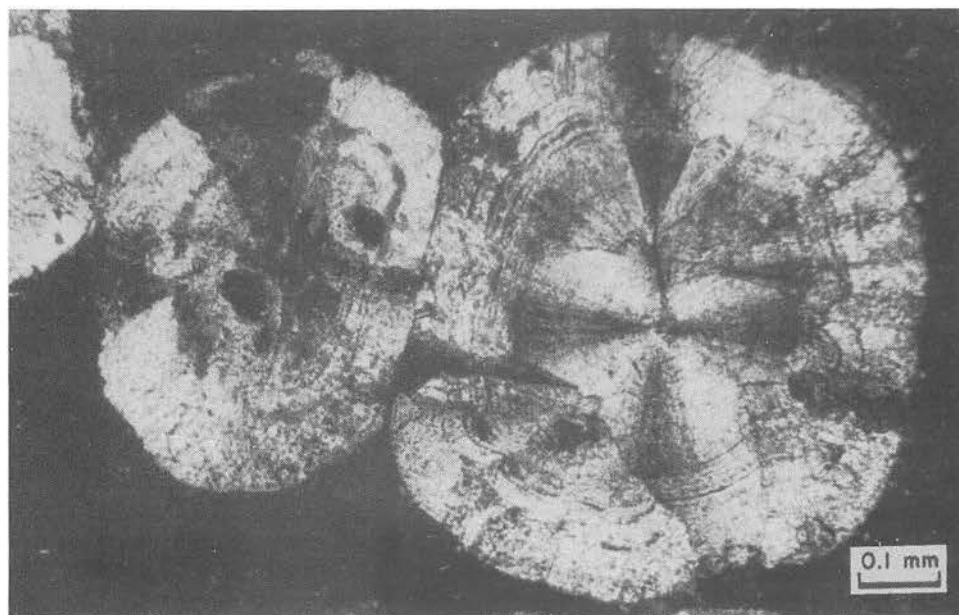

Fig. 22   A photomicrograph of a thin section of two joined siderite spherulites under crossed polars. Note the evidence of the radial crystal growth and the almost straight line trace of the junction between the two bodies. Locality: Ayer Hitam, Selangor.
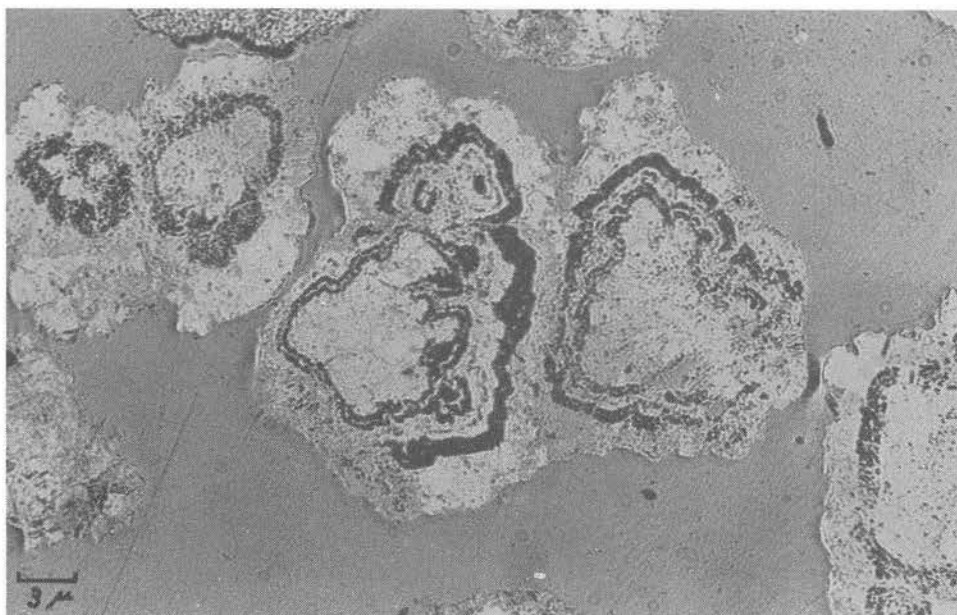
Fig. 23   A photomicrograph of a thin section of joined, irregularly-shaped essentially siderite bodies from Bidor, Perak. The dark annuli in the bodies are composed of iron oxides and reflect changes in the chemical environment during the bodies' development.
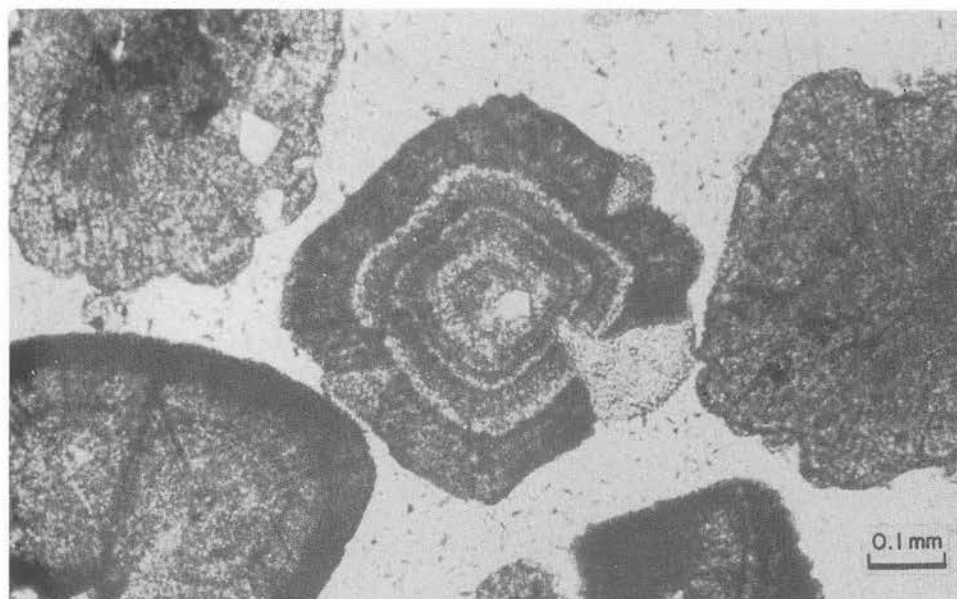

Fig. 24   A photomicrograph of a thin section of siderite bodies from Ayer Hitam, Selangor. The near rhomb shape of the central body is one often adopted by authigenic siderite.

example, grains of quartz, may be, and often are partly or entirely included in the siderite body. These inclusions may be fractured and the little-displaced fragments cemented by siderite (Figure 25).

There is little doubt that the nature of the host largely determines the final shape of the siderite body by dictating the degree of ease with which the radiating crystals can grow in any given direction.

In thin section siderite spherulites, and the equivalent irregularly shaped bodies, commonly display 'concentric' colour bands indicating, in part, variations in the composition of the carbonate and, when brownish or reddish, that the siderite has been locally oxidized. Sometimes, as in the case of spherulites from Wadieburn (near Kuala Lumpur) and Manggor (Belitung) each spherulite consists of an outer rim of iron oxide and a siderite core, and it is obvious that the rim has developed by oxidation of siderite. As both of these highly oxidized samples were collected years before I examined them, possibly the oxidation took place after they had been recovered from the alluvials. It is certain, however, that similar material occurs 'naturally'. Thin sections of some freshly mined spherulites have revealed essentially siderite bodies with hematite rims and internal hematite annuli joined by radially disposed iron oxide veinlets. Clearly, in such cases haematitisation wholly post-dates siderite formation. In contrast, sometimes essentially siderite spherulites contain internal iron oxide annuli. Such a pattern suggests that the developing siderite spherulites were temporarily exposed to an oxidising environment, possibly as a result of partial removal of the overlying sedimentary cover, and an iron oxide rim developed on the spherulites by replacement. Then the spherulites were covered so that conditions were reestablished for siderite deposition and siderite was laid down on the iron oxide rims noted above (Figures 26 and 27).

