GEOCHEMISTRY OF SOME SULPHIDES AND SULPHO-SALTS FROM PARYS MOUNTAIN, ANGLESEY

by

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Geochemistry of some sulphides and sulpho-salts from Parys Mountain, Anglesey.

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SUMMARY

Sulphide mineralisation occurs at Parys Mountain, Anglesey, associated with Ordovician and Silurian sedimentary and volcanic rocks. Pyrite, chalcopyrite, sphalerite and galena are the sulphide minerals with minor quantities of arsenopyrite and pyrrhotite. Tetrahedritetennantites, and Pb and Bi sulpho-salts also occur as interstitial and fracture infillings in sulphides, mainly in pyrite. Pyritic mineralisation shows conformable features with the host rocks, whereas other sulphides and sulphosalts show epigenetic features.

Sulphides have been analysed for essential and trace elements namely Fe, S, Cu, Pb,Zn,Co, Ni, Ag, As,Sb,Sn,Ba,Mo,Te,Cd,Mn and Bi. Sphalerite and galena are comparatively more enriched in trace elements than pyrite and chalcopyrite. The Co/Ni ratio in pyrites is generally greater than 1.00, suggesting that the deposits are related to volcanism. Substantial quantities of Fe are present in sphalerites in solid solution.

Sulphosalts have been quantitatively identified by electron microprobe analysis to be tetrahedrite-tennantites, bournonites, kobellite, galenobismutite and lead sulpharsenides.

Unit cell edge measurements of sphalerite have been made by X-ray and electron diffraction, and a good linear relationship between mol%/ FeS and unit cell edge is shown. Microhardness, reflectivity, infrared and d.t.a. data for sulphides are given - attempts to correlate the physical-optical characteristics with composition resulted in no significant conclusions, except the relation between microhardness and Fe content in sphalerite.

Diabantite, ripidolite, grochauite, clinochlore and aphrosiderite are the chlorite species occurring in the matrix associated with sulphide minerals; chlorite (1b species) has been identified in the matrix where no sulphide minerals occur.

The mineralogical and chemical results in the present study are interpreted to show that the mineralisation at Parys Mountain is a volcanogenic sedimentary process later enriched by hydrothermal processes.

Key words:

Sulphide mineralogy, composition, trace-elements, sulpho-salts.

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CHAPTER 1

INTRODUCTION

1.1 Geology of Parys Mountain

Parys Mountain lies in the north-east corner of Anglesey (Fig. 1) in North Wales. Situated about 4 km south of Amlwch port it forms a prominent topographical ridge aligned in ENE-WSW direction, rising to over 150m above sea level.

The geology of Parys Mountain has been studied by many investigators for a number of reasons. Structurally and stratigraphically it is a very complex area (Manning, 1959; Bates, 1966) and hence the relationship between its sedimentary and volcanic rocks has been variously interpreted. Its mineral deposits have been compared with other mining fields in the southern Caledonides, such as Avoca (southeastern Ireland), and Coniston (Lake District), because of similar age and comparable tectonic and stratigraphic positions (Williams, 1969; Fitton and Hughes, 1970; Wheatly, 1971a, b). It has a close analogy in its depositional environment to other conformable polymetallic deposits (Wheatly, 1971a), and the close relationship between mineralisation and petrology, especially the volcanic succession of the area, has been well exemplified (Thanasuthipithak, 1974).

The most comprehensive and detailed account of the geology of Parys Mountain was given by Greenly (1919). Later various aspects of its geology, namely stratigraphy, structure, lithology, and mineralisation, were described by Manning (1959), Derry (1961), Bates (1964, 1966), Hawkins (1966) and Wolfenden (1967) - in Thanasuthipithak (1974), Williams (1969), Wheatly (1971a, b) and Thanasuthipithak (1974). A simplified geological map after Thanasuthipithak (1974) is given as Fig. 2.

The general stratigraphic sequence and lithologies proved from the bore holes, and described by Hawkins (1966) and Thanasuthipithak (1974) is given in Table 1.

Parys Mountain is underlain by the Precambrian Mona complex (Fig. 2) which is represented by chlorite schists in the northern and eastern parts of the area, and by micaceous granitoid and quartzitic gneisses in the south. The Ordovician, best exposed in the northern side of the mountain consists entirely of Shales (Table 1). They were named as Parys Green Shales by Greenly (1919), Parys Shales by Hawkins (1966) and 'Slates' by Thanasuthipithak (1974) as they possess a well developed slaty cleavage.

Silurian rocks form the core of the mountain (Fig. 2) and consist of highly cleaved and silicifed shales. Surrounding the core, except to the east, are exposures of highly silicified and sheared rocks forming a hair-pin shaped outcrop. These were called 'Felsites' by Greenly (1919) and were considered by him to be intrusive. Thanasuthipithak (1974) described these felsitic rocks as a succession of extrusive volcanic rocks of Ordovician age consisting of dacitic and rhyolitic volcanic fragmental rocks and some siliceous sinter, a similar conclusion to that of both Hawkins (1966) and Wheatly (1971).

The rocks of the Precambrian Mona Complex are thrust over younger rocks along several low angle thrust faults called the Carmel Head, Corwas, and Nebo Thrusts (Fig. 2).

Although the structural relationship between shales and 'felsitic' rocks and the resultant structure of Parys Mountain has been variously interpreted, it is now generally agreed that the structure is an east-north-easterly trending, single syncline overturned to the north, with shales in the core (Fig. 3) (Thanasuthipithak, 1974).

1.2 Mineralisation

The mineralised belt trends between 060° and 070° following the general strike of the enclosing strata and dips 30-50° to the north. It extends for some 1500 m, and is some 400 m wide and has been worked to a depth of 300 m. The mineralisation occurs as a series of lenticular to tabular ore zones, in the folded sequences of Ordovician and Silurian sedimentary and volcanic rocks. The mineralisation is generally concentrated on both sides of the northern outcrops of the rhyolitic rocks. It is present both in the rhyolitic rocks and in the rocks which are in contact with them, namely the siliceous sinter, parts of the Ordovician slates in the north, and the Silurian slates on the south side of the northern limb (Fig. 4) (Thanasuthipithak, 1974). Based on the host rock and the mineralogy, four types of ores were distinguished by Wolfenden (1967) (in Thanasuthipithak, 1974), and a slightly different division was given by Wheatly (1971a). The former division is made use of in the present study. These ore types are given in Table 2 and the lodes in which they occur are shown in Fig. 4.

The origin of these mineral deposits was regarded by earlier workers to be epigenetic, based on the notion that the 'felsite' was intrusive and probably supplied hydrothermal ore-bearing fluids. Deposition was thought to have been modified by metasomatic pyritization,

chalcopyritization and some lead-zinc metasomatism (Greenly, 1919; Manning, 1959). The controls of ore deposition were thought to be both shear zones and lithological interfaces.

Wheatly (1971a, b) suggested that, at Parys Mountain as well as in other mining fields in the southern Caledonides (Avoca, south-east Ireland; Coniston, Lake District), the conformable lenticular, pyritic zones associated with volcanic sequences, reacted with later hydrothermal fluids to produce the complex galena-sphalerite-pyrite mineralization. He further suggested that the mineralisations in these fields, including Parys Mountain, have a pulsatory metasomatic sequence related to tectono-stratigraphic controls. The ore localisation was thought to have been controlled by suitable structures and the pyritic shale horizons. Thus, Wheatly concluded that the main mineralisation was of an epigenetic hydrothermal enrichment type on a 'prototype' syngenetic mineralisation.

Thanasuthipithak (1974) studied the relationship of mineralisation to petrology and concluded that because there was a close association of ore bodies as lenses and tabular bodies, generally conformable with the Ordovician volcanic host rocks, they could be interpreted to have synsedimentaryexhalative origin. According to him the deposits were later modified by remobilization of some sulphides to produce apparent epigenetic features during the Caledonian orogeny.

1.3 Summary of geological events at Parys Mountain

The main geological events including the mineralisation at Parys Mountain, according to Thanasuthipithak (1974), are a) Deposition of Ordovician sediments in a marine environment with volcanism producing acidic rocks, b) Continued Ordovician sedimentation with some mineralisation, c) Main stage volcanism with some mineralisation, d) Erosion, submergence and deposition of Silurian sediments, e) Deformation of sediments and volcanics during the Caledonian and Variscan orogenies along with remobilization of the sulphides.

1.4 The present investigation

It is hoped that further mineralogical and geochemical studies on sulphide minerals can supplement geochemical information and thus help the various interpretations on the genesis of Parys Mountain mineral deposits. Previous interpretations were based on structural, petrological and mineralogical observations and no investigation of the geochemistry of the ore minerals was made. Similarly no systematic and detailed

investigations of the composition of the ore minerals, trace element distribution patterns, partition behaviour of trace elements, if significant, have been made, and although sulpho-salt minerals were recognised, no quantitative determination of them have been made. Also no previous correlation has been done relating the observed quantitative and qualitative reflected light properties of the opaque minerals with composition.

In fact, there are only a few areas in the British Isles where the major and trace element geochemistry of the ore minerals has been investigated to interpret the metallogenesis. El Shazly (1951), El Shazly et al (1957), Bishara (1966), Kakar (1971) were the few to make systematic investigations on trace elements in sulphide minerals mainly sphalerite and galena. Trace elements in pyrite, chalcopyrite, sphalerite and galena mainly from Avoca and a few from the Parys Mountain, and Coniston areas were studied by Wheatly (1971a) who showed a similarity in trace element in all these areas. The geochemical investigations at Parys Mountain by this author were however not detailed and systematic. He also pointed out that work in progress on the geochemical atlas of Great Britain has delineated an anomalous tin area associated with copper at Parys Mountain, the explanation for which is not properly understood.

The present study was a systematic one of the geochemistry of the ore minerals and some of the physical and optical characteristics of the sulphide minerals. To this end studies were made using electron probe microanalysis, atomic absorption spectrophotometry, X-ray diffraction, electron diffraction, quantitative and qualitative reflected light microscopy, infra-red spectroscopy and differential thermal analysis.

CHAPTER 2

MINERALOGY AND PARAGENESIS

2.1 Introduction

The mineralogy and paragenesis of sulphide and sulpho-salt minerals from Parys Mountain has been described by both Wheatly (1971a) and Thanasuthipithak (1974). A description of the textural and paragenetic features observed in 58 polished sections from bore holes not previously studied (bore hole numbers A15, 27, 19, 36A, 32; mainly of pyritic and Bluestone ore types) is given here in addition to descriptions of those observed in some sections previously studied by Thanasuthipithak (1974). Textural features and optical characters of the opaque minerals were examined in reflected light using a Reichert Zetopan Ore Microscope with a micrometer ocular for grain size measurement.

Pyrite is the most abundant of the sulphides followed by chalcopyrite, sphalerite, galena and minor quantities of microscopically identifiable tetrahedrite-tennantite, arsenopyrite, pyrrhotite, lead and bismuth sulphosalts. Megascopically the specimens studied show 4 or 5 distinct forms. The general features of these forms and the corresponding ore types are summarized in Table 3, and Fig. 5 shows sketches of these forms. 2.2 Microscopic features

Only primary minerals are described here, although some secondary minerals, such as covellite and bornite, have been described by Wheatly (1971a) and Thanasuthipithak (1974). A list of ore minerals present, and their general characters are presented in Table 4. Pyrrhotite, from Parys Mountain, has been described by Wheatly (1971a) and Thanasuthipithak (1974), and arsenopyrite has been described by the latter author, but in the present study only their compositions have been determined and these are given in Chapter 3.

2.2.1 Pyrite

Pyrite is the most abundant of all the sulphides, and is most abundant in the pyritic ore type, being present both in the layered sulphide and in disseminated forms, and is relatively least abundant in the Bluestone Ore type. Pyrite grains show both primary fabrics, representing the original depositional features, and secondary fabrics representing deformational and recrystallised features. Euhedral-subhedral, anhedral and framboidal type pyrite grains comprise the primary type. Colloform pyrite was also described by Thanasuthipithak (1974). Cataclastic, radial and recrystallised textures comprise the secondary type.

2.2.1.1 Euhedral-Subhedral pyrite

This type is mainly associated with black shale and dacite as disseminations through the rock. The following three divisions can be made: a) Isolated simple pyrite euhedra in which the grain size varies from about 0.05 mm to about 2 mm with some chalcopyrite replacement at the margins. Pyrite euhedra are associated with rutile and in some instances are seen to replace it (Plate IA). It is therefore paragenetically later than rutile. b) Spherically arranged aggregates of pyrite cubes forming pseudomorphs after framboidal pyrite. As many as 14 pyrite euhedra are present forming a spherically arranged aggregate of pyrite cubes homogenised at the centre of the aggregate but retaining their cube outlines at the periphery (Plate IB). c) Pyritohedra with intense deformation textures, the pyrite grains being heavily fractured (Plate IC). In most instances the fractures are filled by other sulphides.

2.2.1.2 Anhedral pyrite

Anhedral pyrite is less abundant than the euhedral/subhedral type. It is generally fine-grained (0.01 mm to 0.05 mm) and forms allotriomorphic granular aggregates commonly enclosing euhedral pyrite which implies a generation gap between the two types. 2.2.1.3 Framboidal pyrite

Framboidal pyrite was seen mainly in the Bluestone ore type associated with galena-sphalerite mineralisation. Generally three kinds of framboids are present:- a) Isolated framboid microcrysts ranging in size from 2 microns to about 40 microns in diameter. Quantitative studies of framboid grain size were made and the distribution is seen to be positively skewed (Fig. 6). The maximum occurs at 30 microns and the majority of the framboids occur within 15 microns diameter. The size distribution is similar in sections from the different bore holes. There is some clustering of framboids and a plot of the number of framboids per cluster against frequency (Fig. 6d) shows an iiregular pattern with the frequency maximum at 10 framboids/cluster. b) The second type has the framboidal grains in the form of a network whose interstices are infilled mainly by sulpho-salts. This feature was described as atoll texture (Thanasuthipithak, 1974) in which the framboidal grains are extensively replaced, enclosed, and cemented by tetrahedrites (Plate I E, F). c) The third type has the form of a recrystallised

aggregate. The framboids form clusters (Plate ID) and lose their form where they are joined. The loss of shape is attributed to the result of growth of later pyrite between the granules (Raybould, 1973).

In some specimens the core of the framboidal cluster is replaced by sphalerite, and in some instances by tetrahedrite. Radiating textures have also developed in some framboidal pyrites (Plate II C).

Some pyrite grains in the types described above are compositionally zoned (Plate II E). The radiating textures (Plate II C) and irregular fracturing (Plate I C) exhibited by some pyrites are interpreted as resulting from cataclasis. In most specimens the fractures are infilled by other minerals namely sphalerite, and tetrahedrite-tennantites. Pyrite is comparatively free from inclusions; however, in some grains, small quantities of chalcopyrite and some gangue material are present as inclusions.

Pyrite occurs in minor quantities as fine-grained anhedral to subhedral grains forming a distinct vein or fracture filling in the matrix. 2.2.2 Chalcopyrite

Chalcopyrite most commonly is anhedral in form. It occurs: a) as a fracture filling in and replacing euhedral to subhedral pyrites; b) as a matrix material enclosing the pyrite grains; c) as mutual intergrowths with sphalerite, galena and pyrite; d) isolated anhedra embedded in rock matrix; and e) as exsolution bodies in sphalerite. Little chalcopyrite is associated with euhedral pyrite with most being associated with other kinds of pyrite and with other sulphides.

Chalcopyrite, where it is associated with pyrite generally replaces it. It is replaced by sphalerite although there is depositional overlap shown by intergrowths with sphalerite and galena.

2.2.3 Sphalerite

Sphalerite most commonly occurs in the fine-grained Bluestone ore type. The grain size varies between 0.02 mm to 0.5 mm. It is present as anhedral and irregular grains intergrown with other sulphides mainly chalcopyrite, and in lesser quantities filling fractures in cataclastic pyrite.

Two types of sphalerites are recognised: a) sphalerite with exsolutions of chalcopyrite and b) sphalerite without exsolutions. The first type is far more abundant than the second. Both the types are intergrown with chalcopyrite. Bournonite is found as inclusions or

infillings in sphalerite. Sphalerite generally shows mutual replacement textures and intergrowths with galena (Plate II A and B) and this is interpreted to indicate co-deposition.

2.2.4 Galena

Galena is present mainly in the Bluestone ore and Copper ore types and is not present in the Pyritic ore type. The grain size varies from 0.05 mm to 0.2 mm. It forms allotriomorphic masses and most commonly is intergrown with sphalerite and chalcopyrite.

Mutual replacements of sphalerite and galena are also present. A little galena, however, clearly replaces sphalerite, and paragenetically is therefore later. Inclusions or infillings of some sulphosalts are present in galena.

2.2.5 Tetrahedrite-tennantite

The tetrahedrite group is the most abundant of the sulpho-salts at Parys Mountain and it is found only in the Bluestone ore type. These minerals occur as a) fracture fillings in pyrite grains (Plate II D); b) an interstitial cementing matrix for some subhedral pyrite grains (Plates II E and III A); c) inclusions in some sphalerites and chalcopyrites along the peripheries of, and extensively replacing, pyrite framboids. The tennantite end member has a lower reflectivity value than that of tetrahedrite. The tetrahedrite has a reflectivity of between 34.3 and 36.5% at 589 nm in air, and tennantite between 29.5 and 31.7%. The microhardness value ranges 279-328 Kg/mm² for both minerals and their grain size varies from 0.005 mm to 0.01 mm. 2.2.6 Bournonite

Bournonite occurs as very small (grain size 30 microns) inclusions in sphalerite (Plate III B). The reflectivity is generally high (38 - 42%) but could not be precisely estimated because of the very small grain size. 2.2.7 Lead Sulpharsenides

These minerals generally are very similar to galena and it is very difficult to distinguish between them optically. They are distinguished from galena only by an absence of cleavages and triangular pits and by anisotropism (seen only in oil immersion). Electron microprobe analysis showed these minerals to be lead sulpharsenides. They are white in colour, have irregular shapes and generally occur replacing sphalerite and galena along with other sulpho-salts. The reflectivity values are similar to those for galena (about 39.3 - 43.5%) and the

microhardness was not determined because of the very small grain size (about 0.05 mm).

2.2.8 Bismuth sulpho-salts

These are very similar in appearance to the lead sulpho-salts; however, they have a more greyish white colour, are more anisotropic, and the reflectivity (34.5 - 37%) is slightly lower than that of the lead sulpharsenides. They were identified, from electron microprobe analyses, as kobellite and galenobismuthite. Grain shapes are anhedral and irregular and they are generally present only as infillings in other sulphides mainly sphalerite and pyrite.

Mutual replacements between the sulpho-salt minerals are absent and it is difficult to infer paragenetic differences between them. The occurrence as inclusions, and as interstitial infillings in sulphides, is interpreted to indicate that they are later than the sulphides.

2.3 Textural features

The textural relationships outlined fall into two distinct categories. To distinguish between them, here they are called: a) Primary fabrics - developed in the original precipitation or depositional processes, and b) Secondary fabrics - developed either superimposed on an original primary fabric (e.g. cataclastic texture in pyrite) or formed due to some epigenetic process (e.g. fracture infilling of sulpho-salts in pyrite). The two types of fabrics are summarized in Table 5.

2.4 Paragenesis

A simplified paragenetic diagram for the ore minerals, based on the textural relationships outlined above, is presented in Table 6. This is in general agreement with that of Wheatly (1971a) and that of Thanasuthipithak (1974). It should be noted that the information on pyrrhotite and arsenopyrite is from Thanasuthipithak (1974). 2.5 Stratiform features of Parys Mountain ores

Stanton (1972) described stratiform ores as those that occur as layers concordant with the stratification of the enclosing rocks. They are thus confined stratigraphically snd occur in preferred horizons. A comparison of mineralogical features of Parys Mountain ores with those of New Brunswick described by Stanton (1959, 1960 Parts I and II) as a typical conformable stratiform deposit brings out the following coincident features:-

- a) Imperfect alignment of ore lenses parallel to the bedding plane or schistosity
- b) Dominance of pyrite as iron sulphide with pyrrhotite being very local and minor
- c) Dominance of sphalerite among non-ferrous minerals
- d) Galena, although important, is subordinate to sphalerite
- e) Presence of trace quantities of minerals such as arsenopyrite, tetrahedrite-tennantite and other sulpho-salts.

Further the close association of the ores with pyroclastic volcanic rocks, tuffs and siliceous sinter as one of the stratiform type characters (Stanton 1960 Part I) can also be demonstrated in case of Parys Mountain ores (Thanasuthipithak, 1974).

Stanton (1964) considered that the textural features observed in stratiform ores are not depositional but result from growth during diagenesis and metamorphism. This is supported by experimental studies (Stanton and Gorman 1968). This hypothesis can explain the isolated uninhibited growths of euhedral and framboidal pyrites and intergrowths of other minerals with mutual boundary configurations. It cannot, however, account for fracture and interstitial infillings because of the fact that availability of mineral matter at such vacant spaces cannot be a coincidence, but it is a depositional feature along the available channel ways.

At Parys Mountain, the association of mineralisation with characteristic acidic volcanic rocks, megascopic conformable characters, mineralogical assemblages, close similarities to well established stratiform deposits such as Avica, all point to the fact that it is a synsedimentary stratiform conformable mineralisation. Replacement fabrics and fracture and interstitial infillings, favour some deposition at a later date superimposed on the original minerals as a later process of epigenesis. Pyrite represents the major conformable mineralisation with a little chalcopyrite. Microscopic evidence suggests that the minor sulphides and sulpho-salts were deposited at a later date as a process of epigenesis.

CHAPTER 3

SULPHIDE INVESTIGATIONS

3.1 Introduction

The essential and trace element contents of the sulphide minerals and their physical and optical characteristics, namely the reflectivity, microhardness, infra-red spectra and differential thermal analysis were determined to see if they could be correlated with composition and/or to compare with the published data. Table 7 lists the techniques employed and the nature of information obtained from the various minerals.

Samples for the present study were obtained from diamond drill cores, and selection and preparation techniques are described in Appendix 1.