Occasionally polished sections of siderite spherulites reveal that some of the bodies have been locally thinly rim-replaced by pyrite and, in addition, here and there radially disposed veinlets of pyrite occur. Such samples suggest that some of the siderite spherulites temporarily experienced a change of environment, one suitable for pyrite development. That further environmental changes occurred locally during the periods of active authigenic iron minerals' formation is indicated by the appearance, in polished sections, of pyrite framboids in siderite spherulites. Such occurrences are rare, and often the framboids display a pull-apart texture for which, I think, the force of crystallisation of the developing siderite was responsible. In polished sections I have also seen tiny reticulate masses of pyrite in siderite spherulites. It is my view that these rarely observed, and last-mentioned sulphide bodies developed after the spherulites in which they occur had formed, and that they owe their shape to the disposition of easy passage-ways for mineralising agents between some of the radiating siderite crystals and the preferred movement of the mineralising agents along some of the cleavage planes of the siderite.

All the phenomena recorded immediately above were noted, for example, when siderite spherulites from Ayer Hitam, Selangor, were examined in thin and polished sections and, in addition, the following bore log data shows where, in the sediment sequence, the spherulites occurred (Hosking, 1972a, p. 1):-
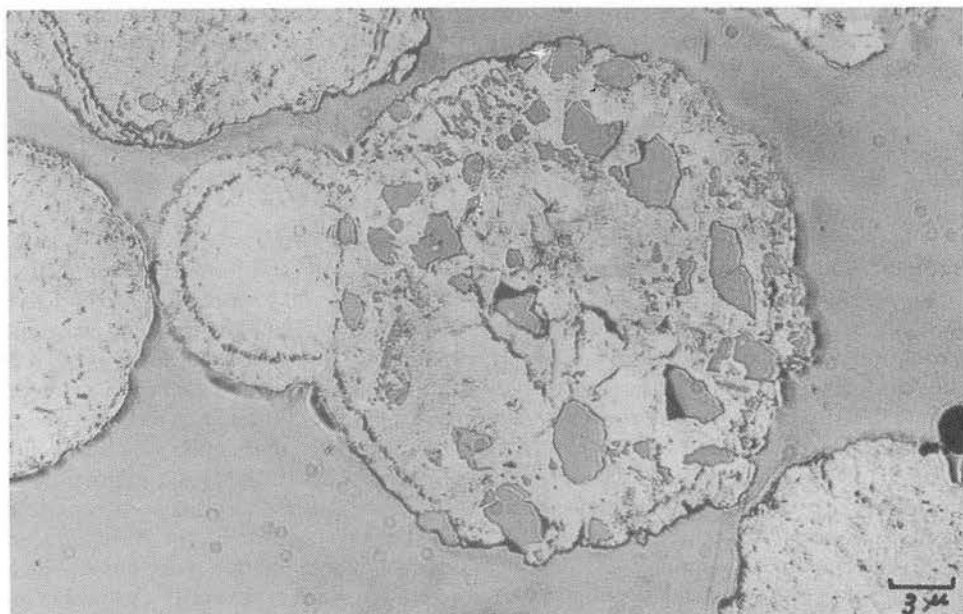
Fig. 25.   A photomicrograph of a thin section of siderite spherulites showing one laden with inclusions. Locality: Ayer Hitam, Selangor.
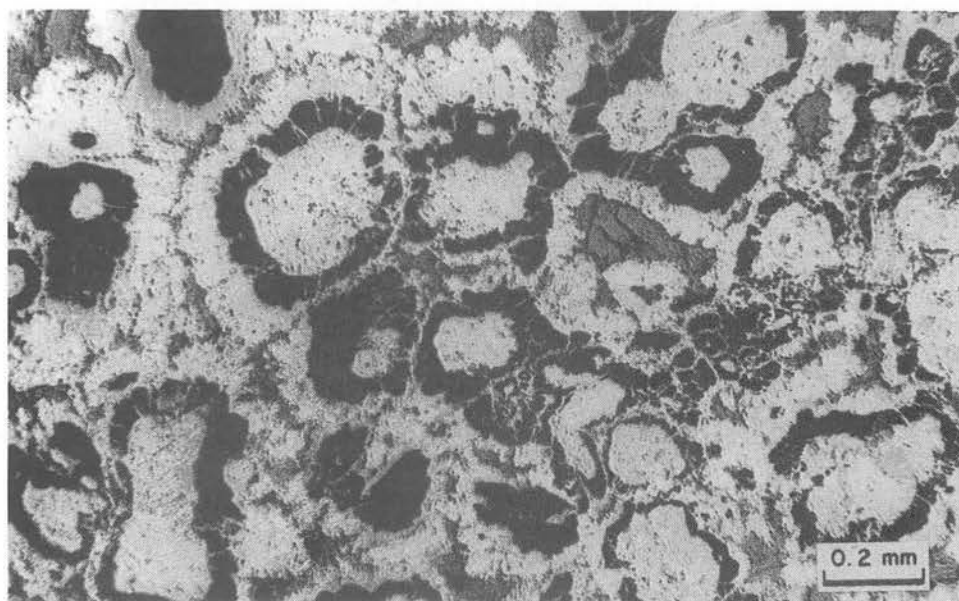

Fig. 26.   A photomicrograph of a thin section of "siderite rock" composed of a mosaic of bodies, each of siderite with an inner annulus of iron oxide. Locality: Wan Yuen Mine, East of the Kledang Range, Perak. (Photo by Too, H.K.)

Depth from surface in feet

  0 - 15 Decomposed vegetation with some brown clay.
 15 - 25 Brown clay with some fine sand.
 25 - 30 Brown clayey sand.
 30 - 35 Brown, mainly coarse sand.
 35 - 45 Brown clayey sand.
 45 - 50 Grey sandy clay.
 50 - 55 Grey peaty sandy-clay.
 55 - 60 Grey sandy-clay.   ⎤ siderite
 60 - 65 Grey clayey-sand   ⎥ spherulites
 65 - 75 Grey clay with some fine sand.   ⎦ present
      78 Limestone bedrock.

b. "Massive" siderite

Whilst single spherulites of siderite and their polygonal and irregularly shaped equivalents are often found in the crude cassiterite alluvial concentrates, particularly when the bedrock is limestone, masses of siderite rock are not uncommonly encountered in the rock piles of opencast mines, as, for example, in Eu Jen Choon mine, near Tanjong Tualang (Perak) and at Sungai Way (Selangor). In addition, such masses are, on occasion, recovered during dredging, as, for example, at Ayer Hitam (Selangor). Generally, examination of thin sections of such masses reveals that they consist of poorly cemented siderite crystals, with or without associated spherulites, and the whole being rich in voids. Inclusions of quartz etc., may be present which are commonly fractured and recemented by siderite. In addition, occasionally pyrite framboids occur in some of the voids as, for example in some masses from Ayer Hitam.