Analaysis for essential and trace elements was done by Atomic Absorption Spectrophotometry (A. A. S.) and Electron Probe Microanalysis. Fe, Cu, Zn, Pb, Co, Ni, Mo, Ba, Cd and Te were analysed by A. A. S. This technique was used because of its high sensitivity and minimum interference from other elements for the elements determined (McLaughlin, 1967; Volborth, 1969) and its simplicity and rapidity of operation (Kahn, 1968; Angino and Billings, 1972). A Perkin Elmer model 460 Atomic Absorption Spectrophotometer was used for all analyses. Details of the technique and sample solution preparation method are given in Appendix 2.

Electron Probe Microanalysis was used to analyse the more finely grained sulphides which could not be recovered in the powdered form, and for the quantitative determination of the sulpho-salt minerals. Some 74 analyses were made on various sulphides and sulpho-salts from some 43 polished sections (Tables 8-12) for the elements Fe, S, Cu, Pb, Zn, Co, Ni, As, Sb, Bi, Mo, Sn, Ag, Cd, Mn and Se. Instrumental and analytical details are given in Appendix 2.

Techniques for reflectivity, microhardness measurements, and sample preparation, along with instrumental details of infra-red and differential thermal studies are given in Appendix 2.

3.2 Pyrite

3.2.1 Composition

Pyrite (FeS₂) has a theoretical composition of 46.6 wt% Fe and 53.4 wt% S. Specimens of euhedral, subhedral, anhedral, and

framboidal pyrites were analysed for both essential and trace elements by electron microprobe and atomic absorption spectrophotometry and the values are given in Table 8. S was not determined in the samples analysed by the latter technique. The mean, minimum and maximum values are given in Table 13. The Fe content was found to fall in the range from 43. 16 to 48.25%, with a mean value of 45.01% which is lower than the theoretical one. The S content ranges from 52.35 to 55.38% with a mean of 54.14% which is slightly higher than the theoretical value.

Trace quantities of Cu, Pb, and Zn are present in nearly all the samples analysed. Cu is a common trace element in pyrite, and in the present study the majority of the samples contain less than 2000 ppm of Cu. The high quantities 1.08% and 1.27% of Cu measured in samples H 14/186, and A 15/971 respectively (Table 8) are probably due to some slight contamination by chalcopyrite. Pb and Zn have a similar distribution pattern with mean values close to each other (Mean Pb 482 ppm and mean Zn 528 ppm). The samples analysed by A. A. S. were free from galena and sphalerite and the analysis in the electron microprobe was done only on pure pyrite grains. Therefore Pb and Zn are probably present in solid solution. Zn, however, is not unexpected in pyrite as Fe and Zn commonly substitute for one another in many min erals.

Co and Ni were present in nearly all the samples. Co substitutes for Fe in the pyrite structure (Rankama and Sahama, 1950), and Ni can exist in solid solution in pyrite (Fleischer, 1955). In the present study these two elements were found in almost all the samples analysed by A. A. S., but they were present in quantities below measurable limits in the samples analysed by probe. Analysis by A. A. S. showed the Co content to range from 30 to 2075 ppm (Table 8) with the majority of the samples containing less than 800 ppm. Although the distribution of Ni is irregular it has the comparatively narrow range of 16-696 ppm. The Co content is thus generally higher than that of Ni.

The Co/Ni ratios determined are given in Table 8. The majority of them show Co/Ni ratios to be greater than 1. High Co values and a Co/Ni ratio > 1 were found to be characteristic of pyritic deposits associated with volcanism (Loftus-Hills and Solomon, 1967). Those deposits in which the Co/Ni ratio is < 1 for pyrites are considered to

be sedimentary in origin. Hawley, and Gavelin and Gabrielson, (in Fleischer, 1955) found separately that the Co content and the Co:Ni ratio were generally high in high temperature deposits. Analysis of Parys Mountain pyrites by Wheatly (1971a) showed a high Co content and Co/Ni ratio > 1.00 and so he concluded the deposits to be associated with volcanism. In the present study, since the majority of the samples showed a consistent Co/Ni ratio > 1.00 it is concluded that pyritic mineralisation is related to volcanism at Parys Mountain.

Notable quantities of As have been reported in pyrite (Rankama and Sahama, 1950). However, in the present study probe analyses showed As to be present in quantities below measurable limits except in 3 samples where it is greater than 0.1% (Table 8).

Cd occurs in pyrite in lower concentrations than in sphalerite (Vlasov, 1964). In the present study only about 40% of the samples analysed contain Cd and in quantities generally less than 1000 ppm.

Ba cannot usually substitute for Fe because of its larger ionic radius and is therefore not common in pyrite (Rankama and Sahama, 1950). In the present study, however, Ba was found in most of the samples analysed by A.A.S. although most of the samples contained below 500 ppm (Table 8).

Mo is not a common trace element in pyrite, though it was reported in syngenetic pyrites by El Shazly (1951). In the present study it was found in some 25% of the samples in quantities less than 500 ppm.

Te, because of physical and chemical similarities, commonly substitutes for S, and as much as 0.1% of Te has been reported in pyrites (Vlasov, 1964). In the present study the majority of the samples analysed by A. A. S. contain less than 200 ppm Te (Table 8). Te is relatively more common in pyrite than in other sulphides.

Other elements detected, although present in below measurable quantities by probe analysis, are Ag, Mn, Bi and in a few samples Se. Sb and Sn were looked for but were not detected.

3.2.2 Physical-optical characteristics

3.2.2.1 Microhardness

The microhardness values for the pyrites determined are given in Table 19. For a load of 100 gm Bowie and Taylor (1958) reported values of 1027-1240 kg/mm² for pyrite. Pyrite from Parys Mountain

has a hardness range of 1031-1483 kg/mm². Higher hardness values of 1186-1836 kg/mm² are quoted by Young and Millman (1964). The measurements made in the present study are thus well within this region. The indentations obtained were all fractured as has been observed by other authors. The weight percentages of Fe in pyrites were plotted against microhardness number (Fig. 7a); however, no relationship was found.

3.2.2.2 Reflectivity

Results of reflectivity measurements on pyrites in the wavelength region 400nm - 700nm at intervals of 20nm including 589nm are given in Table 23, and the spectral reflectivity profiles are shown in Fig. 6a. The profiles show a regular pattern generally increasing sharply with wave length until about 520nm and then increasing very gently (Singh, 1965). However, no significant differences could be observed with different types of pyrites namely the framboidal, euhedral, anhedral and subhedral pyrites (Fig. 8a). Reflectivity values at 589nm were plotted against weight percentage Fe in pyrite (Fig. 9a), but no conclusion could be drawn about their relationship.

3.2.2.3 Infrared studies

The infrared spectra produced for pyrite are given in Fig. 10. The pyrites show poor resolution, and this has been previously reported by Hunt et al (1950). The two absorptions shown by pyrite are in the wave length region 2.8-2.9 microns and 6.1-6.2 microns (Fig. 10). It can be seen in the figure that, compared to the sample A 15/924 which has Fe content of 43.98%, the two samples 36A/1617 and 32-1108, which have Fe content of 45.23% and 45.71% respectively, have more prominent absorptions in the wave length region 6.0-6.2 microns. In sample IM 6/1231, which has Fe content of 46.78%, the absorption in the wave length region 6.2 microns although more prominent than sample A 15/924, is less prominent than the other two samples. This probably indicates that variations in composition may have some role in the absorption patterns. 3.2.2.4 Differential thermal analysis (d.t.a.)

The d.t.a curves obtained for 6 pyrite samples are given in Fig. 11. Comparison with the curves obtained by Kopp and Kerr (1957) show that the present curves are in good agreement in that the pyrites show a broad exothermic peak in the region of 400-500°C. The endothermic

reactions are present at about 550°C. Samples studied have Fe content ranging from 43.19 to 46.78% but no significant differences in the exothermic or endothermic behaviour of these pyrites was observed. 3.3 Chalcopyrite

3.3.1 Composition

The theoretical composition of chalcopyrite in wt.percent. is 34.6% Cu, 30.4% Fe, and 35.0% S. In this study 19 samples were analysed and the results are given in Table 9. Out of these, 8 were analysed by A.A.S., and 11 by electron probe. Four samples analysed by the latter technique were also analysed by A.A.S. S was determined only in the probe analyses. The mean values for Cu, Fe and S of 34.53%, 29.62% and 35.78% (Table 14) respectively are close to the theoretical values given above, although there is a considerable range. The maximum frequency of Cu occurs in the range of 34-36%, Fe in the range of 29-31%, and S in the range of 36-37% (Table 9).

Zn was found in all the samples analysed, ranging from 1000 to 5600 ppm, with a mean around 1900 ppm; this is attributed to the closely associated sphalerite, which commonly occurs as small inclusions in chalcopyrite. However, chalcopyrite is structurally similar to sphalerite and some Zn may also be present in solid solution in the chalcopyrite structure.

As and Bi have been reported in chalcopyrite (Fleischer, 1955), and probe analyses in the present study show that most of the samples contain these two elements (Table 9). Three samples contain more than 0.1% As, and another 3 samples contain more than 0.1% Bi (Table 9). These samples are from the ore types in which arsenopyrite and bismuth sulpho-salts occur respectively. None of the samples which have a high As content contain arsenopyrite. The high As content does not result from contamination but probably is due to its presence in the structure of chalcopyrite. Bismuth sulpho-salts are present as very fine-grained minerals (Chapter 4) in some of the sections (H 4/491, IM 9/269) that have a high Bi content. Thus these minerals probably have contributed to the high Bi values in the form of tiny inclusions.

Co and Ni are present in most of the samples analysed. Analysis by A.A.S. showed that Co ranges from 60 to 710 ppm and Ni from 12 to 1060 ppm (Table 9). Trace quantities of Co and Ni are not unexpected

in chalcopyrite although Ni tends to be concentrated in pyrite relative to chalcopyrite (Vaughan 1971).

Cd commonly is present in chalcopyrite, although in lower quantities than in sphalerite, because of the structural similarities between them (Vlasov, 1964). Analysis by A.A.S. showed Cd to be present in the range of 98 to 446 ppm.

Pb was found in most of the samples analysed in the range of 313 to 1045 ppm.

Te was found in only a few samples, ranging from 55 to 192 ppm, probably substituting for S.

Ba (A.A.S. analysis) was found in quantities ranging from 165 to 1653 ppm, with a mean of 737 ppm. It is not a very common trace element in chalcopyrite and its presence in the chalcopyrites at Parys Mountain is difficult to explain.

Mo (A.A.S. analysis) was also found in some 50% of the samples, in quantities ranging from 28 to 510 ppm, with a mean of 217 ppm.

Ag, Mn, Sb, Se and Sn were all below the limits of measurement of the electron probe.

3.3.2 Physical-optical characteristics

3.3.2.1 Microhardness

Microhardness values measured for chalcopyrite are given in Table 20. This hardness range of $171-221 \text{ kg/mm}^2$ with perfect indentations, is in close agreement with that of 186-219 by Bowie and Taylor (1958). Weight %s of Fe in the chalcopyrites were plotted against microhardness number (Fig. 7b), however, as in the case of pyrite, the relationship is not pronounced.

3.3.2.2 Reflectivity

Reflectivity measurements for chalcopyrite in the wave length region 400-700nm including 589nm are given in Table 24. The spectral reflectivity profiles are given in Fig. 8b. Like pyrite, chalcopyrite also has a regular spectral reflectivity profile, generally increasing sharply with wave length until about 520nm and then increasing very gently. Reflectivity values at 589nm plotted against weight % Fe showed no relationship.

3.3.2.3 Infrared studies

The infrared spectra produced for chalcopyrite are given in Fig. 12.

Chalcopyrite has a poor resolution and one sample (A 15/1193) showed absorption in the vicinity of 6 and 7 microns region. In the two samples studied No. A 15/1193 has Cu 35.05%, Fe 32.37% and S 34.20% and the other (M 10/1521) has Cu 34.73%, Fe 27.73% and S 35.96%. The sample A 15/1193 has a very much higher Fe content than the other and this probably is responsible for its having a more pronounced absorption pattern in the region 2.85-2.9 and 6.0 microns regions. 3.3.2.4 Differential thermal analysis (d.t.a.)

The d.t.a. curves obtained for chalcopyrite are given in Fig. 13. The five samples studied showed marked exothermic behaviour in the vicinity of $450-460^{\circ}$ C. as part of a broad exothermic reaction starting at 400° C and continuing up to 500° C. No significant differences in differential thermal behaviour with compositional variations were observed. The sample with a lower Fe content (sample M 10/1521 with Fe content 27.73) than the others (which have Fe contents ranging from 28.55% to 32.37%), has a smoother curve. This is probably because reactions with higher Fe contents become more vigorous than those with lower Fe content. Further detailed investigations are necessary for significant conclusions.

3.4 Sphalerite

3.4.1 Composition

Sphalerite has a theoretical composition of 67.10% Zn and 32.90% S by weight, but in nature this is not found because the sphalerite structure is remarkably tolerant of substitutions by Fe, Cd and Mn for Zn. Nearly all natural sphalerites are diadochic compounds of ZnS with FeS (up to 42%), Cd (up to 2%), and MnS (up to 9%) (Boyle and Jambor, 1963). Both Zn and S can be isomorphously replaced by substantial quantities of other elements (Vaughan, 1971). The Fe content in particular has received a very considerable attention (Kullerud, 1953; Kalliokoski, 1959; Sims and Barton, 1967; Benson, 1960; Barton and Skinner, 1967; Campbell and Ethier, 1974; Williams, 1974). Trace elements in sphalerite have also been studied in greater detail than in any other sulphide.

In all, 22 sphalerite samples were analysed by electron probe and A.A.S. The Zn content was found to range from 51.68% to 64.74% (Table 10), with a mean of 58.46% (Table 15), and the S content ranges

from 32.23% to 38.66% with a mean of 35.29%. The Fe content ranges from 0.67% to 18.32% (Tables 10 and 11) with a mean of 6.42%. In addition to the analyses listed in Table 10, Fe and Cd were also determined using electron probe on 4 samples to enable calculation of the cell edges (discussed later).

There is a good antipathetic relationship between Zn and Fe content (Fig. 14) allowing the interpretation that Fe has substituted for Zn. The Fe content is believed to be present in sphalerite in solid solution and is not due to any contamination because most of the samples analysed were pure grains.

Cd was found in all the samples analysed in quantities ranging from 215 ppm (A.A.S. analysis) to 0.33% (probe analysis) (Tables 10 and 11).

Cu is present in all samples in quantities ranging from less than 0.1% to 2.75% (Table 10) as analysed by probe and A.A.S. The very high Cu contents of some samples can probably be attributed to submicroscopic inclusions or exsolutions of chalcopyrite, though the Cucontent of sphalerite is present in variable quantities (Rankama and Sahama, 1950).

Pb was found in some 11 samples ranging from 286 ppm to 1468 ppm (Table 10). However, this is probably due to intimate admixtures with galena as has been reported elsewhere (Fleischer, 1955).

Co has been reported in sphalerite and in a very few instances Ni also has been reported (Fleischer, 1955). A.A.S. analysis of Parys Mountain sphalerites showed Co to be present in 5 samples ranging from 206 to 967 ppm and one probe analysis showed 0.1% of Co. Ni was found in 3 samples in the range of 340 ppm to 433 ppm.

Sb, As and Bi have been reported from sphalerites although in most instances only qualitatively (Fleischer, 1955). As and Bi are present in trace quantities (below 0.1%) in most of the Parys Mountain sphalerites analysed by probe, although 4 samples contained more than 0.1% As, and another two more than 0.1% Bi (Table 10). Sb was not detected. It is likely that these quantities are from sulpho-salts containing As and Bi admixed in the sphalerites.

Mn is present in most samples but below measurable limits (0.1%) by electron probe, and in only 3 samples was it found to be more than 0.1% (Table 10).

Ba was found in the samples analysed by A.A.S. ranging from 174 to 7222 ppm (Table 10). As in the case of other sulphides its presence is unexplained.

Mo was found in trace quantities and in a few instances more than 0.1% (Table 10).

Ag and Sn were found not to be present by electron probe. 3.4.2 Unit cell edge measurements of sphalerite

In the present study the reason for the measurement of unit cell edges was two-fold: 1) To investigate whether there is a linear relationship between Fe content and measured cell edges of sphalerite by X-ray diffraction; 2) To investigate the possibility of using a single crystal electron diffraction technique to obtain Fe content in the same way as in X-ray diffraction, if confirmed that there is a linear relationship between cell edge and Fe content.

Kullerud (1953) reported that the effect of FeS (and the other common trace impurities MnS and CdS) is to cause an increase in the unit cell dimensions in a linear way. This then allows for accurate measurements of cell dimension to be used as an indicator of Fe content. Skinner (1961) presented an equation for this:

a = 5.4093 + 0.000456 X + 0.00424 Y + 0.00202 Z where X, Y and Z are the contents of FeS, CdS and MnS in mol% and a is the cell edge in angstroms. Krause, and Van Aswegen and Verleger (in Boyle and Jambor, 1963) have, however, reported that Fe content has no increasing effect on unit cell edge and Williams (1965) has argued that the equation is the least squares fit to the experimental data and is therefore subject to possible error. The concept is, however, supported by Boyle and Jambor (1963) and by Evans et al (1968), and is used in this study.

The unit cell dimensions of 17 sphalerite specimens were measured using a Debye-Scherrer Powder Camera (114.59 mm diameter) fitted to a Phillips Norelco X-ray Diffractometer with Ni filtered CuK_K radiation ($\lambda = 1.5405$ Å). No correction for film shrinkage was applied and the diffraction patterns were measured on a Central Scientific Instruments' Linear Comparator with a vernier having a least count of 0.05 mm (Straumanis' method as described by Zussman, 1967). X-ray diffraction angles (9) calculated by this method were tabulated and the

interplanar spacings were read from tables. Corresponding hkl values were obtained from an X-ray diffraction data file (Berry, 1974), and unit cell edges calculated.

Unit cell edges of sphalerite were also calculated by substituting the mol% values of FeS, MnS and CdS in the equation by Skinner (1961). In general there is a good agreement between measured and calculated cell edges (Table 17) but there is a systematic trend of measured edges being greater than calculated edges, as also noticed by Evans et al (1968); Skinner 1961, found the opposite. A plot of measured cell edges against measured Fe content (mol% FeS) (Fig. 15) shows a good linear relationship between the two. This is interpreted to show that unit cell edge increases with increasing Fe content. The increase in cell edge at lower Fe contents is very pronounced, however, as higher values for Fe content are reached the rate of increase is less pronounced and the curve flattens out slightly. This observation is in agreement with the observations of Boyle and Jambor (1963), although it is a little less pronounced than that found by Evans et al (1968). It is concluded from these results that the accurate measurement of cell edge can be utilised to obtain FeS content. Mol% CdS plotted against cell edge showed no significant relationship (Fig. 16), because the electron probe was not able to measure accurately the trace quantities of Cd present in sphalerite. Mol% Mn was not plotted against cell edge as the data was insufficient.

Cell edge measurements were also made on 12 sphalerite samples by an electron diffraction technique for comparison purposes. Specimens were prepared using the technique described by McConnell (1967) and single crystal electron diffraction patterns were obtained using a Jeol JEM 100 E Transmission Electron Microscope at 100 kV. The diffraction patterns in each case were photographed and the 'd' spacings were calculated using the formula

$$d_{hkl} = c.f.$$

 γ_{hkl}

where dhkl is the lattice interplanar spacing

 \mathbf{v}_{hkl} is the measured distance from origin 000 to spot hkl on the electron diffraction photograph. c.f. is the Camera Factor, a constant

provided (which depends on the camera length (L) and the wave length of the electron beam (λ) (c.f. = λ L).

hkl values were obtained from X-ray powder file and the cell dimensions calculated as in the case of X-ray diffraction.

The cell edges measured are given in Table 18 and it can be seen that all the electron diffraction measurements are higher than those from X-ray diffraction. This is a systematic error in the electron diffraction measurements, probably resulting from an inaccuracy in the assumed Camera Factor. The accuracy could be improved by estimating this Camera Factor at the time of measurement by using an internal standard. Provided an internal standard is used an electron diffraction technique for cell edge measurement has many advantages: 1) It requires less sample than that required by X-ray diffraction; 2) Diffraction patterns can be obtained from several selected spots on a specimen and the Fe content obtained from several measurements might be used to indicate variations in Fe content within a specimen; 3) Diffraction patterns can be readily seen and photographed immediately and thus it is much quicker than X-ray diffraction; 4) Very sharp reflections can be obtained, unlike X-ray powder patterns where measurements are sometimes inaccurate because of obscure reflections and blackening of the film in the back reflection region.

3.4.3 Physical-optical characteristics

3.4.3.1 Microhardness

The microhardness data for sphalerite show it to have a range of 148-240 Kg/mm² (Table 21). The weight % of Fe in sphalerite was plotted against microhardness number (Fig. 7c), because it had been noticed by previous workers that an increase in Fe content of sphalerite increased its microhardness (Young and Millman, 1964; Bishara, 1966; Vaughan, 1971). In the present study, a good linear relationship between Fe content and microhardness was seen (Fig. 7c). 3.4.3.2 Reflectivity

Results of the reflectivity measurements in the wave length region 400 nm-700 nm including 589 nm are given in Table 25, and the spectral reflectivity profiles are shown in Fig. 8c. Sphalerite in this study was seen to have maximum reflectivity in the wave length region 480-500 nm, as has been reported by Gray and Millman (1962) for sphalerites. In many grains little variation was observed with wave length, but generally the values decrease with increase in wave length. Reflectivity values at 589 nm plotted against weight % Fe in sphalerite (Fig. 9b) showed no significant relation.

3.4.3.3 Infrared studies

The infrared spectra for sphalerite are shown in Fig. 17, and compared with other sulphides, show good resolution. All the sphalerites show clearly two absorption peaks in the vicinity of 2.8-3.0 microns wave length. The 5 samples studied had Fe contents ranging from 1.59% to 18.32% (Fig. 17), and unlike pyrite and chalcopyrite, no differences in absorption patterns with varying Fe content were observed.