There is no doubt that much, possibly all of the massive siderite, was deposited on the limestone bedrock, or on cobbles, etc., (When, as at Sungai Way stalactitic forms are found) or as a cement of sand grains, probably immediately overlying the bedrock in most cases. This does not mean that siderite has never developed by the replacement of limestone in the alluvial environment of Southeast Asia. It means that having examined a number of ferruginous deposits on the limestones of opencast mines, particularly in Selangor and Perak, I have no evidence that unequivocally demonstrates that such, 'skins'are the product of limestone replacement. Indeed, the presence of quartz grains in such skins in the Tanjong Tualang mines suggests that there, at least, they were directly precipitated as siderite, albeit, siderite which was subsequently much oxidised. It is relevant to mention that on occasion such oxidised skins, as occur in the South Tualang Mine, for example, appear to have been fractured and recemented by siderite and calcite. I cannot explain how these 'fractures', if that is what they are, occurred. In the neighbouring and more undulating foothill country on the east side of the Kledang Range, on the exposed, locally steep limestone walls of the Fook Hup Nam tin-mine, the secondary iron encrustation is multi-layered and locally displays small stalactites with a complex internal texture. Thin and polished sections of the stalactitic material indicate that it consists essentially of a core of siderite of complex texture, a number of framboid-rich zones, a little secondary calcite and very minor marcasite and a skin of goethite and limonite (Figure 28). The developmental history of this complex deposit, which has been described by Too (1974) has been by no means completely unravelled. Provisionally I think that the deposit developed within the superficial parts of an alluvial sequence whose
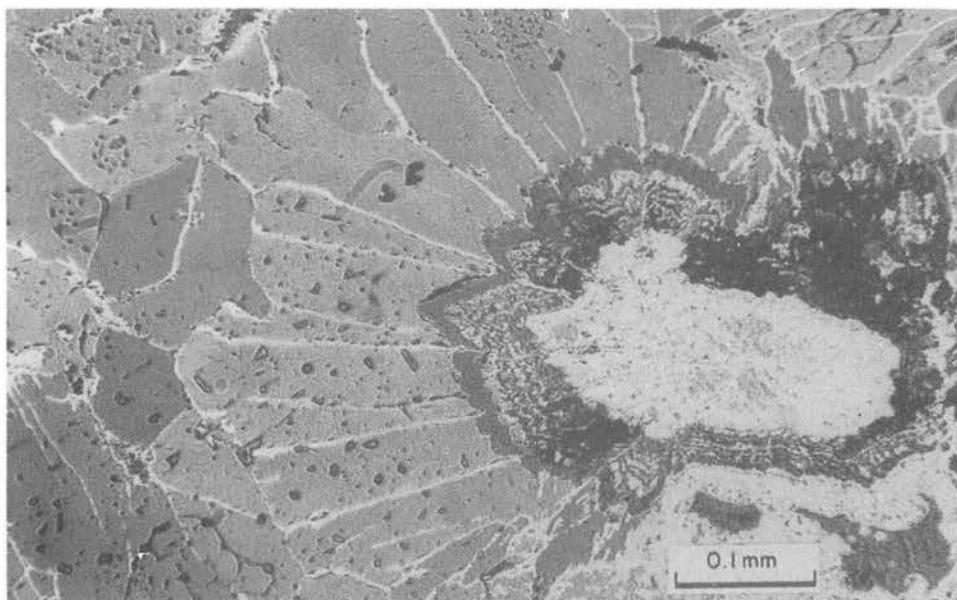
Fig. 27.   A photomicrograph of a thin section of 'siderite rock' demonstrating the complexity of its texture and the rapidly changing chemical environment that occurred during its development and which is reflected by the local alternations of siderite (lights shades of grey) and iron oxides (dark greys to black). Locality: Wan Yuen Mine, East of the Kledang Range, Perak. (Photo by Too, H.K.)
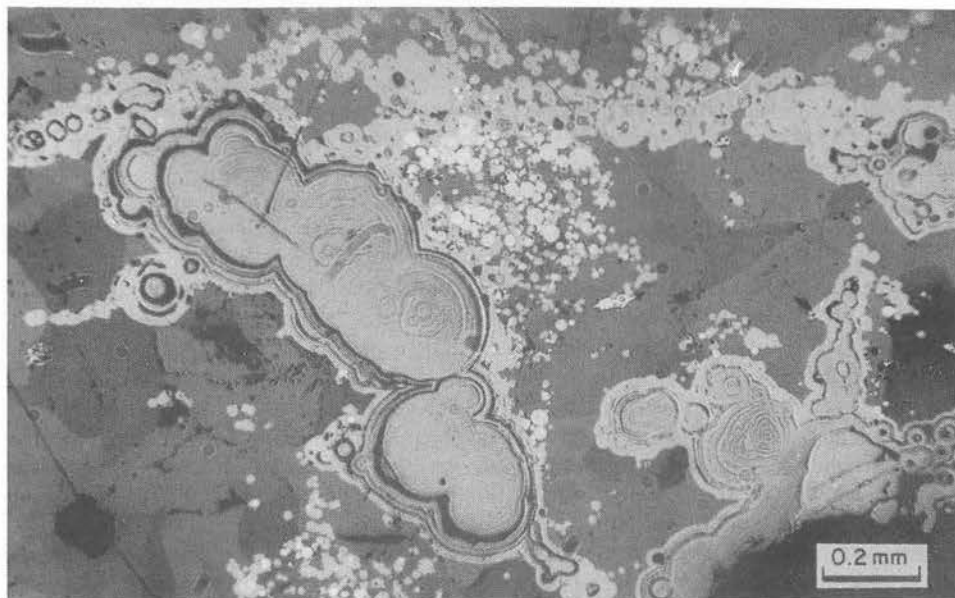