3.5 Galena

3.5.1 Composition

The theoretical composition of galena is 86.6 wt% Pb and 13.4 wt% S. Twelve samples were analysed, and the Pb content found to range from 80.15% to 87.15% (Table 12), with the majority of the samples containing between 82 and 86% Pb. All galenas analysed except one (A 15/1193) have a lower than theoretical Pb content, and have considerable As and Bi contents. The S content ranges from 13.85 wt% to 15.75 wt% (Probe analysis).

As, Sb and Bi are common trace elements in galena (Rankama and Sahama, 1950) and these elements were looked for in the specimens analysed by electron probe. As was found to range from 0.1wt% to 2.85 wt% with a mean of 1.48 wt%. Bi ranges from 0.27 wt% to 3.49 wt% with a mean of 1.58 wt% (Tables 12 and 16), and more than 0.1 wt% Sb was found in all samples. As and Bi sulpho-salts are present in very fine-grained sizes in most of the sections analysed by probe and high values in these analyses are thus probably due to some submicroscopic admixtures of these minerals with the galena. However, since As, Bi and Sb are common in galena, it is likely that they are also present in solid solution. No further information was gained in this study.

Ag is a common trace element in galena (Fleischer, 1955) and it was detected in all the samples analysed by probe and 4 samples were found to contain more than 0.1 wt% (Table 12). As there are no Ag

sulphides in the specimens analysed, the Ag content is not due to contamination but probably is present in solid solution.

Cu, Fe and Zn are all present generally above 1000 ppm or 0.1 wt% (Table 12). Cu occurs in lower quantities than in sphalerites. Fe and Zn although reported by previous workers in galenas, were probably due to contamination by pyrite and sphalerite (Fleischer, 1955). Most of the samples in the present study contain Fe and Zn (Table 12) (Probe and A.A.S. analysis) above 0.1 wt%.

Cd was found in most of the samples in quantities generally below 1000 ppm (Table 12). In 2 samples it was found to be 0.11 wt%. Goldschmidt (in Vlasov, 1964) suggested that admission of Cd into galena is due to the Cd-Pb isomorphism, and trace quantities of Cd in Parys Mountain galenas are probably present in solid solution.

Co and Ni are present only in trace quantities (Table 12) and in the samples analysed by A.A.S. they were found to be below 500 ppm.

Sn was detected in most probe analyses and 3 samples contain more than 0.1 wt% (Table 12).

Ba was measured by A.A.S. in 3 samples and it was found to be present below 500 ppm (Table 12). Its presence as in the other sulphides is difficult to account for.

Mo was also found in a few samples and 2 probe analyses showed more than 0.1 wt% (Table 12).

Te was measured in 4 samples by A.A.S. and was found to be below 100 ppm (Table 12). It has probably substituted for S. 3.5.2 Physical-optical characteristics

3.5.2.1 Microhardness

The measured values for microhardness of galena have a range of 61.7-107 kg/mm² (Table 22) in contrast to Bowie and Taylor's (1958) measurements of 71-84 kg/mm². The wider range in microhardness of Parys Mountain galenas probably results from the presence of considerable quantities of As and Bi. Weight %s of As and Bi were plotted against microhardness (Figs. 7d, e) and there appears to be slight linear relationship between them, though this needs confirmation by more data.

3.5.2.2 Reflectivity

Reflectivity measurements in the wave length region 400 nm-700 nm,

including 589 nm are given in Table 26, and the spectral reflectivity profiles are shown in Fig. 8d. Galena is a highly reflecting species and it shows irregular spectral profiles as reported by Gray and Millman (1962). Reflectivity % at 589 plotted against weight % As and weight % Bi showed no significant relationship probably because of insufficient data. (Fig. 9c, d).

3.5.2.3 Infrared studies

The infrared spectra produced for galena show poor resolution with broad absorption peaks between 2.8 and 3.0 microns wave length and one absorption peak in the vicinity of 6.0 micron wave length region (Fig. 18). No significant difference in absorption pattern was seen between the two samples studied, although one sample (19-424) contains 2.24% of As and the other (sample H 4/491) has only 0.10%, and both of them have nearly similar quantities of Bi (Table 12). 3.6 Arsenopyrite

Two grains of arsenopyrite were analysed by electron probe and the results are listed in Table 27 along with the theoretical value for the ideal formula FeAsS.

Compared with theoretical composition the Parys Mountain arsenopyrite has less As content but more Fe. Co, Ni, Cu, Pb and Zn are present in trace quantities (below measurable limits by electron probe).

3.7 Pyrrhotite

One pyrrhotite grain was analysed by electron probe and it has the following composition

Fe S Co Ni Cu Pb Zn Total 57.33 M 10/1521 40.91 1.30 tr tr tr 99.55

The high Cu content is difficult to account for from a single analysis and no further information was obtained in the present study. 3.7 Summary and implications of sulphide investigations

Investigations on Parys Mountain sulphide minerals have the following significant features:-

 Analysis by electron probe on inclusion free areas showed the presence of substantial quantities of trace elements probably in solid solution.
 The generalisation could be made that Co is concentrated in pyrite relative to other sulphides. Co and Ni are more common in pyrite and chalcopyrite than in sphalerite and galena.

3) Cd is concentrated in sphalerite relative to other sulphides, and there is a wide range of Fe content in sphalerites.

As, Bi and Ag are concentrated in galena relative to other sulphides.
 Sn is also present in galena but is absent in others.

5) Mo is concentrated more in sphalerite and galena than in pyrite and chalcopyrite. Ba is concentrated in chalcopyrite relative to pyrite. The significance of these two elements is not clear.

6) Correlation of trace element assemblage with the different types of the same mineral are inconclusive, such as between euhedral, anhedral and framboidal types in case of pyrite (Table 8), and in sphalerite grains those with exsolutions and without exsolutions (Table 10).
7) Concentration profiles for essential and trace elements were observed while analysing the sulphides by electron probe. It was noticed that variations of essential and trace elements within the same grain were more pronounced in case of sphalerite and galena than in the case of pyrite and chalcopyrite.

8) The Co/Ni ratio in pyrites (> 1) relates the deposits to volcanism

High quantities of Cu in pyrites have been used by Frenzel and Ottemann (1967) in Fiji deposits to indicate a subvolcanic origin. High quantities of Cu in some Parys Mountain pyrites may be related to volcanism, though in some, contamination by inclusions is likely. 9) High Ag, Sb and Bi in galena indicate high temperature of formation as low quantities of these have been reported only from low temperature deposits (Fleischer, 1955; El Shazly et al 1957). Marshall and Joensuu (1961) also found that galenas having poor trace element assemblage predominantly form at lowest temperatures and vice versa. From this point of view the Parys Mountain galenas may throw some light on temperature of formation. However, it requires more data to draw any conclusions on this.

10) A linear relationship was observed between Fe content and unit cell edges of sphalerite and between microhardness and Fe content in sphalerite.
11) Attempts to correlate composition with some physical and optical characteristics of the sulphides allowed no significant conclusions, although some of this was due to insufficient data.

CHAPTER 4 SULPHO-SALTS

4.1 Introduction

The sulpho-salt minerals are intimately associated with the major sulphides at Parys Mountain. Their optical properties and textural relationships with the sulphides have been discussed elsewhere (Chapter 2). Their physical and optical characteristics are so similar that they are difficult to identify and distinguish optically (Uytenbogaardt and Burke, 1971) and so electron probe microanalysis is the most common method used for their mineralogical determination.

Most of the commonly known sulpho-salts contain one or more of the following elements - Fe, Co, Ni, Cu, Ag, Zn, Hg, Sn, Pb, Mo together with one or more of As, Sb and Bi; S is an essential constituent. These chemically complex sulpho-salts are commonly 'patterned' structurally after the simple sulphides (Ross, 1955) and are modifications of the cubic or hexagonal close packing structures. The sulpho-salt minerals present at Parys Mountain are listed in Table 28 along with their theoretical formulae. In addition to those listed, bismuthinite was reported by Thanasuthipithak (1974).

4.2 Tetrahedrite-tennantite

Many workers do not regard the tetrahedrite-tennantite group of minerals as sulpho-salts and there is considerable disagreement in assigning a chemical formula to them. Springer (1969), from the analyses of world wide material, concluded that the general formula (Cu, Ag, Fe, Zn, Hg)₃ (As, Sb, Bi, Te)S_{3.25} is valid for tetrahedrite although the majority corresponds to (CuAg)_{2.50} (Fe Zn)_{0.50} (As Sb)S_{3.25}. Later Maske and Skinner (1971) proposed a formula $Cu_{12+x}As_{4+y}S_{13}$ where $O \ll x \ll 1.72$ and $O \ll y \ll 0.08$ for tennantite. Skinner et al (1972) proposed $Cu_{12+x}Sb_{4+y}S_{13}$ for tetrahedrite where $O \ll x \ll 1.92$ and $-0.02 \nsim y \not \sim 0.27$. This complexity is due to extensive substitutions in the structure where Zn, Ag, Hg, Pb, Ni or Co as well as Fe may replace Cu in quantities ranging up to 16% (Vaughan, 1971).

Complex substitutions can occur in tetrahedrite partly because Cu occurs in both mono and divalent states. The first type is tetrahedrally co-ordinated with three S atoms in unusual planar groups (Riley, 1974). Cu in these sites can be replaced by Ag and Hg. In the second type Cu, which is in 3-fold co-ordination in the structure, can be replaced by Zn and Fe (Vaughan, 1971). Other substitutions involve Sb, which can be

completely or partly replaced by As and in minor quantities by Bi, Sn and Ge (Ramdohr, 1969). This complexity is well exemplified by the Parys Mountain minerals (Table 29).

Analyses of 6 tetrahedrites and 3 tennantites from Parys Mountain are shown in Table 29, and these represent the average analysis taken from 2 or 3 points in each grain. The atomic proportions (Table 30) were calculated by making the total of Cu + Ag + Fe + Zn equal to 12, Sb + As + Bi equal to 4 and obtaining the relative proportion for S based on the total of these two groups (Petruk et al., 1971). Analyses of tetrahedrites from Parys Mountain and Avoca, reported by Wheatly (1971a) are given in Table 29, for comparison.

Comparison of the compositions determined in the present study with those reported by Wheatly (1971a) (Table 29) shows that Ag content in Parys Mountain minerals in the present study is low, the maximum Ag value being 1. 28 wt% from bore hole H4/491 (Bluestone ore) as compared to Wheatly's maximum Ag value of 5.4 wt%. The Fe content in the present study ranges from 3.16 to 10.18 wt% and is higher than that shown by Wheatly's (1971a) analyses. The zinc content ranges from 1.29 to 8.18 wt% and this range is quite in agreement with the analyses of Wheatly (1971a). All tetrahedrites contain some As and tennantites some Sb (X-ray images in Plate IV). Cu and Sb contents are in good agreement with Wheatly's (1971a) analyses. Bi is observed in both tetrahedrites and tennantites, the maximum content being 1.42 wt% from bore hole 27-145. There is a compositional break between tetrahedrite and tennantite as shown in Fig. 19. Such break was also noticed by Wheatly (1971a) at Avoca.

Deviations from the stoichiometric formula are illustrated by the atomic proportions of S given in Table 30. Such deviations have been noted in analyses elsewhere (Petruk et al., 1971) and are considered to be the result of complex metal substitutions with the whole complex forming an extensive solid solution series.

4.3 Bournonite

The theoretical formula for bournonite is CuPbSbS₃. Analyses of specimens from Parys Mountain, Avoca and Idaho are compared with the theoretical values in Table 31, along with atomic proportions for the analyses in the present study. The compositions and atomic proportions are at variance with the stoichiometric values. This is especially true of specimen 2 (sample M 10/1548) which contains appreciable quantities of Bi, Fe and Zn and has a Cu content very much higher than the theoretical value. The analysis of specimen (H4/465) however is in good agreement with the theoretical values and with the analyses of Avoca minerals (Wheatly 1971a). Analyses of specimens from Parys Mountain show As to be present in considerable quantities probably substituting for Sb. A solid solution series exists between Sb end member (Bournonite) and the As end member seligmannite (CuPbAsS₃) and this is considered to account for the As content in Parys Mountain analyses. 4.4 Bismuth sulpho-salts

Kobellite $(Pb(Bi, Sb)_2S_5)$ and galenobismuthite $PbBi_2S_4$ were identified at Parys Mountain in the Bluestone ore type. Kobellite is a disordered Bi-Sb-Pb sulpho-salt of composition $Pb_{6-x}(Bi, Sb)_{7+x}$ (Fe, Cu)S_{17.5} with $O \swarrow x \measuredangle 1$ (Weunsch, 1974). Weight percentages and atomic proportions for kobellite and galenobismuthite are given in Tables 32 and 33 along with theoretical values and some comparative analyses.

Comparison with theoretical composition shows the analytical data on Parys Mountain kobellite to be in good agreement with theoretical compositions. As is present substituting for Sb, and appreciable quantities of Cu and Fe are also present in the Parys Mountain kobellites. The deviation in composition from the theoretical composition of Parys Mountain galenobismuthite is due to a high Zn content which is probably present in solid solution.

4.5 Lead sulpharsenides

Mineral grains optically very similar to galena with high As values are classed here as lead sulpharsenide minerals. Analyses of these and calculated atomic proportions are presented in Table 34.

Chang and Bever (1973) have outlined the various disagreements on formulae for the lead sulpharsenide group of minerals. The calculated atomic proportions (Table 34) roughly correspond to jordanite which has a formula Pb₁₄As₇S₂₃ or Pb₁₃As₇S₂₃. However, since there is no standard and accepted formula for jordanite, Parys Mountain minerals are classed as lead sulpharsenides only, rather than comparing them to any of the theoretical formulae.

4.6 Implications of sulpho-salt geochemistry

The complexity and uncertainty of the sulpho-salt geochemistry at Parys Mountain is due to the extremely local and minor abundance of these minerals and their fine grain size. Textural relationships with the major sulphides as outlined in Chapter 2 suggest that they are later than the conformable pyritic mineralisation. There is no geochemical evidence from sulpho-salt studies to assign any environment or temperature of formation for the Parys Mountain mineralisation.

Experimental studies by Maske and Skinner (1971) showed that the ideal composition for tennantite $Cu_{12}As_4S_{13}$ is probable only at lower temperature, i.e. below 300°C, and above this temperature, it deviates. Chang and Bever (1973) pointed out that lead sulpho-salt minerals are essentially restricted to hypogene deposits, particularly in the mesothermal intensity range. Minerals such as galenobismuthite have been described as occurring in high temperature areas (550 - 610°C) of volcanic fumaroles in the Lipari Islands (Palache et al., 1944 in Craig, 1967). Czemanske and Hall (1975) have reported that the Darwin lead-zinc-Silver deposit where lead sulpho-salts occur, is a high temperature deposit.

If comparisons are made with Parys Mountain minerals, then a high temperature, at least a relatively higher temperature phase than earlier conformable pyritic mineralisation has to be assigned for the Parys Mountain sulpho-salts. Nevertheless, strong similarities in mineralogy, host rock geology and sulpho-salt assemblage exist between Parys Mountain deposits and the Kuroko deposits of Japan (Lambert and Sato, 1974) which are not considered to be of high temperature mineralisation.

CHAPTER 5

WALL ROCK STUDIES

5.1 Introduction

Despite the widespread occurrence of chlorite associated with mineralisation areas, little use has been made of its development in mapping metal distributions (Tuddenham and Lyon, 1959), and zoning in mineral deposits. In the present study 12 chlorites from wall rocks in mineralised sections, and 6 from non-mineralised sections, were studied, using X-ray diffraction techniques to identify them and to determine any differences which might be present between the different sections. Eight of the chlorites from the mineralised sections and 3 from non-mineralised ones were also subjected to infra-red absorption spectroscopy to discover any differences that might be present. Of the chlorites from mineralised sections 11 were largely from materials associated with pyritic and chalcopyritic mineralisation and in one case with sphaleritic mineralisation (sample IM 9/269).

5.2 X-ray diffraction studies

Powder samples used were either obtained from rock chips which were ground in a tungsten carbide mill or directly from the core samples using a vibrating needle.

Diffraction patterns were obtained on a Phillips Norelco X-ray diffractometer, with Ni filtered CuK radiation, and quartz as an The measured 'd' spacings of the chlorites are internal standard. given in Tables 35 to 40. It was noticed that, while there is a variation in chlorite species from place to place in the case of the mineralised sections, in general there was no variation in specimens from the nonmineralised sections. A variation in chlorite species was also noticed in mineralised sections from the same bore hole (bore holes 36A and IM 6) (Tables 35, 36 & 38 to 40). Diabantite, clinochlore and grochauite varieties of chlorite were found mainly associated with pyritic mineralisation with some chalcopyrite and sphalerite. Ripidolite was found associated with pyrite and chalcopyrite, and aphrosiderite with pyrite. Chlorite 1b species was found in all the non-mineralised sections Comparison of the chlorites at Parys Mountain with the studied. classification of the chlorites given by Hey (1954) as in Fig. 20 shows

that they are closely related varieties in terms of Si, total iron and Fe /(Fe + Mg). These different varieties of chlorites which have slightly different compositions probably are the result of the wall rock alteration associated with epigenetically formed sulphides. The differences may have been caused by the proposed secondary hydrothermal sulphide mineralisation rather than by the early sedimentary pyrite mineralisation. Determination of composition of chlorites in terms of major and trace elements and the identification of the species by X-ray study on a greater number of samples would be a useful investigation to find whether the above observation is localized or whether it is a general feature with the mineral deposits at Parys This is particularly important in establishing the Mountain. relative ages of mineralisation and metamorphism because premetamorphism chlorites would likely be destroyed.

5.3 Infra-red studies

Specimens used were 11 chlorites directly recovered from core samples and free from other minerals such as quartz. These were subjected to infra-red absorption spectroscopy, using the technique described in Chapter 3, and the spectra obtained were compared with those obtained by Tuddenham and Lyon (1959). They all fall under group 1 of the classification proposed by the above authors in that each spectrum has one strong absorption band in the wave length region between 9.3 and 11.0 microns and two to three clearly visible absorption bands between 2.6 and 3.0 microns (Fig. 21). It was, however, not possible to distinguish the chlorites from mineralised and nonmineralised sections because no significant differences in absorption patterns were seen.

CHAPTER 6

DISCUSSION AND CONCLUSIONS

6.1 Discussion

The mineralogical, textural and geochemical features discussed in the previous chapters can be used to add to discussion of the metallogenesis of these sulphide minerals. Interpretations of mineralisation should account for (a) Source and availability of various essential and trace elements, (b) Mode of transportation and availability of sites for precipitation or deposition (environment of formation), (c) Genetic relationship with the host rocks, (d) Post depositional characteristics. These are discussed below for Parys Mountain in the light of information derived in this study.

6. 1. 1 Source and availability of elements

As outlined in Chapter 2, the Parys Mountain deposits can be considered as stratiform type based on field, megascopic and mineralogical characteristics. These stratiform deposits, because of a close association with a volcanic succession, and generally having a Co:Ni ratio of > 1, are thought to be related to volcanism. Hutchinson (1973) defined volcanogenic sulphide deposits as strata bound lenticular bodies of massive pyrite mineralisation, containing variable amounts of chalcopyrite, sphalerite and galena in layered volcanic rocks. They are believed to have been formed subsequently by volcanic fumarolic activity which occurred periodically during volcanism. The Parys Mountain deposits have close similarities to the Type II of Hutchinson (1973), in metals, volcanic rocks, volcanic activity, tectonic position and geological age.

Hutchinson Classification Type II is as follows :-

Type II	Pb-Zn-Cu Pyrite	
Associated volcanics	Intermediate to felsic, calc-alkaline volcanic suites; andesite, dacite-rhyolite tuff etc.	
Type of volcanism	Felsix centres of explosive, Pyroclastic and ignimbritic activity. Subaqueous to subaerial.	
Associated Epiclastic predominates sediments		
Tectonic position	Later eugeosynclinal orogenic stage	
Examples	Mt. Isa (Proterozoic) New Brunswick (Ordovician)	

Petrological studies by Thanasuthipithak (1974) has established the presence of all these characteristics at Parys Mountain and that the volcanics belong to an orogenic-calcalkaline magma series formed in a continental margin/ island arc environment.

That many of the world's economically workable sulphide deposits have been derived from volcanic processes is firmly established by many workers throughout the world. Detailed discussions of individual deposits are given in Stanton (1960), (1965), Hutchinson (1965), Krauskopf (1967), Schermerchorn (1970), Ferguson and Lambert (1972), Lusk (1972), Goosens (1972), Constantinove and Govett (1973), Sillitoe (1973), Strauss and Madel (1973), Roberts (1975), Thurlow et al., (1975), Spence and Spence (1975), Spence (1975), Jenks (1975) and Angus and Davis (1976).

6.1.2 Environment of formation

Many of the volcanogenic deposits quoted above, though related to volcanism are thought to have been formed by an interplay of volcanic-sedimentary or volcanic-hydrothermal processes. It has to be postulated that there existed a sedimentary volcanic basin at Parys Mountain in which thick volcanic products accumulated. The sulphide metallic phases, mainly iron sulphide from volcanic emanations, were also deposited along with the volcanic successions within certain restricted environments. Thanasuthipithak (1974) called such a process 'synsedimentary-exhalative'. However, as pointed out by Anderson and Nash (1972) the word 'exhalative' implies vapour transport and there is no evidence at Parys Mountain that the metals were carried in the vapour phase. Alternative terms given by Anderson and Nash (1972) are volcanogene-sedimentaire, volcano-sedimentaire, and submarine volcanic sedimentary. The term volcanogenic-sedimentary (Ilavsky 1976) is perhaps the most suitable for the Parys Mountain mineralisation.

However, microscopic features discussed in Chapter 2 suggest that the mineralisation at Parys Mountain was not a single simple episode. Although much of the copper ore has been removed by previous mining operations, its paragenesis is clear and it is only the pyritic mineralisation that has obvious conformable or syngenetic features. The leadzinc sulphides and sulpho-salts are later and they apparently show features of deposition from a multi-component hydrothermal system, though they could have resulted as complex substitutions in other sulphides. Where

deposition has occurred from such a system the mobility of ore metals is in decreasing order as experimentally given by Barnes and Czemanske (1967) Pb-Cu-Zn-Sn-Ni-Fe-Co; (this coincides with the general paragenesis). All these epigenetic minerals were formed in fractures, and interstitial infillings and replacements of the earlier pyritic mineralisation.

6.1.3 Relationship with the host rocks

As outlined above the pyritic mineralisation is reported to be conformable and syngenetic with the host volcanic succession. Epigenetic mineralisation though, complex mineralogically, shows some crosscutting features consistent with later formation or remobilisation, presumably during metamorphism.

6.1.4 Post depositional characteristics

The earlier pyritic mineralisation shows post depositional charactieristics mainly the evidence of deformation and remobilisation. These are the cataclastic textures, fracturing recrystallisation of framboid pyrites, etc. which became vacant sites for the subsequent epigenetic mineralisation. Either both these phases, or the earlier pyritic mineralisation, were remobilised during the Caledonian orogeny (Thanasuthipithak, 1974).

Both in the earlier syngenetic mineralisation and later hydrothermal deposition the source for the metallic sulphide is believed to have been volcanic. This repetition of ore formation is not uncommon in volcanogenic sulphide deposits.

It can therefore be concluded that the Parys Mountain mineralisation is consistent with a volcanogenic-sedimentary deposit of a stratiform type later enriched by hydrothermal processes. This deposit was later remobilised during the Caledonian orogeny to produce many of the crosscutting features.

6.2 Summary of conclusions

In the present study of mineralogy and geochemistry of Parys Mountain sulphides and sulpho-salt minerals, the following conclusions are reached:

1) The mineralogy, paragenesis and association with a volcanic succession of rocks allow the interpretation that the deposit is both stratiform and conformable associated with volcanism. An earlier synsedimentary pyritic mineralisation has been enriched by an epigenetic

complex sulphide and sulpho-salt mineralisation.

2) The deviations in composition of the major sulphide minerals pyrite, chalcopyrite, sphalerite and galena from their stoichiometry are interpreted as due to presence of appreciable quantities of trace elements and complex substitutions.

3) Pyrite and chalcopyrite have relatively low trace element content and they mainly contain Co, Ni, Ba, As, Pb, Zn, also Cu in pyrite. The Co/Ni ratio in pyrites is generally > 1. This is interpreted to indicate that the deposits are related to volcanism.

4) Sphalerite and galena are rich in As, Ag, Bi, Sb contained in solid solutions.

5) The iron content in sphalerite varies widely, and this is interpreteted as being due to solid solution.

6) Measurements of cell edge of sphalerites, using both electron diffraction and X-ray diffraction techniques, showed it to vary linearly with iron content. Electron diffraction is thus an alternative method for measuring the iron content of sphalerites.

7) There is a good relationship between iron content and microhardness in sphalerite. However, this was found not to apply to the other sulphides, namely pyrite and chalcopyrite.

8) The chlorite group minerals, diabantite, ripidolite, grochauite, and aphrosiderite were formed in wall rocks at the contacts of the mineralisation. Chlorite 1b species was found in non-mineralised sections.

APPENDIX I

SAMPLE SELECTION AND PREPARATION

All the sulphide samples studies were taken from the diamond drill cores including some previously studied by Thanasuthipithak (1974), and only fresh looking material was selected. Two types of samples were required: a) sections of mineralised parts for polishing (reflected light microscopy, reflectivity, microhardness, and electron probe measurements); b) powdered sulphide minerals for chemical analyses, infrared and differential thermal studies. In the latter case, only mineral grains which were sufficiently coarse (average size >about one mm) to be liberated with considerable amount of purity were selected. More finely grained minerals were analysed by electron probe on polished sections.

Sulphide mineral grains were liberated directly from the core specimen using an electrically vibrating needle. They were then thoroughly washed using acetone and distilled water and dried. They were examined under a binocular microscope and impurities were removed by hand. In some instances a heavy-liquid technique was used (Muller, 1967) to separate less coarse grained sulphides from fine grained gangue. In some cases the core chip was polished on a coarse grade abrasive paper to allow grain boundaries to be clearly seen before the grain was liberated. Most of the sphalerite samples were recovered in this way.

A certain amount of mineral impurity was, however, unavoidable. This was especially true of sphalerites and pyrites with some chalcopyrite exsolutions. Also some very fine grained gangue inclusions in sulphide minerals could not be separated.

APPENDIX 2

LABORATORY METHODS

2.1 Atomic Absorption Spectrophotometry (A.A.S.)

Solutions for A.A.S. were prepared by dissolving the sulphide samples in concentrated Hcl and concentrated HNO3 (Strasheim et al. 1960; in Angino and Billings, 1972). About 200 mg of powder was weighed accurately into a conical flask and 8 to 10 ml of concentrated Hcl was added. This was allowed to stand for approximately one hour for the initial reaction to take place before adding 8 to 10 ml of concentrated HNO3. This method was used in preference to direct use of aquaregia to prevent basic nitrates being formed on the surface of the sulphide grains (Dolezal et al. 1968, in Ghosh, 1972). After adding HNO₂ some 3 hours were allowed for a clear solution to form. The solutions were stirred and then transferred to 150 or 250 ml volumetric flasks, made up to volume with double distilled water, and quickly transferred to polythene bottles. The solutions were analysed within three days of preparation because elements present in low concentrations are lost by absorption on to the sides of the bottle, if stored for longer periods.

Standards were prepared from stock solutions containing 1000 ppm of the element in each case. These stock solutions, except Mo were supplied from BDH Chemicals Limited. The Mo standard was prepared by dissolving 1.840g of ammonium paramolybdate ($(NH_4)_6 Mo_7O_{24} 4H_2O$)) in 1 litre of 1% ammonium hydroxide (NH_4OH), for 1000 ppm concentration.

Analyses for Cd, Co, Cu, Fe, Ni, Pb, Te and Zn were done using an air acetylene flame, and Mo and Ba were determined using a nitrous oxide acetylene flame. An integrated period of 0.5 seconds was allowed for each aspiration. At the beginning of each run, standard solutions were aspirated starting from lower concentration to higher concentration, followed by the sample solution. At least 4 readings were taken for each sample solution. The mean of these concentrations was taken and from it the weight % in the sample was calculated. 2.2 Electron probe microanalysis

Analyses were done on carbon coated polished sections and in some instances on the sections mounted in conducting bakelite. The standards used were either pure metals/elements or compounds (Table 41).

Analyses were done using a Cambridge Microscan V with a constant accelerating potential of 15 kV, a sample current of 0.3 mA and a beam current of 0.05 mA. The crystals used were PET (Pentaerythritol) and LiF (Lithium fluoride). Both crystals were used because readings were obtained simultaneously in two separate channels thus allowing two elements to be determined simultaneously. Counting rates were measured for intervals of 10 seconds. Peak intensities for various elements determined in each grain were read at least twice, and the mean taken. Similarly background readings also were taken at least twice.

A dead time correction was applied for counts more than 2000/ second, though for count rates below 10,000 counts /second, the error is considered to be less than 1% (Adler, 1970). Dead counts were read from the graph supplied and were added to the measured counts. The concentration after applying dead time was calculated using the formula

 $Wt \% = \frac{Peak-Background + Dead time (counts/second) of specimen x C}{Peak-Background + Dead time (counts/second) of standard}$ where C is the weight percentage of the element in the standard.

The measured concentrations were subjected to corrections described by Long (1967), Adler (1970). Corrections for Atomic Number (Z), Fluorescence and Absorbance, were made using a computer programme produced in the Department of Metallurgy, University of Aston. 2.3 Reflectivity

Measurements of reflectivity were made on a Reichert Zetopan Ore Microscope equipped with a reflex microphotometer (Singh, 1965). Comparative quantitative measurements were made against Tungsten Titanium Carbide (WTiC) and silicon carbide (SiC), standards with reflectivity being calculated from the formula

 R_{λ} % of Mineral = $\frac{\text{Deflection Value of Mineral}}{\text{Deflection Value of Standard}} \times K$

where K = calibrated reflectivity % of standard

 λ = monochromatic wave length

R% = Reflectivity percentage

All measurements unless otherwise specified were made at a wave length of 589 nm in air. A glare correction was applied before calculating R% to compensate for reflections from the back of the objective (Bowie and Henry, 1964).

2.4 Indentation microhardness

Measurements of microhardness were made with a Leitz Durimet Microscope with an attached indenter. Varying loads of 50, 200 and 300 gm were applied to obtain a sharp indentation and an indentation time of 30 seconds was allowed for each specimen. The diagonals of the projected impression on the polished surface were measured using a travelling micrometer ocular. The hardness number was calculated using the formula

$$VHN = \frac{1854.4 \text{ x L}}{d^2}$$

where VHN =' Vickers microhardness number in kg/mm²

L = Load applied

d = Indentation diagonal

2.5 Infrared Absorption Spectroscopy

Samples for infrared studies were prepared by potassium bromide pellet method (Tuddenham and Lyon, 1959; and Lyon, 1967). Spectra were obtained on a Perkin-Elmer 237 Grating Infra red Spectrophtometer in the wave number region 600-4000 cm⁻¹. 2.6 Differential Thermal Analysis

Analyses were made on samples of pyrite and chalcopyrite on a Dupont-900 Differential Analyser using a sample preparation technique described by McLaughlin (1967). Glass beads were used as standard. A heating rate of 50°C/minute was applied, with the scale for chart paper of 100°/inch.

Sulphides contain corrosive elements such as S and As (Kopp and Kerr, 1957). Special techniques of diluting the samples with alumina to avoid corrosion by S or As were not employed because the maximum temperature reached was only 600°C.

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Aspects of structure and bonding in the iron

le 1 Stratigraphic sequence at Parys Mountain

	(Hawkins, 1966)		(Thanasuthipithak,	1974)
Age	Lithology	Thickness	Lithology	Thickness
Silurian	Grey shales with graptolites	530	Dark-grey to black slates	
Ordovician	Fine-grained sediments with a few occurrences	600 ft	unconformity ?	
	of tuff in felsitic zone of silicification		Rhyolitic volcanic rocks	200m
			Grey to greenish-grey slates	600m
	Parys shales	720 ft		
	Black shales * Grey shales weather- ing to brown and green			
	Grey micaceous shales with beds of sedimen- tary breccia	1200 ft		
	Carmel I	Head Thru	st	
Pre- Cambrian	Amlwch beds Pale-green phyllites		Chlorite schists, micaceous and granitoid gneisses, quartzitic gneisses.	

* Note: These are the Parys Green Shales of Greenly

Table 1

Table 2. Classification of Ore Types.

Author	Mineralisation Type	Host rock or matrix	Mineralogy Major Minor		Example	
Wolfenden (1967) (in Thanasu- thipithak 1974)	Copper ore	Northern rhyolites and its contacts	Pyrite Chalco- pyrite	Sphalerite Galena	Great ore Opencast lode, Hill Side open case, Black rock lode	
	Bluestone ore	Dacite, silicified silurian slates and in rhyolites in contact with Ordovician slates	Argent- iferous galena, Sphalerite	Chalco- pyrite Pyrite e	Clay shaft lode Black rock lode	
	Pyritic ore	Within rhyolitic rocks	Pyrite	Chalco- pyrite	Golden venture lode Carreg-y-doll lode, Middle lode, South branch lode North dis- covery lode	
	Low grade Galena-Sphalerite ore	Disseminated in Orodovician slates	Calena Sphalerite	e	Not mined be- cause of low grade	
Wheatly 1971a	Pyritic zone	Black shale (Ordovician slates)	Pyrite Chalco- pyrite	Pyrrhotite Sphalerite Galena	Disseminated in shale units	
	Siliceous zone	Shales and tuffs (silicified Silurian slates and rhyolitic tuffs + siliceous sinter)	Pyrite Chalco- pyrite Sphaler- ite Galena	Pyrrhotite Tetra- hedrite Bismuth- inite Native Bismuth	Carreg-y-doll, Golden Venture lode Charlotte lode, North discovery lode.	
	Lead-zinc zone	Shales and tuffs	Sphaler- ite Galena Pyrite Chalco- pyrite	Tetra- hedrite Bournon- ite	Morfa-dee and Black rock lodes, clay shaft lodes (Bluestone)	
	Veins	Shales, tuffs and lavas	Galena, Sphaler- ite Chalco- pyrite	Tetra- hedrite	Great cross Cowis Carreg-y-doll lode.	

Ore Type	Form	Description	Minerals Major Minor	Grain size/ dmsns	Matrix/ host matrix
Pyritic ore	a) Layered sulphide form	Continuous and dis- continuous layers conformable with the quartz and chloritic matrix parallel to foliation of the host rock. Some layers have a lenticular shape, major lens made up of smaller lenses giving rise to en- echelon arrangement	Pyrite Sphal- chal- erite copyrite	Thick- ness of the layer 2mm- l cm.	Quartz- chlor- itic rocks
	b) Disseminated form	Well developed euhedral and sub- hedral pyrite grains disseminated in host rock.	Pyrite Chal- co- pyrite	-2 mm	Black shale, Dacite
Copper ore	a) Massive form	Irregular, coarse granular inter- growths	Pyrite Sphal- Chal- erite co- Galena pyrite	to	is the main matrix
	b) Vein and stockwork form	Intersecting con- tinuous and dis- continuous veins of chalcopyrite	Chal- Pyrito co- pyrite	Aver- age width of the vein about 5 mm	Sili- ceous rocks
Blue- stone ore	Fine-grained	Microscopic gran- ular intergrowths	Sphal- Sulpho erite salts Galena Chal- co- pyrite Pyrite	o- Aver- age size Z 1 mm	Shales and tuffs (Sili- ceous/ sinter)

Table 3 Summary of some mineral forms at Parys Mountain

Name	Form	Microhardness range (Kg/mm ²)	Reflectivity % range at 589nm (air)	Special association
Pyrite	Euhedral, subhedral anhedral and fram- boidal	1027 - 1483	45.9 - 56.5	Euhedral pyrite with rutile
Chalco- oyrite	Anhedral, allotrio- morphic	174 - 221	38.2 - 42.6	
Sphaler- te	Anhedral, rounded and as intergrowths with chalcopyrite	148 - 240	16.3 - 22.1	
Galena	Anhedral, sometimes intergrows with sphalerite	61 - 201	37.3 - 41.3	
Arseno- oyrite	Euhedral to subhedral			
⁹ yrrho- ite	Anhedral, irregular			
Γetra- nedrite- Γennantite	Fracture and interstitial infillings mainly in pyrite	279- 328	34.3 - 36.5 (Tetra- hedrite) 29.5 - 31.7 (Tennan- tite)	Pyrite
Bourn- mite	Inclusions - white in colour and anisotropic	-	-	Sphalerite
vead ulpho- alts	Inclusions and intergrowth with mainly sphalerite and galena		39.3 - 43.5	Sphalerite and galena
Bismuth sulpho- salts	Interstitial infillings in pyrite, sphalerite	-		

Table 4	Table	showing	the	ore	minerals	at	Pary	s Mountain
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P	rimary			Secondary	
Texture	Description	Mineral/s	Texture	Description	Mineral/s
1) Panidio- morphic	Euhedral grains	Pyrite	1) Cataclastic	Fractures and other deform- ative features are present	Pyrite
2) Framboid- al	A spherical or subspherical aggregate of pyrite granules or microcrysts	Pyrite	2) Vein filling	A distinct and narrow filling of pyrite in the matrix in the form of a vein	Pyrite
3) Allotrio- morphic granular	Irregular and anhedral grains	Pyrite Chalco- pyrite Sphaler- ite Galena & sulpho- salts	3) Inter- stitial fillings	Later formed minerals are present in the interstitial spaces of the previously formed grains	Sphaler- ite in Pyrite Tetra- hedrite - Tennan- tite in Pyrite
4) Mutual intergrowths	The two minerals are usually inter- grown with no distinct boundary between them		4) Replace- ment	Later formed minerals re- place previously formed minerals along peripheries	Chalco- pyrite replaces pyrite
			5) Recryst- allisation and homo- genisation	An aggregate of framboidal or euhedral grains homo- genised at the centre, retaining their respective out- lines at the periphery	Pyrites

Table 5 Summary of Textures shown by ore minerals at Parys Mountain

Table 6 Simplified Paragenetic diagram of Primary Sulphides and Sulpho-salts at Parys Mountain

Time	· · · · · · · · · · · · · · · · · · ·
Rutile	
Euhedral Pyrite	
Anhedral, framboidal Pyrite Vein-filling Pyrite	
Pyrrhotite ——	
Arsenopyrite	-
Chalcopyrite -	
Sphalerite	
Galena	
Tetrahedrite - Tennantite Bournonite	
Lead sulpharsenides	
Bismuth sulpho-salts	

Name of the No. technique samp			Minerals		Information
Reflected Light Microscopy	58		Sulphides and Sulpho-salts		Identification, Des- cription and Paragenesis
Reflectivity	71 grains	a)	Sulphides	a)	Plotting of spectral reflectivity profiles.
		ь)	Sulpho- salts	ь)	For identification
Microhardness	56 grains		Sulphides		Quantitative measurement
X-ray diffraction (Powder Camera)	17		Sphalerite		Unit cell measurement
Electron diffraction	12		Sphalerite		Unit cell measurement
Atomic Absorption spectrophotometry	55		Sulphides		Major and trace element analysis
Electron Probe Microanalysis	74		Sulphides and Sulpho-salts		Major and trace element analysis
Infra-red absorption spectroscopy	13		Sulphides		To compare with published data and to see if related to composition
Differential thermal analysis	11		Pyrite, Chalcopyrite		To compare with published data and to see if related to composition

Table to show the techniques employed and the nature of information obtained

Table 7

Explanation for Tables 8 - 12

A. A. S.	Atomic Absorption Spectrophotometry	
ЕРМА	Electron Probe Microanalysis	
A	Anhedral	
F	Framboidal	
Е	Euhedral	
S	Subhedral	
х	Not determined	
XX	Looked for but not detected	
tr	traces	

Results of EPMA are quoted in %

Results of A. A. S. are quoted in % for essential elements, and in parts per million for trace elements. Where EPMA and AAS analyses have both been done on the same sample, the analyses for essential elements are those done by EPMA and the trace elements unless quoted in % are those analysed by A.A.S.

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Te	49	52	30	133	15	XX	XX	23	XX	68	xx	31	55	88	24	27	xx	xx	128	132	XX	1
Pb	107	208	XX	38	429	1300	808	535	411	390	xx	595	500	873	536	485	293	316	xx	xx	361	
Ni	xx	46	400	37	47	349	158	253	16	26	541	62	208	84	969	556	50	xx	xx	xx	59	
Mo	xx	хх	xx	xx	xx	xx	46	37	193	241.	256	39	xx	13	19	168	хх	442	xx	xx	xx	
Cu	2873	1025	300	335	760	650	12715	454	348	137	380	540	2575	120	568	957	479	2487	2875	1563	340	
°C	39	99	1900	222	683	742	125	340	206	xx	455	590	143	105	583	958	487	795	36	66	269	
Cd	xx	хх	хх	128	216	xx	105	16	76	xx	хх	хх	xx	хх	33	XX	хх	45	XX	хх	275	
Ba	xx	386	235	645	761	хх	171	108	150	349	148	205	103	xx	267	105	112	ХХ	394	268	827	
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Jampte Method 1ype of Number grain	A15/911	A15/916	A15/924	A15/928	A15/935	A15/953	A15/971	A15/980	A15/1193	IM6/516' 6''	IM6/770	IM6/1044' 8"	IM6/1101	IM6/1108	IM6/1160	IM6/1179	IM6/1231	IM6/1393	36A/1611	36A/1617	32-1108	0011 00
No. P	1 A	2 A	3 4	4 1	5 A	6 A	7 A	8 A		10 IN	11 IN	12 IN	13 IN	14 IN	15 IN	16 IN	17 IN	18 IN	19 36	20 36	21 32	~~ ~~

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Te	x	xx	62		xx	×	×	×	39	36	×	169	×	×	×	×	×	×	×	×	×	×	×
РЪ	697	804	490	305	152	ħ	1300	ħ	156	589	ħ	440	ţ	ħ	ħ	ħ	tr	xx	xx	xx	tr	xx	tr.
Ni	133	50	19	185	563	ħ	ħ	ħ	552	276	ħ	410	ħ	tr	tr	tr	tr	tr	xx	xx	xx	xx	xx
Mo	120	xx	xx	xx	xx	tr	tr	tr	230	68	Ħ	100	ţ	ħ	XX	xx	XX	xx	xx	xx	xx	XX	tı
Cu	200	210	9	_	ţ	ħ	0.12	0.10	2875	1260	0.11	Ħ	0.12	tr	tr	ħ	tr	ħ	ţ	tr	ţ	ħ	ħ
ů	136	789	36	2075	268	tr	ħ	ħ	83	160	Ŀ	69	ħ	ħ	Ħ	ħ	ħ	0.12	ħ	H	5	ħ	H
Cd	xx	хх	xx	xx	320	ħ	хх	4	260	249	ħ	180	0.10	0.13	0.11	tr	0.10	tr	tr	ţŗ	ţ	ţ	tr
Ba	хх	130	xx	125	хх	×	×	×	хх	×	×	195	×	×	×	×	×	×	×	×	×	×	×
As	×	×	×	×	0.21	0.11	5	ħ	×	5	t	×	tr	tr	tr	tr	tr	tr	tr	tr	ħ	ţ	xx
Total				98.61		99.44	98.50	98.92		98.16	98.43		98.64	99.70	98.07	98.17	99.19	99.07	100.44	98.06	98.43	100.64	99.56
S	×	×	×	53.97	55.38	52.88	53.61	54.62	×	54.97	54.82	×	54.53	54.17	53.34	53.28	52.35	54.69	55.07	53.34	53.66	54.68	54.37
ы	48.25	47.65	45.91	44.64	43.60	46.56	44.89	44.30	43.75	43.19	43.61	44.85	44.11	45.53	44.73	44.89	46.84	44.38	45.37	44.72	44.77	45.96	45.19
Type of grain	A	A	S	A	A	S	A	A	A	A	A	S	A	A	A	A	A	A	Ŀı	ц	£4	ц	A
Method Type of grain	AAS	=	=	EP MA & AAS	=	EPMA	=		AAS	EPMA & AAS	EPMA	AAS	EPMA	EPMA	=	=	=			=			
Sample Number	HMA/1510	H ₄ 3A/1837	A14/1534	H14/186	H14/265	IM9/264	IM9/269	IM9/285	IM9/288	1M9/2921	IM9/294' 6"	IM9/364' 6''	M10/1512	M10/1540	M10/1548	M10/1589	M10/1599	M10/1608	H4/456	H4/464	H4/465	H4/474	C4/960
SI No.	23 I	24 I	25 /	26 I	27 1	28 1	29 1	30 1	31]	32]	33]	34	35	36	37	38	39	40	41	42	43]	44	45 (