Fig. 28.   Colloform siderite with included zones of goethite (black) and pyrite framboids (near white) in a matrix of coarse siderite crystals. A photomicrograph of a polished section of 'siderite rock' from Fook Har Lam Mine, Perak. (Photo by Too, H.K.)

Eh/pH character varied repeatedly over a short interval of time and in such a way that a number of generations of siderite and sulphide were deposited. Finally, and perhaps as a result of exposure during mining operations, the deposit was superficially oxidized. I believe the stalactitic parts of the deposit developed centrifugally within a fine-grained host whose components were pushed aside and rejected by the siderite crystals. The marked variations, with time, in the size of the siderite crystals probably depended on variations in the concentration of the carbonate-depositing agents. It is also noteworthy that commonly the pyrite framboids in the stalactites are within zones of beautiful colloform siderite. It is this siderite which I think may well have developed from a gel in which Liesegang rings were established, and which subsequently crystallised. The presence of very minor amounts of marcasite within the bodies under discussion suggests that briefly the environment must have become unusually acid, and serves to draw attention again to the fact that the chemical environment was constantly changing, due largely, perhaps, to rapid changes in the drainage patterns of the area. The high siderite/sulphide ratio of the bodies may be due to the Eh/pH conditions but also to a paucity of sulphur components necessary for the generation of sulphides. The latter might be expected in the mine area where the alluvial deposits were probably developing in freshwater systems and so where the sulphur sources were limited to plant material and perhaps, oxidising sulphide-bearing primary mineral deposits.

Bi. View concerning the chemistry of the genesis of authigenic siderite

Sellwood (1971, p. 855) summarises what he believes to be the generally held view of the geochemical requirements for the formation of siderite as follows:- "... *it seems that negative Eh, low sulphide ion concentrations, high ferrous ions activities, and the presence of $CO_2(HCO_3^-)$ are all required. Clay particles entering sedimentary basins bring in iron in an oxidized insoluble state. On reduction, these ferric compounds become reduced to soluble, mobile ferrous ions.*" Sellwood (op. cit. p. 855) also makes what is probably a valid point, that immediately below the sediment/water interface there is a zone of oxidation which overlies the zone of reduction. He further remarks (op. cit., p. 858) that *"during compaction, iron-bearing pore solutions would migrate upwards towards the sediment surface ... Thus the ferrous ions which encountered an oxidizing environment near the sediment/water interface would again be oxidized and precipitated, particularly in sediments through which open burrow systems penetrated and extended the oxidising conditions downward into the substrate.*" At South Tualang tin mine, mentioned earlier, we found a portion of a branch of a tree, the cells of which had largely been infilled with goethite, which might provide some support for Sellwood's view. Polished sections of the stem revealed that generally the internal cellular texture had been very well preserved and only locally had there been some distortion and obliteration of the cell walls. Too (1974) figures and describes this specimen and observes that the nature of the distribution of the iron oxide within the body suggests that the mineralising solution had passed through the vessels of the wood. It seems reasonable to propose that the portion of stem was lying in the oxidising zone and was so orientated that it provided a local easy access route for ascending ferrous ions which on entering the stem were oxidised and deposited as goethite.