	Table 9	Table showing the essential and trace element composition of Chalcopyrite	ng the es	sential	and trac	e elemen	ut com	positio	n of C	halcop	yrite	1					
SI. No.	Sample Number	Method	Cu	Fe	S	Total	As	Ba	Bi	Cd	°C	Mo	IN	РЪ	Te	Zn	
1	A15/920	AAS	34.37	31.16	×		×	924	×	xx	133	28	41	XX	xx	680	-
2	A15/965	AAS	36.11	29.36	×		×	276	×	xx	60	140	12	325	62	395	
3	A15/1193	EPMA & AAS	35.05	32.37	34.20	101.62	ħ	576	X	250	405	510	500	155	55	2140	
4	M10/1410	AAS	34.59	29.92	×		×	1653	×	xx	440	260	069	410	xx	1790	
5	M10/1521	EPMA & AAS	34.73	27.73	35.96	93.42	0.27	1385	x	1	710	Ħ	726	x	74	1895	
9	M10/1589	EPMA	35.81	28.15	36.15	100.11	tr	×	0.13	tr	ţ	xx	5	ħ	×	tr	
2	A14/1534	AAS	33.87	30.98	×		×	260	×	180	275	405	122	820	192	1388	
80	IM6/762		33.70	30.12	×		×	742	×	235	344	280	215	285	xx	969	
6	IM6/1392		32.40	30.34	×		×	210	×	446	486	85	190	1045	xx	851	
10	IM6/1393	EPMA	33.66	31.19	34.85	99.70	0.12	×	хх	tt	tr	ţ	H	ħ	x	ţŗ	
11	H4/464	EPMA & AAS	34.64	30. 15	36.58	101.37	0.11	xx	5	211	410	300	510	ħ	XX	345	
12	H4/465	EPMA	34.72	25.80	36.49	97.01	t	×	tr	H	tr	tr	ħ	ţ	×	2100	
13	H4/491	EPMA & AAS	34.54	27.75	36.61	93.90	4	165	0.24	198	625	Ħ	446	656	xx	911	
14	H4/581	EPMA	35.19	32.12	33.29	100.60	ħ	×	t	tr	tr	xx	ħ	ţ	×	0.38	
15	IM9/264		32.07	29.25	36.93	98.25	tr	×	ħ	xx	tr	XX	ħ	Ħ	×	0.27	
16	IM9/269		37.09	28.76	35.61	101.46	t	×	0.13	xx	5	X	Ħ	5	×	0.56	
17	H14/171	AAS	32.27	30.69	×	•	×	368	×	98	290	xx	1060	316	x	1100	
18	H14/186	EPMA	35.25	32.81	32.81	100.54	XX	×	хх	다	tr	xx	ħ	ħ	×	0.47	
19	H43A/855	AAS	35.25	28.55	×		×	1526	×	xx	236	xx	xx	313	xx	1295	

Meitod			Lable 10		lable	snowing	lable snowing the essential and trace element composition of Sphalerite	ntial a	nd trac	e elem	ent con	ipositio	ide io n	lalerite	-				
FPMA & 58.99 4.21 35. 21 98.47 0.12 2189 tr 0.17 206 2980 tr xxx xxs 1468 105 mAS 53.01 13.77 x xx xxx	Sample number		Method	Zn	ъ	S	Total	As	Ba	Bi	Cd	°	Cu	Mn	Mo	Ni	Pb	Te	Type
	H4/456		EPMA & AAS	58.99	4.21	35. 27	98.47	0.12	2189	ħ	0.17	206	2980	ħ	xx	xx	1468	105	Exsolutions of Chalco- pyrite present
AAS 53.01 13.77 x 138 x x 128 x <	H4/460			64.74		34.63	100.49	0.10	7222	ħ	0.12	668	15360	tr		433	1286	xx	
EPMA 61.70 1.16 55.59 98.45 tr x 0.11 tr x w 0.11 x " 56.12 9.1235.83 101.07 tr x 0.13 tr 2.28 0.10 tr x xx	H4/467		AAS	53.01	13.77			×	1383	×	876	296	3157	×		385	315	16	
" $54, 87$ $12, 47, 32, 23$ $99, 57$ tr x 0.13 tr 2.28 0.10 tr 20.14 xx 0.14 xx " $56, 12$ $9, 12$ $35, 33$ $101, 07$ tr x 0.14 xx xx 0.12 xx xx <td>H4/473</td> <td></td> <td>EPMA</td> <td>61.70</td> <td></td> <td>35.59</td> <td>98.45</td> <td>tr</td> <td>×</td> <td>xx</td> <td>0.15</td> <td>ħ</td> <td>0.33</td> <td>xx</td> <td>xx</td> <td>xx</td> <td>0.11</td> <td>×</td> <td></td>	H4/473		EPMA	61.70		35.59	98.45	tr	×	xx	0.15	ħ	0.33	xx	xx	xx	0.11	×	
	H4/474			54.87	12.47	32.23	99.57	tr	×	xx	0.13	tr	2.28	0.10	0.12	xx	0.14	×	
FPMA & 51.66 14.21 35.28 101.17 tr 174 0.11 0.28 tr 4600 tr 2100 tr 286 149 AAS 64.31 1.66 34.33 100.23 tr tr<	H4/481			56.12		35.83	101.07	tr	×	0.14	0.13	tr	0.26	xx	0.12	хх	xx	×	
	H4/491		EPMA & AAS	51.68	14.21	35.28	101.17	ħ	174	0.11	0.28	ţ	4600	\$	2100	ħ	286	149	
" 60.43 2.75 37.08 100.26 tr x tr 0.11 tr 0.30 tr tr </td <td>IM9/283</td> <td></td> <td>EPMA</td> <td>64.31</td> <td>1.65</td> <td>34.33</td> <td>100.29</td> <td>tr</td> <td>×</td> <td>tr .</td> <td>tr</td> <td>tr</td> <td>0.65</td> <td>ţ</td> <td>tr</td> <td>tr</td> <td>0.12</td> <td>×</td> <td>=</td>	IM9/283		EPMA	64.31	1.65	34.33	100.29	tr	×	tr .	tr	tr	0.65	ţ	tr	tr	0.12	×	=
EPMA & 61.84 2.86 35.67 100.37 tr 108 tr 388 tr 2870 tr ASS 11 <t< td=""><td>IM9/285</td><td></td><td></td><td>60.43</td><td>2.75</td><td>37.08</td><td>100.26</td><td>tr</td><td>×</td><td>tr</td><td>0.11</td><td>tr</td><td>0.30</td><td>t</td><td>tr</td><td>tr</td><td>ħ</td><td>×</td><td></td></t<>	IM9/285			60.43	2.75	37.08	100.26	tr	×	tr	0.11	tr	0.30	t	tr	tr	ħ	×	
	IM9/285'2"	5	EPMA & AAS	61.84	2.86	35.67	100.37	ħ	1088	5	388	ħ	2870	ħ	ħ	ħ	ħ	×	=
" 62.07 5.09 33.94 101.10 tr x tr xx x x x <	1M9/2921611	9	EPMA	62.66	1.59	35.19	99.44	0.12	×	tr	tr	xx	0.18	ħ	хх	xx	ħ	×	
EPMA & 61.87 2.96 36.15 100.98 tr 569 tr 215 135 136 365 340 85 260 AAS 54.56 11.58 35.61 101.75 xx xx 0.12 xx 0.22 tr xx 0.12 x EPMA 52.11 10.65 38.16 100.92 tr xx 0.12 tr xx xx 0.12 xx xx xx 0.12 xx xx 0.12 xx xx xx 0.12 xx xx 0.12 xx xx </td <td>'49/294'</td> <td></td> <td></td> <td>62.07</td> <td>5.09</td> <td>33.94</td> <td>101.10</td> <td>ţ</td> <td>×</td> <td>Ħ</td> <td>ħ</td> <td>хх</td> <td>0.40</td> <td>t</td> <td>xx</td> <td>xx</td> <td>ħ</td> <td>×</td> <td>=</td>	'49/294'			62.07	5.09	33.94	101.10	ţ	×	Ħ	ħ	хх	0.40	t	xx	xx	ħ	×	=
EPMA54.5611.5835.61101.75xxxxx0.12xx0.22trxxxx0.12xEPMA52.1110.6538.16100.92trxxx0.14tr0.10trxxxxtrx"62.783.7332.9799.480.37xxx0.110.10trxxxxtrx"62.783.7332.91100.69trxxx0.12trtrtrtrtrx"53.8112.5635.58101.95trxtrtr1.080.13trxxx"58.562.3938.6699.61trxtrtrtrtrtrxAAS57.912.19x-x168x228886330x384trxAAS57.2611.7832.98100.02trxtrtrtrtrxtrxAAS57.2611.7832.98100.02trxtrtrtrtrxtrxxTANA55.2611.7832.98100.02trxtrtrtrtrxtrxxtrxxTANA55.2611.7832.7733.74100.33tr413trtrtrtrtr <td< td=""><td>1M9/294161</td><td>9</td><td>EPMA & AAS</td><td>61.87</td><td>2.96</td><td>36. 15</td><td>100.98</td><td>ţ</td><td>569</td><td>ħ</td><td>215</td><td>135</td><td>1088</td><td>xx</td><td>565</td><td>340</td><td>85</td><td>260</td><td></td></td<>	1M9/294161	9	EPMA & AAS	61.87	2.96	36. 15	100.98	ţ	569	ħ	215	135	1088	xx	565	340	85	260	
EPMA52.1110.6538.16100.92trxxx0.14tr0.10trxxxxtrxx"62.783.7332.9799.480.37xxx0.110.10trtrtrtrxx"52.9110.8736.91100.69trxtrtrtrtrtrtrtrtrx"52.9110.8736.91100.69trxtrtr1.080.13trtrtrx"53.8112.5635.58101.95trxtrtrtrtrtrxtrx"58.562.3938.6699.61trxtrtrtrtrtrtrxxtrAAS57.912.19x-x168x228886330x384trtrxEPMA & 55.2611.7832.98100.02trxtrtrtrtrtrx19053EPMA & 63.822.7733.74100.33tr413trtrtrtrtrtrxtrxxx"52.8810.733tr413trtrtrtrtrtrtrxxtrxxxxxxxxxxx <t< td=""><td>IM6/1160</td><td>-</td><td>EPMA</td><td>54.56</td><td>11.58</td><td>35.61</td><td>101.75</td><td>xx</td><td>×</td><td>xx</td><td>0.12</td><td>хх</td><td>0.22</td><td>tr</td><td>хх</td><td>xx</td><td>0.12</td><td>×</td><td>No exsolutions</td></t<>	IM6/1160	-	EPMA	54.56	11.58	35.61	101.75	xx	×	xx	0.12	хх	0.22	tr	хх	xx	0.12	×	No exsolutions
" 62.78 3.73 32.97 99.48 0.37 x xx 0.11 0.10 0.13 tr tr tr tr x x " 52.91 10.87 36.91. 100.69 tr x tr 0.12 tr 2.75 tr tr x x " 53.81 12.56 35.58 101.95 tr x tr tr x tr xx	IM6/1392	~	EPMA	52.11	10.65	38.16	100.92	ţ	×	хх	0.14	tr	0.10	ħ	xx	xx	ħ	×	
" 52.91 10.87 36.91. 100.69 tr x tr 0.12 tr 2.75 tr tr xx tr x " 53.81 12.56 35.58 101.95 tr x tr tr tr tr tr xx tr	M10/1548	80	=	62.78		32.97	99.48	0.37	×	xx	0.11	0.10	0.13	ħ	ħ	ħ	ħ	×	Exsolutions present
" 53.81 12.56 35.58 101.95 tr x tr tr tr 1.08 0.13 tr xx tr x " 58.56 2.39 38.66 99.61 tr x tr tr tr tr tr tr x tr x tr xx tr x AAS 57.91 2.19 x - x 168 x 228 886 330 x 384 xx 190 53 EPMA \$ 55.26 11.78 32.98 100.02 tr x tr tr tr 0.47 tr tr xx tr 990 x	M10/1589	6		52.91	10.87	36.91.	100.69	ħ	×	H	0.12	tr	2.75	tr	ħ	xx	ħ	×	E
" 58.56 2.39 38.66 99.61 tr x tr tr tr tr tr tr x x tr x x tr x AAS 57.91 2.19 x - x 168 x 228 886 330 x 384 xx 190 53 EPMA 55.26 11.78 32.98 100.02 tr x tr tr tr 0.47 tr tr xx tr xx tr x EPMA & 63.82 2.77 33.74 100.33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	A15/971			53.81		35.58	101.95	tr	×	tr	tr	tr	1.08	0.13	ħ	. xx	ħ	×	
AAS 57.91 2.19 x - x 168 x 228 886 330 x 384 xx 190 53 EPMA 55.26 11.78 32.98 100.02 tr x tr tr tr tr tr xx tr	A15/1193		=	58.56		38.66	99.61	ħ	×	tr	ţ	tr	tr	ħ	Ħ	xx	ţ	×	No exsolution s
55.26 11.78 32.98 100.02 tr x tr tr tr 0.47 tr tr xx tr x 63.82 2.77 33.74 100.33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	A15/1194		AAS	57.91	2.19	×		×	168	×	228	886	330	×	384	xx	190	53	=
63.82 2.77 33.74 100.33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	27-145		EPMA	55.26	11.78	32.98	100.02	tr	×	tr	tr	tr	0.47	tr	ħ	xx	ħ	×	Exsolns pre-
	H14/265		EPMA &	63.82		33.74	100.33	tr	413	tr	1600	tr	4020	0.10	tr	tr	066	×	sent

Table showing the essential and trace element composition of Spha

able 1

Sample	Fe%	Cd%	
H 4/581	2.03	۷۵.۱	
IM 9/269	18.32	0.33	
IM 6/1044'8''	8.77	0.11	•
M 10/1512	1.69	0.18	

Table 11 Fe and Cd contents of Sphalerites

Table 12. Table showing the essential and trace element composition of Galena

Cu Fe Mo Ni Sb Sn	1.17 0.39 0.11 xx 0.21 tr	0.10 0.12 0.12 tr 0.11 tr	0.29 0.12 6.80 tr 0.10 tr	0.38 tr xx tr 0.15 tr	359 487 xx xx x x	5680 1025 xx xx x x	6100 913 386 145 0.19 0.13	tr 0.11 xx xx 0.37 tr	0.14 tr tr tr 0.16 tr	933 1236 xx 210 x x	1.65 tr tr xx 0.14 0.13	0 14 44 44 44 44 0 41 0 11
Co	xx	tr	xx	tr	238	хх	497	tr	tr	хх	tr	
Bi Cd	1. 18 0. 11	0.34 tr	0.27 xx	0.37 tr	xx x	× 775	0.98 683	3.49 tr	0.38 tr	× 412	3. 17 0. 11	1 07 +++
As Ba	2.33 x	1.78 x	0.10 233	2.85 x	xx x	x 455	1.26 xx	0.17 x	2.24 x	x 396	1.18 x	•
ul Ag	18 0.12	53 0.11	77 tr	28 tr	×	×	33 0.28	15 0.15	49 tr	×	10 tr	44 44
S Total	81.61 14.87 96.48	83.88 15.75 99.63	15.65 98.77	80.15 15.13 95.28	×	×	14.60 99.83	14.87 97.15	98.	×	81.25 13.85 95.10	14 67 07 86
Pb	81.61	83.88	83.12 15.65	80.15	84.77	85.14	85.19 14.60	82.28 14.87	83.68 14.81	87.75 x	81.25	83.19 14.67
Method	EPMA	=	EPMA & AAS	EPMA	AAS	AAS	' EPMA & AAS	EPMA		AAS	EPMA	=
Sample Number	H4/464	H4/474	H4/491	H4/581	IM9/269	IM9/283	IM9/29416"	H14/265	19-424	A15/1193	M10/1584	M10/1589
Sl. No.	1	2	3	4	5	9	2	80	6	10	11	12

Table 13. Table showing the statistical data of Pyrite (in p. p. m. & %)

	Fe%	S%	As	Ba	Cd	ů	Cu	Mo	Ni	Pb	Te	Zn	
Mean	45.01	54.14		314	395	523	1946	138	264	482	78	528	
Minimum	42.83	52.35		103	33	30	120	13	16	38	15	17	
Maximum	48.25	55.38	•	827	1300	2075	1.271	442	969	1300	230	3280	

Table 14. Table showing the statistical data of Cha. copyrite (in p. p. m. & %)

	Cu%	Fe%	S%	As	Ba	Bi	Cd	ပိ	Mo	Ĩ	4D	Te	U.Z
Mean	34.50	29.85	35.38		737	0.16%	231	401	217	410	481	95	1907
Minimum	32.40	25.80	32.48	•	165	1000	•	60	28	12	1000	55	1000
Maximum	37.09	32.81	36.93	•	1653	0.24%	446	710	510	1060	1045	192	5600

Table 15. Table showing the statistical data of Sphulerite (in p.p.m. & 70)

Te	116	16	260
Pb	874	190	1468
Ni	382	340	433
Mo	951	285	2100
Mn	1157	1000	1300
Cu	5996	3.30%	2.75%
°	588	206	1000
Cd	1190	215	2780
Bi	0.12%	1000	0.13%
Ba	1651	168	7222
As	0.17%	1000	0.37%
5%.	35. 29	32. 23	38.66
Fe%	6	1.12	18.32
Cu%	58.46	51.68	64.74
	Mean	Minimum	Maximum

Table showing the statistical data for Galena (in p. p. m. & %)Table 16

Zn	2674	1164	5860
Te	33	15	69
Sn	0.12%	1000	0.12%
Sb	0.20%	0.10%	0.37%
Ni	202	145	260
Mo	841	386	1200
Fe	1378	487	3900
Cu	4310	359	1. 65 % 3900
°C	367	238	497
Cd Co	820	412	1130
Bi	361 1.25%	0.27%	3.49%
Ba	361	233	455
As	16.50 1.48%	1000 1.68%	2.85%
Ag	16.50	1000	2800
S(%)	14.91	13.85	15.75
Pb(%) S(%)	83.50	80.15	87.75
	Mean	Minimum	Maximum

S1. No.	Sample: Number	Measured edge in Å	Calculated edge Å	Difference Å
1	H4/456	5.4146	5.4135	-0.0011
2	H4/460	5.4113	5.4107	-0.0006
3	H4/467	5.4221	5.4211	-0.0010
4	H4/473	5.4120	5.4108	-0.0012
5	H4/474	5.4194	5.4202	+0.0008
6	H4/481	5.4162	5.4172	+0.0010
7	H4/491	5.4201	5.4220	+0.0019
8	H4/581	5.4135	5.4109	-0.0026
9	IM6/1044'8"	5.4206	5.4169	-0.0037
10	IM6/1160	5.4198	5.4193	-0.0005
11	IM9/269	5.4249	5.4259	+0.0010
12	'IM9/283	5.4118	5.4107	-0.0011
13	IM9/285'2"	5.4125	5.4118	-0.0007
14	IM9/292'6"	5.4114	5.4106	-0.0008
15	IM9/294'6"	5.4127	5.4118	-0.0009
16	M10/1512	5.4106	5.4114	+0.0008
17	H14/265	5.4152	5.4124	-0.0028

Table 17 Table showing the measured and calculated cell edges of Sphalerite

S1, No.	Sample number	X-ray diffraction Å	Electron diffraction Å	Difference Å
1	H4/456	5.4146	5.4284	0.0138
2	H4/460	5.4113	5.4226	0.0113
3	H4/491	5.4171	5.4248	0.0077
4	IM9/269	5.4249	5.4367	0.0118
5	IM9/283	5.4118	5.4320	0.0202
6	IM9/285'2"	5.4125	5.4177	0.0052
7	IM9/292'6"	5.4114	5.4236	0.0122
8	IM9/294'6"	5.4127	5.4381	0.0254
9	H14/265	5.4202	5.4207	0.0005
10	M10/1512	5.4106	5.4242	0.0136
11	19-424	* 5.4240	5.4196	0.0044
12	A15/1193	* 5.4115	5.4224	0.0109

Table showing the differences in measured cell edges of Sphalerite by X-ray diffraction and electron diffraction Table 18

* calculated edges

S1. No.	Sample number	VHN kg/mm ²	S1. No.	Sample number	VHN 2 kg/mm ²
1	A15/916	1031	9	M10/1548	1097
2	A15/924	1037	10	M10/1589	1123
3	A15/971	1052	11	H14/186	1118
4	· IM6/1044'8"	1063	12	M10/1599	1155
5	IM6/1160	1185	13	C4/960	1110
6	36A/1617	1123	14	H4/464	1168
7	H43A/1837'	1483	15	H14/265	1107
8	M10/1540	1089	16	32-1108	1063

Table 19 Microhardness values of Pyrite

Table 20 Microhardness values of Chalcopyrite

S1. No.	Sample number	VHN kg/mm ²	Sl. No.	Sample number	VHN kg/mm ²
1	A15/920	203	7	IM9/264	221
2	A15/1193	210	8	M10/1548	197
3	A14/1534	201	9	M10/1589	187
4	M10/1521	201	10	H4/465	174
5	M10/1512	187	11	H4/491	194
6	H14/186	194	12	H4/171	210

S1. No.	Sample number	VHN kg/mm ²	S1. No.	Sample number	VHN kg/mm ²
1	A15/971	230	11	IM9/288	206
2	IM6/1160	215	12	M10/1589	195
3	IM9/269	237	13	H4/465	148
4	19-424	203	14	M10/1548	175
5	M10/1512	161	15	H4/481	190
6	A15/1194	172	16	H4/474	210
7	H4/474	195	17	IM9/294'6"	172
8	H4/491	240	18	IM9/285	186
9	IM9/285'2"	168	19	H4/456	203
10	M10/1584	198			

Table 21 Microhardness values of Sphalerite

Table 22 Microhardness values of Galena

S1. No.	Sample number	VHN kg/mm ²	Sl. No.	Sample number	VHN kg/mm ²
1	19-424	61.7	5	H4/491	67.7
2	H4/464	107	6	M10/1584	201
3	H4/474	104	7	IM9/283	96.5
4	A15/1194	77.9	8	H14/265	87.8

			Table 23		able sh	owing t	the spec	ctral r	eflectiv	ity value	Table showing the spectral reflectivity values of Pyrite (R% air)	rite (R	% air)				
No.	400	420	440	460	480	500	520	540	560	580	589	600	620	640	660	680	700
A15/924	41.05	46.1	47.5	50.05	51.8	52.0	52.7	55.0	55.15	56.23	56.45	57.8	56.2	57.3	57.6	57.8	57.7
A15/980	42.5	45.20 45.5	45.5	45.18	47.5	48.2	49.3	49.6	49.8	50. 25	52.1	52.5	52.6	53.8	53.9	53.8	53.7
A15/971	35.05	36.8	37.9	40.10	42.5	43.2	45.05	46.8	47.5	49.0	49.8	50.15	51.2	52.5	54.1	54.6	55.3
A14/1534	36.10			42.5	43.6	46.0	47.5	49.0	49.65	49.75	51.38	52.1	53.4	55.6	55.2	55.3	55.25
27-145	42.5	44.3	47.0	48.3	49.5	50.25	50.05	51.2	52.1	52.1	52.3	52.1	52.5	53.2	53.8	54.0	54.8
H43A/1855	34.8	36.7	37.2	38.3	41.8	42.9	45.5	47.5	48.3	50.6	52.1	52.35	53.68	54.8	54.95	55.0	54.86
32-1108	34.3	37.9	40.15	41.6	42.65	45.73	46.35	46.65	46.75	46.89	47.5	50.05	50.10	50.10	5.05	50.05	51.00
32-1198	36.0	37.5	39.8	42.5	45.05	47.8	48.5	50.05	50.10	50.5	52.01	52.25	52.20	51.85	51.80	51.8	50.75
H14/265	32.5	36.2	37.3	39.4	40.03	41.6	42.5	43.6	45.80	47.2	47.8	48.3	49.6	49.5	49.9	50.05	50.20
H4/456	36.2	41.8	42.6	43.2	45.05	46.7	47.5	48.3	50.15	52.6	53.9	54.8	55.05	55.10	55.20	55.15	55.20
H14/	36. 25	37.5	37.8	40.16	41.68	42.5	43.6	45.2	46.25	46.8	47.6	47.8	49.3	50.2	52.6	52.3	52.2
19-424	38.12	40.10	42.3	42.7	44.3	45.6	46.2	47.6	48.3	48.9	49.2	50.12	50.15	49.8	50.2	49.5	50.05
A15/953	42.5	43.4 47.5 4	47.5	48.2	51.6	52.6	54.8	55.1	55.2	56.2	56.3	56.8	56.4	52.5	57.2	57.6	57.3
A15/950	37.0	37.5	39.5	40.25	45.06	46.3	47.5	49.3	47.25	50.15	50.30	52.2	55.0	55.25	55.6	55.3	55.75
A15/	34.8	35.2	36.8	36.9	37.5	40.2	41.5	42.2	43.8	45.0	46.3	49.8	51.3	52.6	52.7	52.6	53.9
32-1269	33.6	37.6	39.5	42.5	45.0	47.5	50.2	51.8	52.5	52.8	53.6	54.9	55.2	55.1	55.3	55.6	55.4
IM6/1101	35.0	37.8	41.8	44.8	47.5	47.8	51.3	51.85	52.6	53.6	52.8	55.05	55.61	55.3	55.4	55.6	55.0
A15/1193	32.6	34.6	39.6	42.5	45.0	47.2	49.6	49.8	50.1	51.2	51.8	52.5	52.6	52.7	52.9	54.0	55.0
IM6/1160	32.5	35.6	40.04	42.6	45.10	47.5	49.8	50.1	50.25	52.5	52.7	54.0	55.0	55.2	55.05	55.10	55.2
A15/941	36.8	37.5	39.8	42.3	42.8	46.8	47.9	50.0	50.10	50.15	51.28	52.20	52.5	52.8	52.4	52.3	52.0
IM6/231	34.3	35.0	36.2	37.2.	40.02	40.35	42.5	42.6	44.8	46.35	47.21	47.75	48.3	48.4	48.2	48.3	49.5
A15/916	38.35	40.05 44.3	44.3	47.5	48.3	50.1	50.2	52.5	52.7	53.6	54.8	55.0	55.6	55.2	54.9	54.8	54.6
IM6/1392	34.8	35.0	40.35	42.6	46.3	46.2	47.5	47.8	47.9	50. 25	50.20	53.2	52.5	53.2	53.1	53.6	53.78
H4/474	33.6		36.2	37.8	38.3	40.5	42.5	45.0	45.8	46.9	46.92	46.85	47.25	47.05	46.55	47.2	47.4
A15/935	33.8	36.8	38.6	42.6	47.5	48.9	51.6	52.6	53.78	54.2	53.98	54.5	55.2	55.1	52.8	52.3	52.6

200	52.6	50.3	53.2	51.2	49.8	53.6	55.4	53.5
680	52.3	50.2	53.6	50.15	49.5	53.78	55.2	53.2
660	2.8	0.2	54.8	50.25	48.4	53.65 53.78 5	55.0	53.8
640	52.7	49.6	53.4	52.3	47.3	53.8	55.3	54.6
620	52.5	48.4	52.6	51.2	45.8	53.6	55.2	54.8
009	51.26	47.8	52.5 52.6 53.4 5	50.2	45.6	52.5	54.7	52.2
589	50.53	47.6				51.6		
580	50.6	46.8	50.2	45.7	44.5	50.5	54.6	50.2
560	49.35	45.6	49.5	45.2	42.75	48.4	52.6	48.6
540	49.3	45.7	47.5	45.6	42.6	47.5	51.8	47.5
520	48.6	44.6	47.8	44.2	41.8	45.5	50.2	47.2
500	47.5	42.5	45.6	43.6	46.1	44.2	47.5	46.8
480	45.1	41.9	45.2 45.6 47.8 47.5	42.5	39.6	42.6	46.8	42.5
460		39.8				41.5		39.8
440	40.2	37.3	40.15	37.8	37.5	37.5	40.2	37.5
420	37.5 40.2	34.68 37.3	37.39 40.15	35.7 37.8	35.2	35.0	34.6	35.0
400	34.85	32.15	36.18	33.5	32.3	32.2	34.8	32.6
	1M6/779	IM 9/364'2"	M10/1548	A15/965	36.A/1611	H4/491	M10/1610	1M9/2921611

air)
(R %
Chalcopyrite
values of
reflectivity
le spectral
showing th
Table
Table 24

Section No.	400	400 420 440	440	460	480	500	520	540	560	580	589	600	620	640	660	680	200	
32-1198	24.48	27.54	24.48 27.54 29.04		31.71 34.58	37.11	38.23	39.45	40.05	40.25	40.25 41.33 41.39 40.66	41.39	40.66	39.68	39.45	39.68 39.45 38.66	38.73	
A15/1193 25.92 28.85 31.00	25.92	28.85	31.00	33.44	35.40	36.49	37.44	37.79	38.81	39.12	39.12 40.36 39.60 38.31	39.60	38.31	36.8	36.65	36.03	35.93	
IM6/1393 22.75 24.26 26.28	22.75	24.26	26.28	28.54	29.91	31.13	31.32	33.38	34.56	36.15	38.21	38.66	37.81	36.15 38.21 38.66 37.81 36.65 36.2	36.2	34.75	34.2	
A15/924	28.7	29.10	28.7 29.10 31.8	32.7	34.10	35.71	37.19	38.14	38.37	39.83	39.83 40.36	41.18	41.18 38.31	36.8	36.5	36.2	35.85	
A15/943	21.91	22.95	21.91 22.95 24.60	27.45		34.76	30.10 34.76 35.68	36.61	36.61 37.31 38.25 38.65 39.30 40.31 39.58	38.25	38.65	39.30	40.31	39.58	37.61	37.5	36.31	
H14/186	25.10	28.78	25.10 28.78 29.9	30.31		32.36	31.15 32.36 35.29		35.86 36.16	36.24	36.24 38.34	39.47	39.47 40.69	39.68	39.32	38.58	36.8	
A15/965	20.40	22.56	20.40 22.56 25.08		27.81 30.44 32.38 33.98 34.39 36.35	32.38	33.98	3.4.39	36.35	37.12	37.12 38.88 38.56 37.34	38.56	37.34		38.31 36.62	36.12	35.2	
67776 MI	28, 15	29.28	28.15 29.28 30.36	31.38		34.73	32.67 34.73 36.01 37.28	37.28	37.92	39.13	40.62	39.47	40.31	39.13 40.62 39.47 40.31 39.8	38.86	38.05	36.9	
H4/456	23.53	28.01	23.53 28.01 29.36	30.35	31.29	32.75	33.51	35.91	35.91 37.53	38.62	38.62 40.55	39.47	40.31 41.4	41.4	40.38	39.68	39.7	
H43A/ 1855	27.35	28.45	27.35 28.45 28.86		29.81 30.34 33.76 35.29	33.76	35. 29	36.94	36.94 37.92	39.6	39.6 41.35	40.44	40.75	40.4	40.2	39. 65	39.3	
H4/491	26.16	27.36	26.16 27.36 28.71	29.30	30.16	31.35	33.69	3.4.85	3.4.85 32.83	39.65	39.65 41.02 41.37	41.37	40.31	40.31 40.6	40.4	40.2	39.3	
M10/1410 23.6 24.2 26.8	23. 6	24.2	26.8	29.80		33.76	30.34 33.76 36.29	38.94	33.94 39.92	40.15	42.61	43.85	43.05	40. 15 42. 61 43. 85 43. 05 42. 83 42. 65	42.65	41.85	40.38	

Table 25Table showing the spectral reflectivity values of Sphalerite (R% in air)

14.89 13.53 19.6 20.6 19.3 19.3 13.3 19.4 18.9 17.6 700 700 19.46 15.63 19.6 19.87 13.6 19.6 13.53 20.3 19.6 17.6 680 680 15.87 14.53 14.83 15.33 20.32 13.53 16.47 17.15 19.8 20.3 19.8 20.3 17.37 17.25 17.60 18.85 18.64 18.32 18.8 660 660 19.32 15.87 14.83 15.87 14.53 18.13 19.23 23.07 17.01 17.55 17.42 17.96 17.53 17.55 17.00 17.25 17.05 19.57 18.36 20.3 20.3 640 640 Table showing the spectral reflectivity values of Galena (R% air) 18.13 22.67 16.87 16.32 17.8 620 620 17.08 19.65 17.94 17.65 17.08 17.28 23.92 600 600 17.83 17.72 17.89 15.92 15.66 16.78 15.92 15.66 16.35 22.13 16.95 16.98 17.72 17.92 17.63 17.65 17.43 17.35 15.81 16.35 17.7 589 589 22.25 580 580 18.79 16.50 16.07 22.29 560 560 18.62 18.78 17.53 17.6 17.83 17.79 16.52 16.32 15.89 17.79 17.74 22.04 18.28 15.86 15.25 15.4 540 540 22.31 16.40 15.21 17.35 17.93 520 520 15.84 14.85 14.86 17.65 16.58 16.11 16.66 16.11 21.87 18.80 17.89 500 500 18.62 18.07 18.72 19.91 21.95 16.78 16.4 18.6 480 480 22.04 18.9 18.6 460 460 17.85 18.8 16.85 16.73 16.15 18.68 22. 16 16.85 16.76 16.64 19.05 17.4 18.8 440 Table 26 440 18.80 22.20 19.25 19.15 19.03 18.2 18.3 16.85 16.9 18.9 420 420 18.85 18.35 19.31 19.2 18.4 22.24 400 400 IM6/1393 IM9/294' A15/1193 IM9/2851 A15/980 H14/265 32-1198 -9 H4/456 12 Section 27-145 19-424 Section No.

36.68 44.83 40.5 33.2 31.2 45.63 41.2 33.2 37.2 35.57 34.2 36.5 45.8 32. 74 32. 47 31. 87 33. 22 34. 42 36. 35 40.8 32. 15 32. 00 31. 92 32. 38 34. 16 35. 86 37. 31 37. 31 38. 15 37. 7 41.39 41.08 40.68 41.32 42.36 43.06 46.0 37.39 41.4 36.13 36.8 41.18 39.6 40.57 39.45 40.25 42.66 40.65 38.85 39.29 38.91 38.37 37.83 38.3 32.73 41.71 32.79 43.95 42.38 41.96 41.35 33.26 35.69 45.05 45.24 42.84 42.64 35.19 32.8 36.09 32.95 33.45 32.80 43.31 43.15 43.05 45, 15 43.35 38.3 45.92 45.24 43.65 38. 65 43.93 38.75 A15/1193 M10/1584 A14/456 19-424 H4/491

Table 27

Composition of Arsenopyrite

	M 10/1599 %	M 10/1608 %	Theoretical composition %
Fe	36.06	37.11	34.30
As	42.78	43.23	46.01
Co	tr	tr	
Ni	tr	tr	
Cu	tr	tr	
РЪ	tr	· tr	
Zn	tr	tr	
S	20.76	21.25	19.69
Total	99.60	101.59	100.00

Table 28 List of Sulpho-salts found at Parys Mountain

General classification	Name	Theoretical formula
Copper Sulpho-salts	Tetrahedrite-Tennantite	(Cu Fe Zn Hg) ₁₂ (Sb As) ₄ S ₁₃
Copper-Lead Sulpho- salt	Bournonite	Pb Cu Sb S ₃
Lead Bismuth Sulpho- salts	Galenobismuthite Kobellite	Pb Bi ₂ S ₄ Pb (Bi, Sb) ₂ S ₅
Lead Sulpharsenides	Lead Sulpharsenide	Pb-As-S (varying)

Composition of Tetrahedrite - Tennantites

Table 29

13	34.9	2.6	3.9	2.5	29.8	0.8	1	24.7	99.2
12	34.4	1.8	4.9	2.6	29.8	1.1	,	25.0	9.6
:	32.6	5.4	1.3	6.1	28.2	0.8	•	24.5	98.9
10	34.7	3.1	1.7	5.7	25.1	2.7	•	25.2	98.2
9 M10/1548	28.78	xx	3. 16	1. 29	0.12	41.57	xx	25.12	100.04
8 H4/491	31.61	1.28	8.31	5.15	1.38	24.29	0.87	24.63	97.52
7 27-145	37.88	0.23	7.04	4.69	5	22.16	1.42	27.47	100.91
6 H4/474	32.39	ħ	4.31	8.18	23.67	3. 28	xx	26. 66	98.49
5 27-145	39.67	0.55	6.05	4.24	22. 12	1.18	xx	23. 32	97.75
4 H4/456b	36.31	tr	9.61	2.23	22. 85	4.48	tı	25.03	100.51
3 H4/456a	33.76	0.31	10.18	5.36	23.35	2.1	0.67	26.18	101.91
2 H4/464	36.12	tr	8.42	1. 29	28.52	3.2	0.89	23. 25	98. 69
1 H4/473	34.35	0.1	9.54	2.38	24.77	2.1	0.32	25.45	99.01
Sample No.	Element Cu	Ag	Fe	Zn	Sb	As	Bi	S	Total

tr - traces xx not detected

- 1 6 Parys Mountain Tetrahedrites (Present Study)
- 7 9 Parys Mountain Tennantites (Present Study)
- Parys Mountain Tetrahedrite Hill Side open cast, Bluestone adit dump (Analyst: Wheatly 1971a) 10
- 11 Parys Mountain Tetrahedrite, Morfa-du Ida Shaft dump (Analyst:Wheatly 1971a)
- 12 West Avoca Tetrahedrite, South Lode. (Analyst: Wheatly 1971a)
- 13 East Avoca Tetrahedrite (Analyst: Wheatly 1971a).

Table giving the atomic proportions for Tetrahedrites-Tennantites (Present Study) Table 30

M10/1548 S 10.27 1.28 0.45 3.99 0.00 11.50 e 1 1 + •--4 H4/491 R 8.10 0.19 2.42 11.42 0.13 3.82 1.28 0.05 B R R 27-145 e 12.48 8.99 0.03 1.90 1.08 3.90 0.09 0.00 H H4/474 8.59 1.30 2.10 3.26 0.74 13.90 1 ı 3 27-145 e 9.33 0.07 1.62 11.54 0.97 3.53 0.47 + . 1 • – • H 5 H4/456b e 10.59 1.05 0.37 0.97 13.95 3.03 1 ч 1 d H H4/456a + e 7.99 0.04 2.74 1.23 0.50 12.79 3.44 0.06 H H4/464 9.23 2.44 0.32 3.33 0.61 0.06 11.37 . H4/473 8.66 0.01 2.73 0.58 3.49 0.48 0.02 12.93 Zn Cu Fe Ag As Sb Bi S

		Co	mposi	tion			Atomic Prop	portions
	1	2	3	4	5	6	1	2
Cu	15.22	20.72	13.0	13.6	14.2	12.3	1.37	1.58
РЪ	39.81	43.86	42.4	44.6	43.8	42.9	1.10	1.03
Sb	22.84	16.17	24.9	22.7	22.7	25.3	1.07	0.64
As	2.49	3.67	-	-			0.19	0.24
Bi	0.12	0.22	-	-			0.00	0.00
Fe	xx	0.25	-	-			n 2 2 / 5 2 - 3 1	0.02
Zn	0.16	0.14	-	-			0.01	0.01
s	18.17	15.62	19.7	19.3	20.5	19.6	3.25	2.46
- Total	98.81	100.65	100.0	100.2	101.2	100, 1		

Table 31 Composition and atomic proportions of Bournonite

Parys Mountain, H4/465 (Present Study) 1.

Parys Mountain, M10/1548 (Present Study) 2.

Theoretical Composition 3.

1.

East Avoca, Tigroney (Analyst: Wheatly, 1971a) 4.

No. 1A, draw point, Avoca (Analyst: Wheatly, 1971a) 5.

Wood river Lead Silver deposit, Idaho (Analysts: Hall and Czemanske, 1972) 6.

26 86	Compos 2 43.18 2.19	3 44.4	4 47.1	1 5.51	2 8.77
	2.19	-			
			0.9	1.27	1.45
22	32.15	29.9	32.1	4.10	6.47
12	4.23	8.6	4.5	1.43	1.46
12	1.29	-	-	0.65	0.97
31	0.88	-	-	0.05	0.00
18	16.19	17.2	15.7	15.20	21.25
07	100.11	100.1	100.3		

Table 32 Composition and	atomic prop	portions of	Kobellite
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1. Parys Mountain H4/474

1

2. Parys Mountain M10/1548

3. Theoretical Composition

4. West Avoca (Analyst: Wheatly, 1971a)

Table 33 Composition and atomic proportions of Galenobismuthite

	(Compos	ition		Atom	ic Proportions
Bi	1 43.16	2 55.5	3 54.69	4 58.0		1 1.47
Cu	3.18	-				0.36
РЬ	26.47	27.5	27.65	24.7		0.83
Zn	10.12					1.10
Fe	0.39				•	0.00
s	13.78	17.0	17.35	17.0		3.06
	97.10	100.0	99.69	99.7		

1. Parys Mountain H4/474

2. Theoretical Composition

3. Type Material (Analyst: Sjogren (1878) in Berry, 1940)

4. Bally Coog, Avoca (Analyst: Wheatly, 1971a)

Tabl	e 34 Com	position and atomi	ic proportions of Lead Sulp	harsenides
	Compo	sition	Atomic Prop	ortions
	1	2	1	2
Cu	0.18	0.28	0.03	0.06
Pb	69.68	68.18	3.17	4.21
Sb	0.13	0.05	0.01	0.00
As	13.24	15.37	1.66	2.63
Fe	0.16	0.38	0.03	0.09
Zn	1.88	0.19	0.27	0.04
Bi	xx	xx		
S	13.82	14.38	4.06	5.75
Total	99.09	98.83		

1. Parys Mountain 19-424

2. Parys Mountain M10/1589

dÅ (from Tables 7-171)	hkl	d A measured	
7.08	002	7.081	
3.541	004	3.541	
2.458	132, 203	2.458	
2. 271	132, 204	2.276	
1.829	136, 205	1.829	
1.550	331, 060	1.542	
1.360	334, 065, 336	1.368	

Table 35X-ray Powder diffraction data for Diabantite

Table 36X-ray Powder diffraction data for Ripidolite

dÅ (from Tables 7-76)	hkl	d Å measured	
14.1	001	14.119	
7.07	002	7.076	
4.724	003	4.720	
3.537	004	3.534	
2.599	(131, 202)	2.600	
2.450	132, 203	2.452	
1.826	136, 205	1.826	
1.665	137, 206	1.666	
1.547	331,060	1.546	

		the second se
dÅfrom Tables 19-749	hkl .	d Å measured
14.3	001	14.348
7.12	002	7.115
3.56	004	3.559
2. 435	132	2.438
2. 255	133	2.256
1.535	245,060	1.536

Table 37 X-ray Powder diffraction data for Clinochlore

Table 38 X-ray Powder diffraction data for Aphrosiderite

d A from Tables 2-243	hkl	d Å measured
7.05	002	7.047
3.52	004	3. 527
2.83	005	2.822
2.67	200	2.672
1.559	060	1.559
1.559	060	1.559

Table 39 X-ray Powder diffraction data for Grochauite

d Å from Tables 7-165	hkl	dA measured
14.0	001	14.029
7.08	002	7.081
3.545	004	3. 545
2.543	132, 201	2.544
2.842	005	2.844

Table 40X-ray powder data for Chlorite 1b

hkl	d Å measured	
001	14.392	
002	7.155	
203	2. 470	
204	2. 287	
060	1.549	
	001 002 203 204	001 14.392 002 7.155 203 2.470 204 2.287

35	36A/1617 (Pyrite with little chalcopyrite), IM6/1044'8" (Pyrite), 36A/1611 (Pyrite)
36	36A/1670 (Pyrite), M10/1630 (Pyrite), A15/941 (Pyrite with little chalcopyrite), M10/1410 (Chalcopyrite with some pyrite)
37	IM9/269 (Sphalerite with some pyrite), 32-1198 (Pyrite with little sphalerite)
38, 39	IM6/1231 (Pyrite), IM6/1365 (Pyrite, Chalcopyrite with little sphalerite; in this section only grochauite is present)
40	IM6/1359, 36A/1525, 6-527, H17A/1510, H43A/1845 (non-

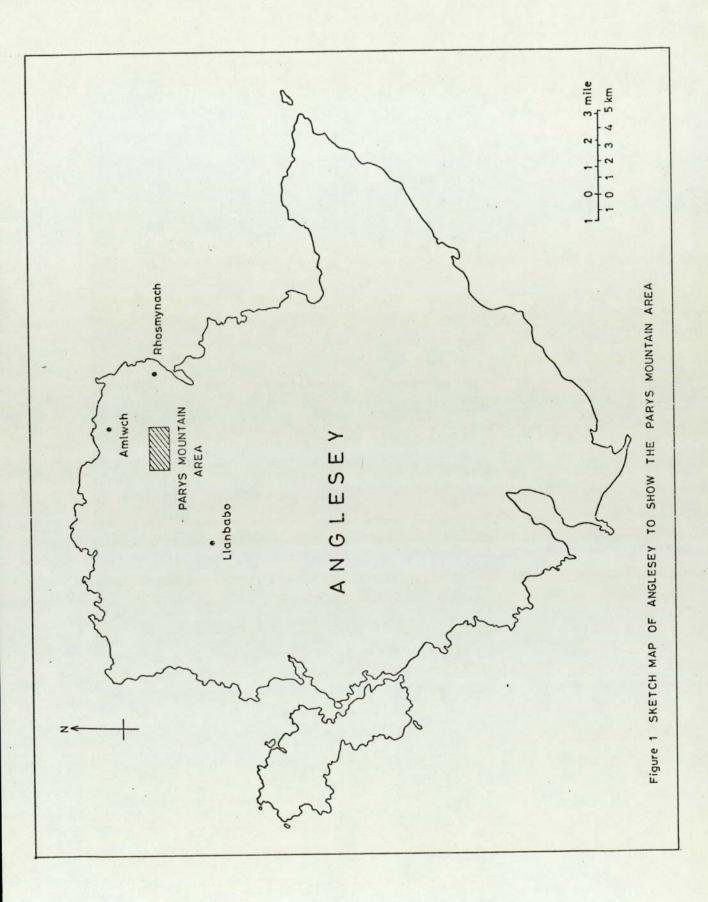
mineralised sections).