As noted earlier, siderite can be deposited in freshwater and brackish- and salt-water environments and, doubtless, siderite that was generated in each of the environments is to be found in the stanniferous alluvials of Southeast Asia. It would help to unravel the history of development of individual alluvial deposits of the region were it possible to establish the

environment in which any siderite present had been generated. This may be possible as Weber *et al.* (1964, p. 818) have shown that the determination of $^{12}C/^{13}C$ ratio of siderites from *ancient* sediments permits the environments in which they were developed to be arrived at. I think it would be rewarding to subject authigenic siderites from Southeast Asia to such a study, as would one involving the S.E.M., the latter organised to provide data re variations in the compositions of individual spherulites from their cores to their outer surfaces. This thought is prompted by the observations of Curtis *et al.* (1975) of a concretionary siderite sheet in the Westphalian of Yorkshire. These workers were able to conclude that the siderite they investigated shows considerable compositional range and that (op. cit., p. 3881) *"the compositional variation is both systematic and symmetrical from centre (early) to outer (late) precipitated carbonate. This precisely parallels the trends seen in carbon isotope constitution and inferred porosity at time of formation."*

C. Native copper

At the outset it must be stated that while native copper has been found in a few opencast tin mines in Southeast Asia its origin is still uncertain. That is, it is not known whether it developed in the alluvials, and so is an authigenic species, or whether it was the product of in situ oxidation of a primary deposit containing copper-bearing sulphides.

Rabelink (Personal communication) mentioned that native copper, possibly authigenic, had been found in a number of kollongs in the vicinity of Selumar (Belitung), but as far as I am aware there are no published details of these occurrences.

In Malaysia native copper has been found on a number of occasions, over a period of many years in several opencast tin mines on the western side of the Kinta Valley. Scrivenor (1928, p. 140) records that *"native copper is found with tin-ore sometimes in the Tanjong Toalang mines and between Batu Gajah and Pusing in Kinta. There was once a deep opencast mine Rotan Dahan, between Batu Gajah and Pusing, ... in which native copper caused much trouble. It occurred as minute and beautifully sharp isometric crystals ... that were invisible when mingled with tin-ore, and their presence was unsuspected until the ore was smelted. The cassiterite and native copper were contained in clay over limestone. A little chalcopyrite was found also, and the copper crystals were clearly a case of reduction from copper sulphate in solution derived from the chalcopyrite, the original position of which was in the limestone".*
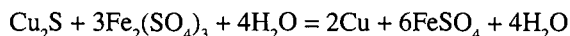
Willbourn (1937, para. 50) noted that *"in February, 1934, the dredge on the South Kampar section of the property owned by South Kinta Consolidated was digging up red clay that was identified as weathered metamorphic shale by the presence of pieces of tourmaline schist and tourmaline-corundum rock. It contained fine-grained cassiterite associated with 'amang' in which crystals and irregularly-shaped flakes of native copper were conspicuous."* Willbourn thought that the schist was mineralised, that it was interstratified with the limestone, and that the granite lay to the west of it. This suggests that Willbourn thought that the red clay and the minerals in it were, collectively, the oxidized zone of a hard-rock Sn/Cu deposit. Later, however, Ingham and Bradford (1960, p. 288) note that *"shapeless grains, sharp crystals and arborescent forms of native copper, similar to those described by Scrivenor from Rotan Dahan, have been found in Perak at Batu Ampor, Gopeng, Changkar Pari, south of Tronoh, and at Tanjong Tualang"*. They conclude that *"the native copper has*

undoubtedly been formed in the alluvium by the reduction of cupreous salts in aqueous solution, formed by the alteration of primary minerals such as chalcopyrite."