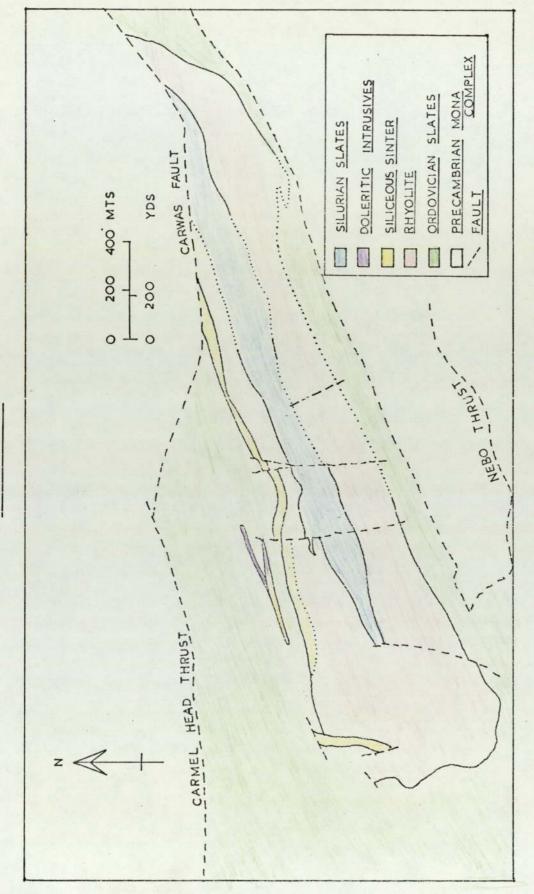
Table 41	Т	ab	le	4	1
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Standards used for Microprobe Analysis

		Sector Sector Sector		
Element	Standard		Radiation	
Ag	Pure Metal		Ag K _X	
As	Pure Element		As K	
Bi	Pure Metal		Bi L _x	
Cd	Pure Metal		Cd L	
Co	Pure Metal		Co Kox	
Cu	Pure Metal		Cu K	
Fe	FeS2	46.55% Fe	Fe K _X	
Mn	Pure Metal		Mn K _K	
Мо	Pure Metal		Mo Lo	
Ni	Pure Metal		Ni K of	
Pb	PbS	86.62% Pb	Pb M _×	
S	FeS2	53.45% S	SKX	
Sb	Pure Element		SbL	
Se	No Standard avai	lable	-	
Sn	Pure Metal		Sn K _K	
Zn	Pure Metal		Zn K _K	

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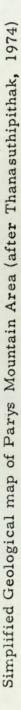
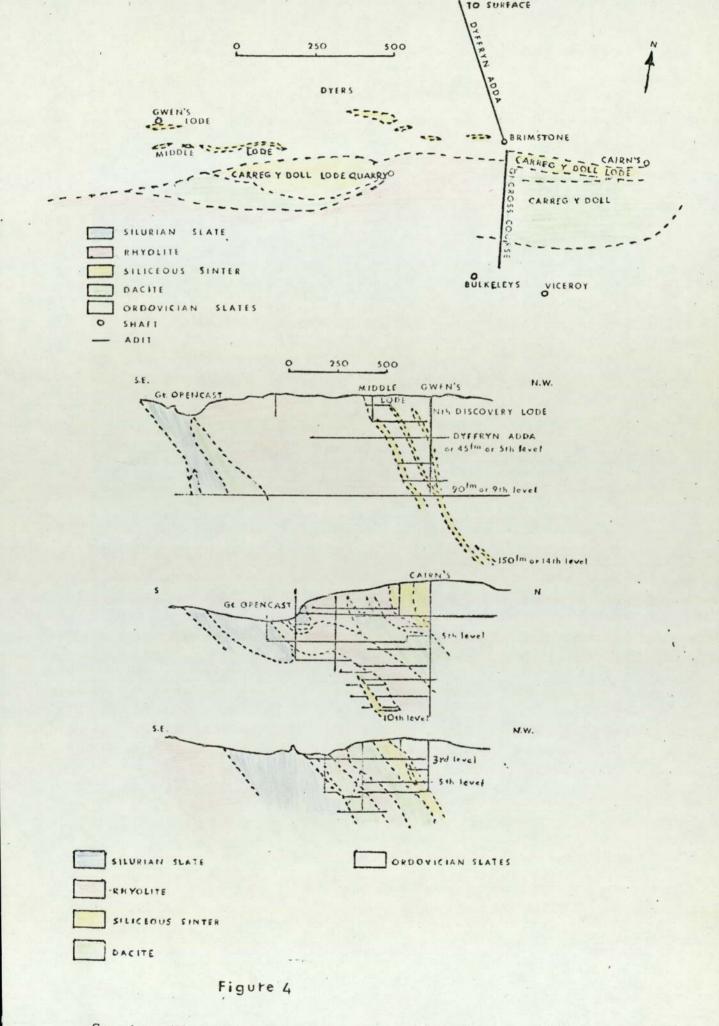


FIGURE 2

. FLGURE 3

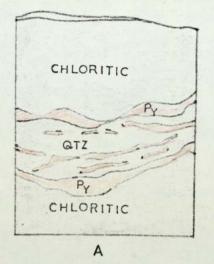
OF PARYS MOUNTAIN
0
CARMEL HEAD THRUST NEBO
RHWNC THRUST L F
CARMEL HEAD 3
RHWNC THINK
THRUST III III
CHAPEL THRUST
HORIZONTAL AND VERTICAL SCALE VERTICAL SCALE VERTICAL SCALE
. (4)
1//////
300 67
1000FT
200M
() SECTION THROUGH THE CENTRAL PART OF PARYS MOUNTAIN (AFTER GREENLY 1919)
(2) SECTION THROUGH THE WESTERN END OF PARYS MOUNTAIN (AFTER GREENLY 1919)
(3) SECTION THROUGH THE CENTRAL PART OF PARTS MOUNTAIN (AFTER MANNING 1959)
4 SECTION THROUGH THE CENTRAL PART OF PARTS MOUNTAIN AFTER THANASUTHIPITHAK 1974
cf. WHEATLEY, 1971)
SILURIAN SLATE
DACITE ORDOVICIAN SLATE
RHYOLITE PRECAMBRIAN MONA COMPLEX

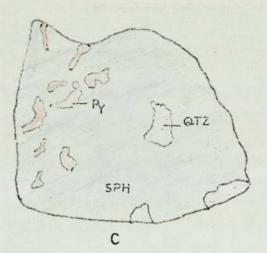
CROSS SECTIONS ILLUSTRATING THE STRUCTURAL INTERPRETATIONS OF PARYS MOUNTAIN



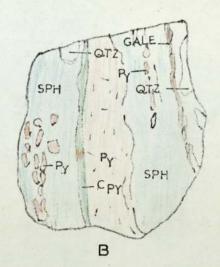
Sections illustrating the various lodes (after Manning, 1959)

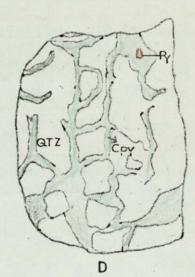


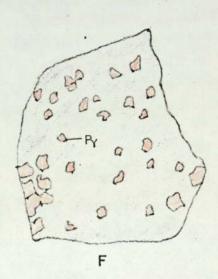






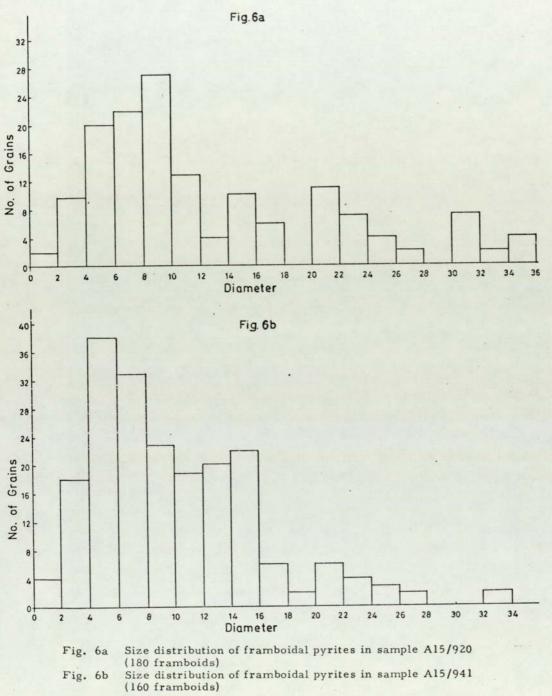


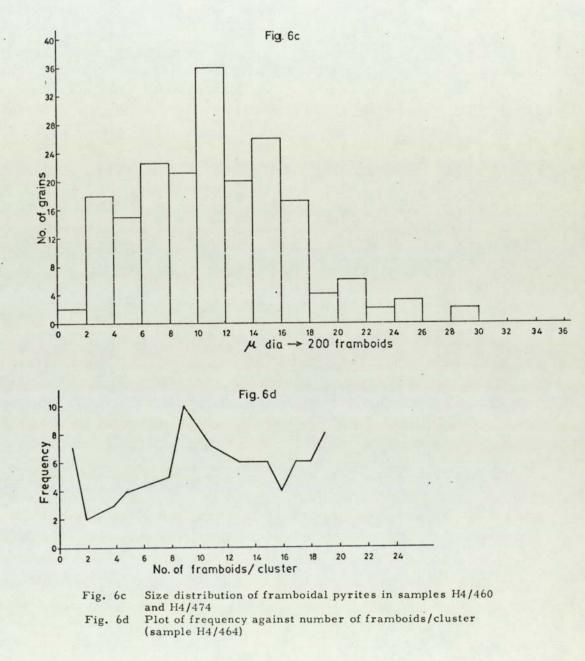


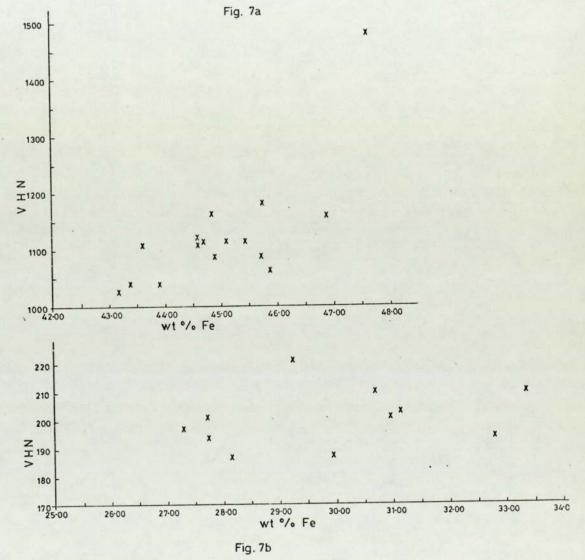


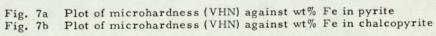
I CM

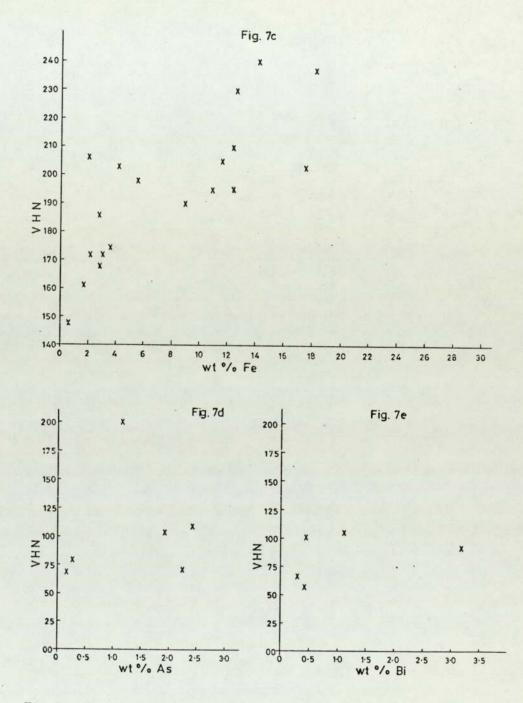
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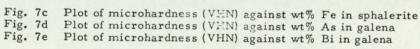


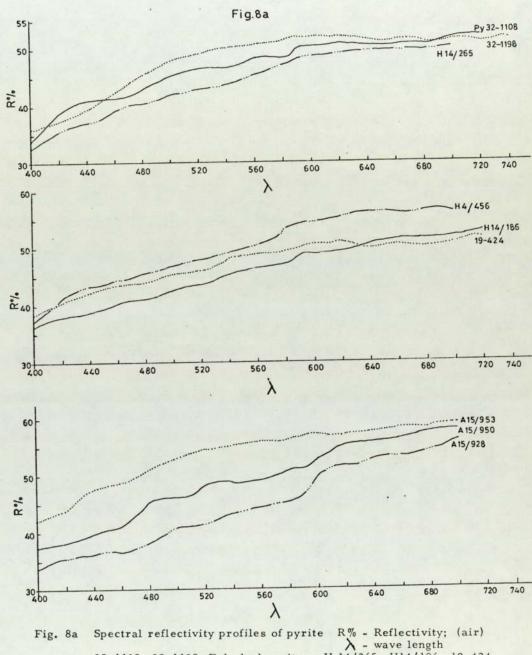




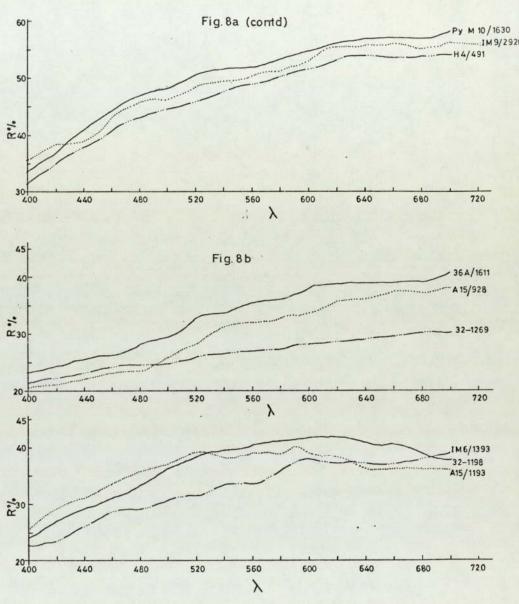


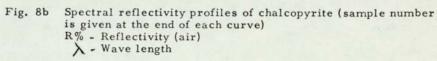






Spectral reflectivity profiles of pyrite R% - Reflectivity; (air) λ - wave length 32-1108, 32-1198 Euhedral pyrites; H 14/265, H14/186, 19-424, A 15/950, M 10/1630, all anhedral pyrites; H 4/456, A 15/953, A 15/928 Framboidal pyrites





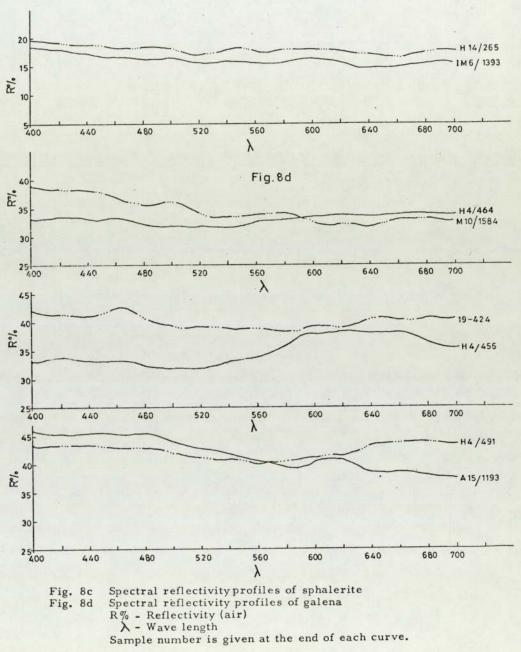
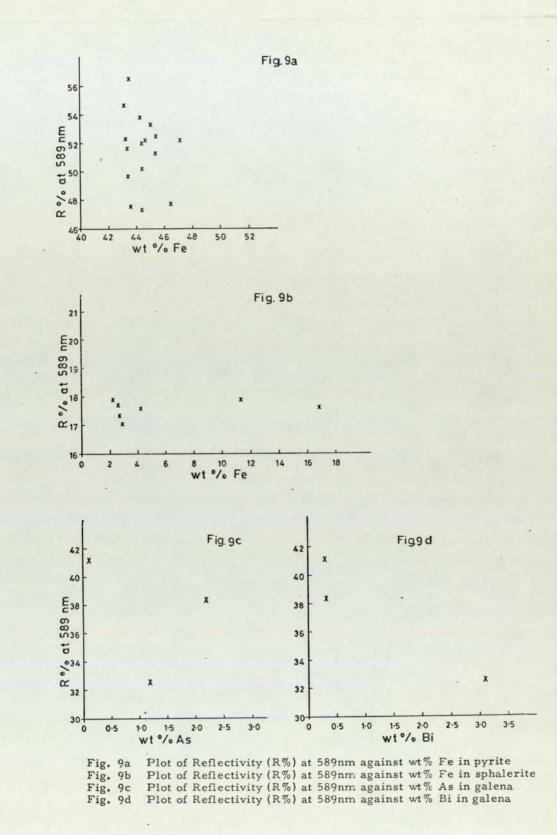
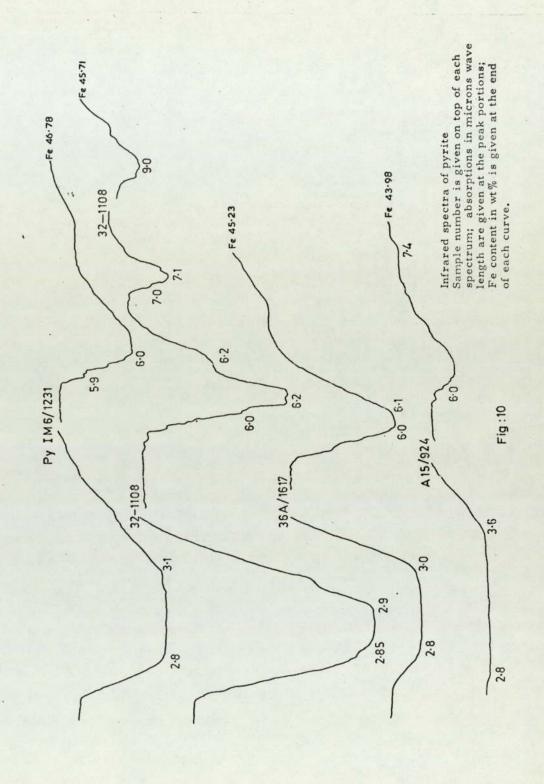