In 1972, Mr. D.Y. Picken, of what was then known as Sharikat Eastern Smelting Bhd., Penang, provided me with a sample of native copper recovered from a tin concentrate from South Tualang Mine, and in the accompanying letter he mentioned that *"several mines around Pusing and Batu Gajah, in the foothills of the Kledang Range, produce it."* He also mentioned that in a consignment of tin concentrate he had received from South Tualang Mine the tin content was 50.03 per cent while the copper content amounted to 33.40 per cent! Also present, in per cent, were As, 0.017; S, 0.20; Pb, 0.073 and Bi, 0.004. Subsequently, during my brief visit to the mine, I saw that the native copper occurred in red clay, and generally the occurrence was virtually the same as at South Kampar, which is noted above. Whether the native copper had developed in the 'hard-rock' or in the alluvium is, in my view, uncertain. Undoubtedly the grains of copper had suffered little or no transportation from their place of origin, as even small and slender ones were rarely deformed or defaced. It is relevant to mention that examination of polished sections of samples of the grains revealed that some had been replaced in part by cuprite. Whilst the replacement of some grains was quite advanced, generally, when oxidation had occurred, it was confined to the rims. I think it is likely that this oxidation occurred after the deposit had been uncovered during mining.

Ci. Views concerning the chemistry of the genesis of native copper

It is generally supposed that syn-sedimentary native copper does occur but the chemical reactions leading to its development, and, indeed to the genesis of native copper in any environment, are, in my view, uncertain. Ramdohr (1969, p. 317), for example, notes that *"the deposits of arid basins often contain native copper, which may have been formed from chalcocite ... but in other instances copper has probably been directly precipitated."* Bateman (1950, p. 177) states that copper *"has been precipitated in sea muds as sulphides and native copper and has been thrown down by micro-organisms."* Bateman further observes (op. cit., p. 271) that *"native copper is also formed, among other ways, by reaction between cupric and ferric sulphate solutions."* Palache et al. (1966, p. 100) remark that some native copper has been formed *"by the reaction of copper solutions with hematite or other iron minerals"*, whilst on page 200 they mention that *"native cooper may form through the reaction of copper solutions with carbonaceous material, as in the action of wood on mine waters."* Edwards (1965, p. 3) notes that *"van der Veen has figured a specimen in which native copper and limonite occur in alternating concentric shells, and he considers that the zonal arrangement resulted from the encounter of copper sulphate solutions with a gel of colloidal ferric hydroxide. He pictures the sulphate ions as able to diffuse freely through the gel, whereas the rhythmically distributed copper ions were precipitated on the surface of the hydroxide. If the copper was deposited as a colloid, the zones mark the rhythmic distribution of some electrolyte through the gel."* Routhier (1963, p. 251) points out that native copper may either be formed by the oxidation of a sulphide or reduction of an oxide according to the following equations:-

$$Cu_2S + 3Fe_2(SO_4)_3 + 4H_2O = 2Cu + 6FeSO_4 + 4H_2O$$

$$\text{and } Cu_2O + 2FeSO_4 + H_2SO_4 = 2Cu + Fe_2(SO_4)_3 + H_2O$$

Routhier also remarks that the deposition of native copper is determined essentially by the oxidation/reduction potential (Eh) and that the field of stability of copper is situated between that of cuprite and chalcocite. Betekhtin (1965, p. 144) sums up the present state of affairs when he expresses the view that the genesis of native copper which is found in sedimentary deposits still remains obscure.

CONCLUSION

It is hoped that this paper will stimulate others to come to grips with the many intriguing problems provided by the authigenic species of the stanniferous alluvial deposits of Southeast Asia. Not only is there still much to be learned about those species that have been the subject of this paper, but others are known to occur, and generally they have received but scant attention from the researcher. I think particularly of authigenic quartz and calcedony, calcite, the iron oxides, chamosite and related species, the clay minerals and those of the cave earths. Vivianite is certain to occur in some of the organic-rich horizons but, as far as I am aware it has not yet been recorded. What rewards await those investigators who enter this field!

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