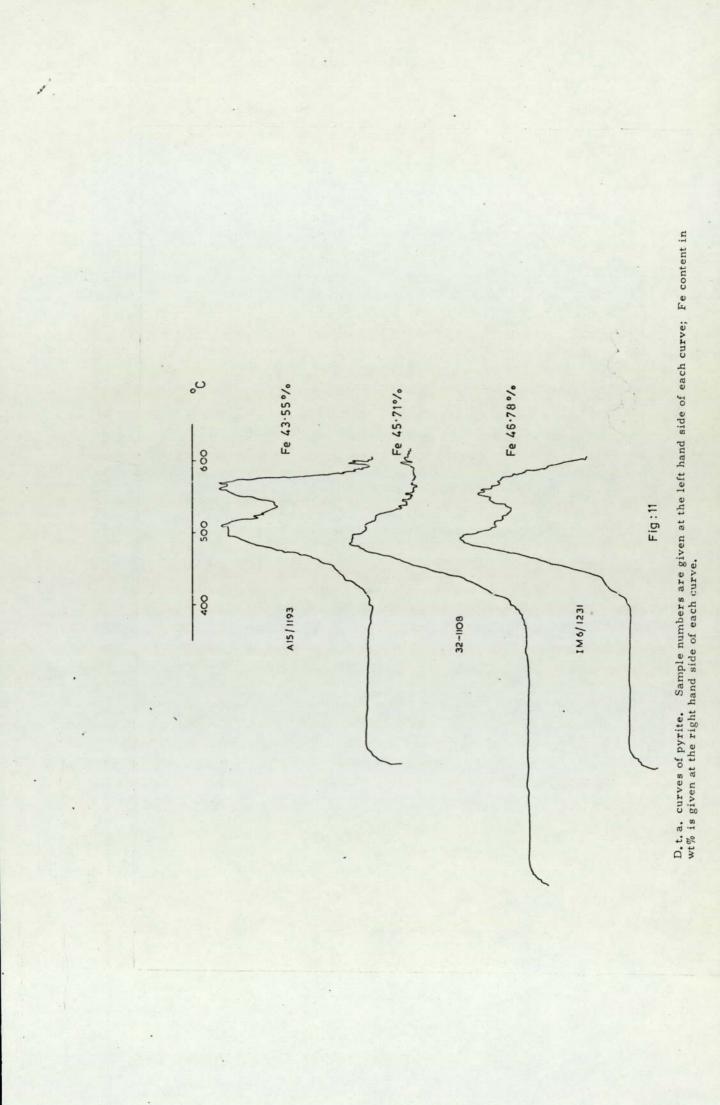
Fig. 8c

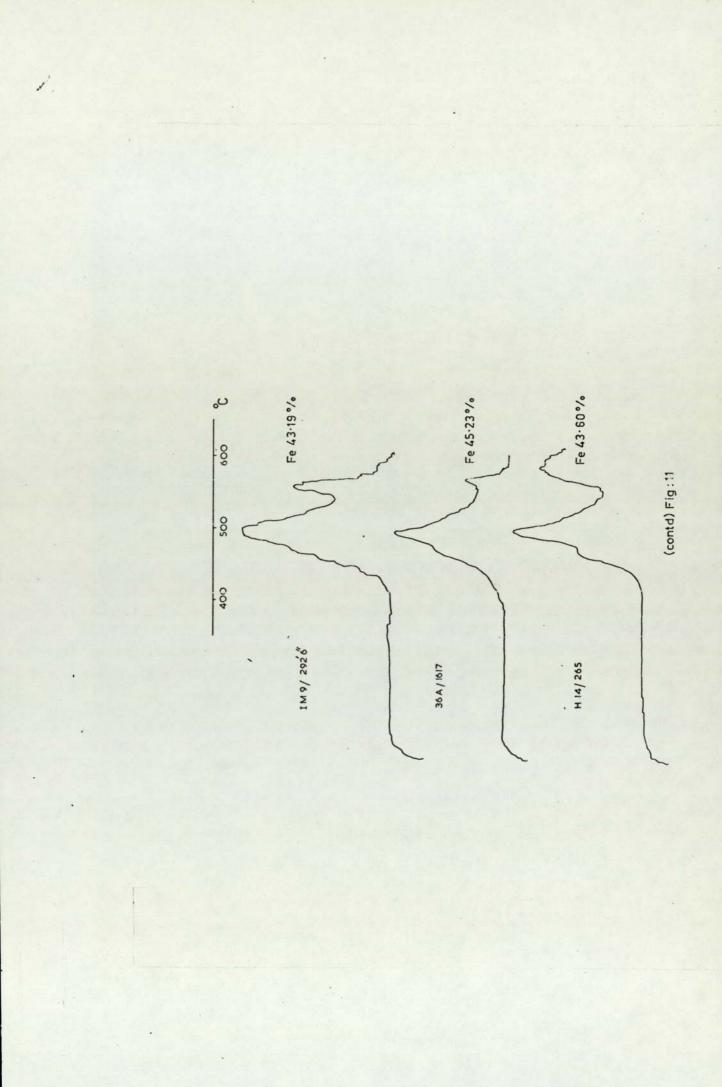
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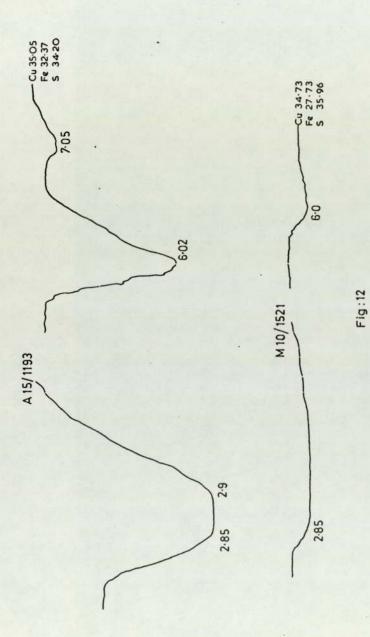




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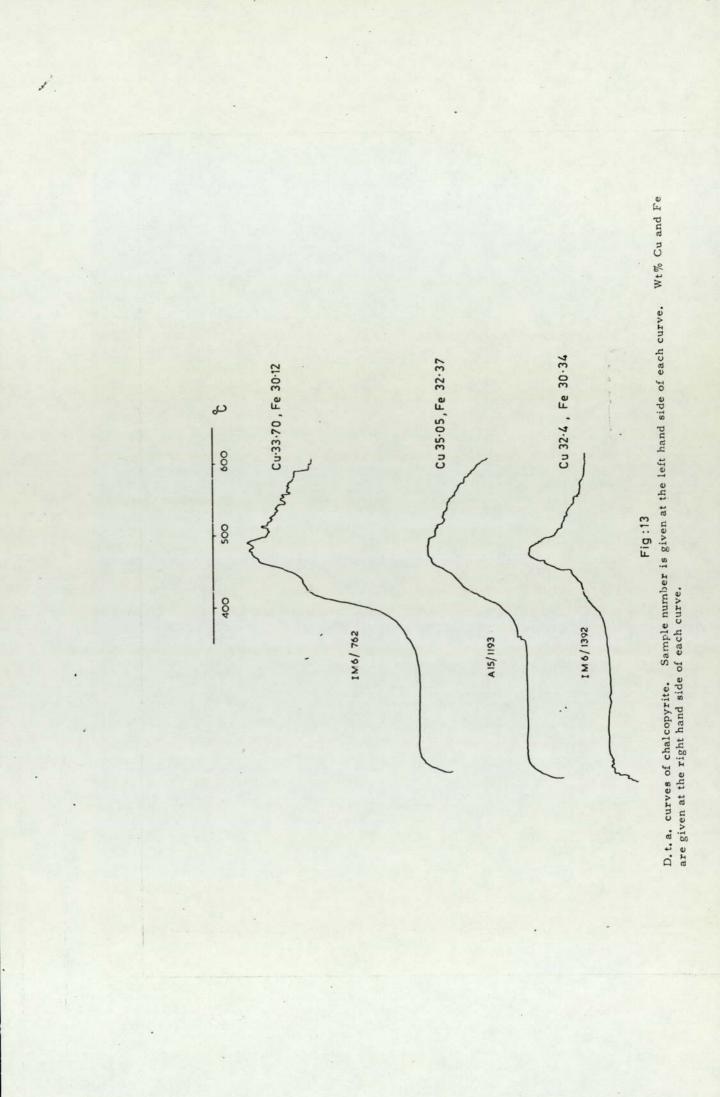


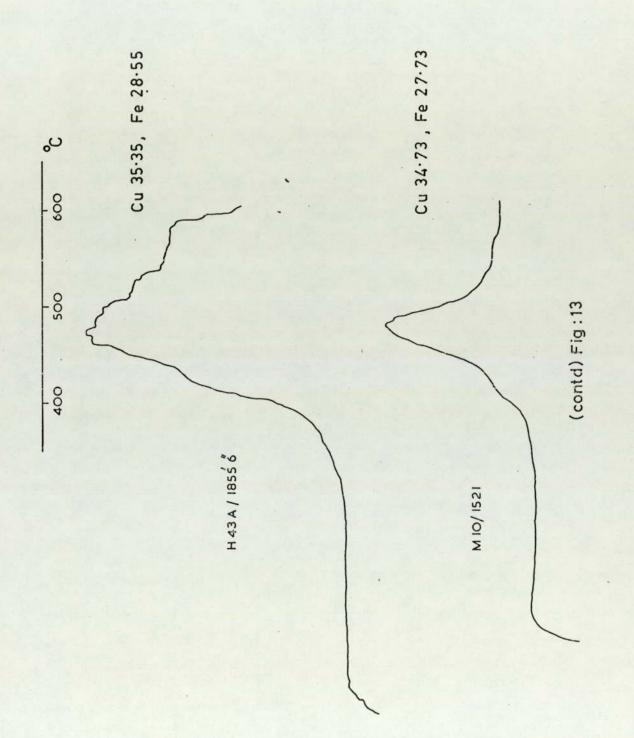


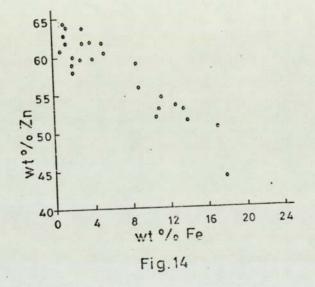


Infrared spectra of chalcopyrite. Sample number is given on top of each spectrum. Absorptions in microns wave length are given at peak portions. Composition in wt % is given at the end of each spectrum.

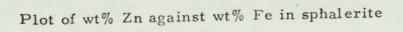
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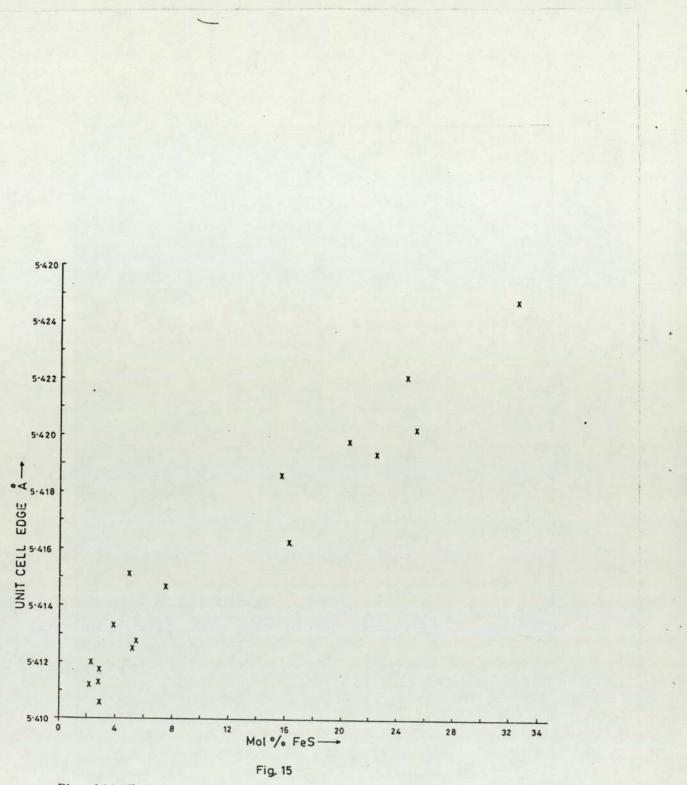






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ä

Plot of Mol% FeS against unit cell edges of sphalerite

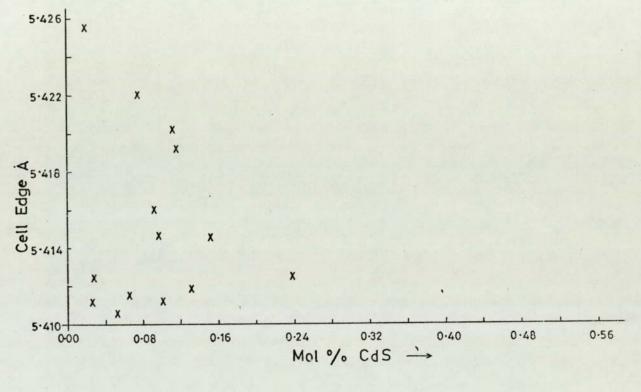
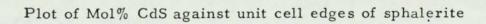
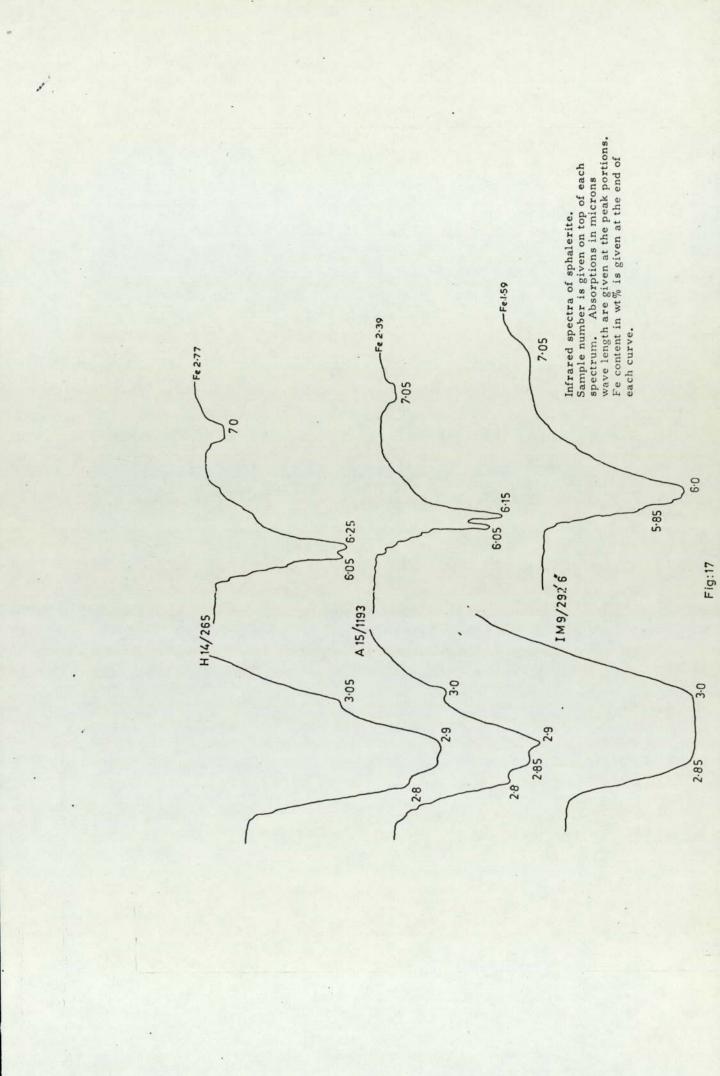
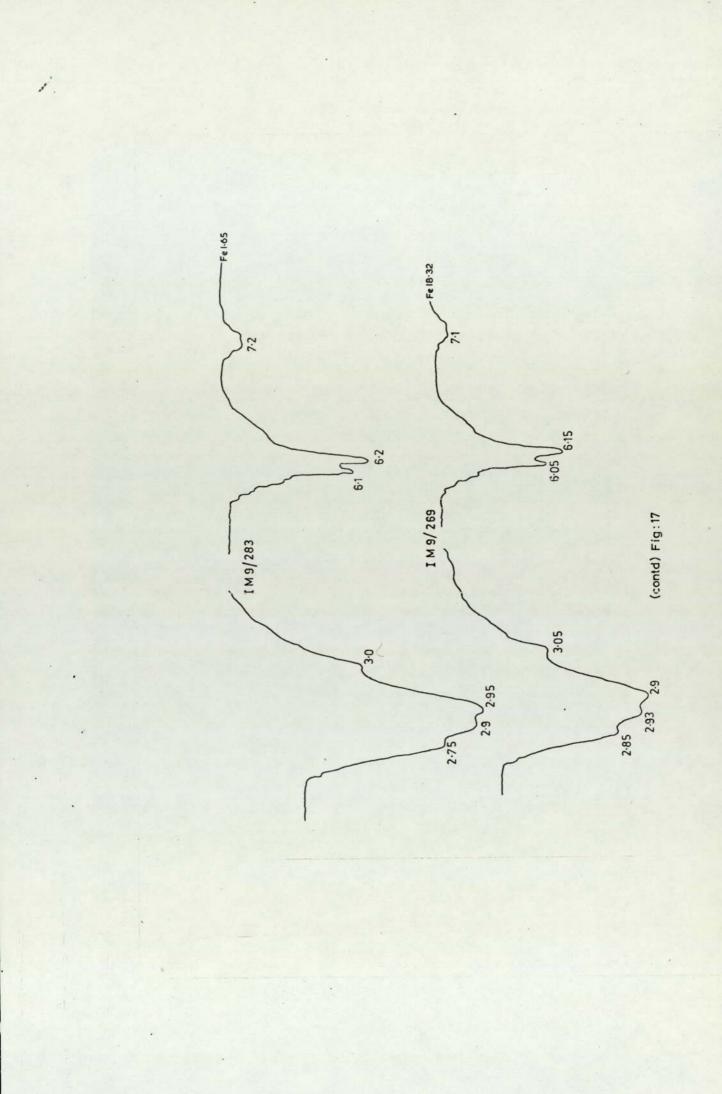
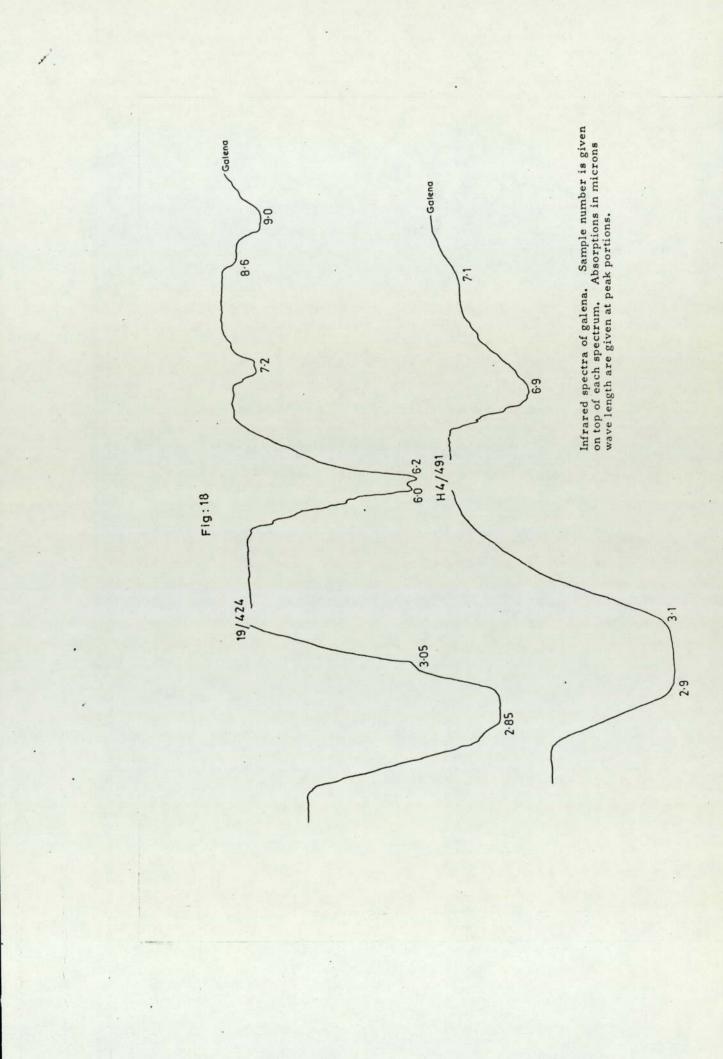


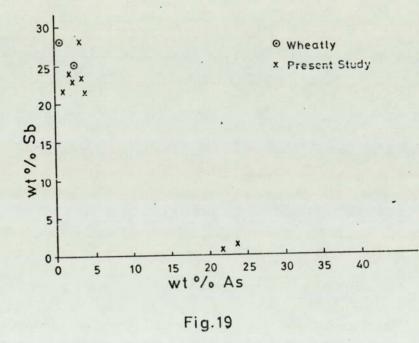
Fig. 16



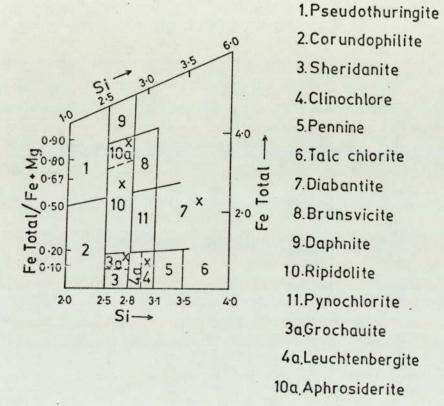






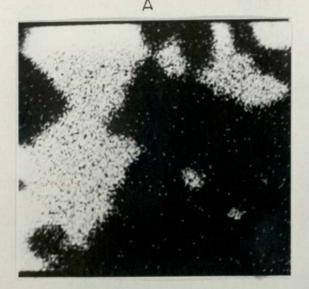


Plot of wt% Sb against wt% As in tetrahedrite-tennantites showing the compositional break.

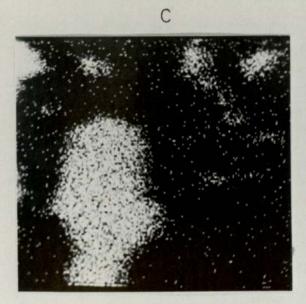


Orthochlorites showing the species and variety boundaries (after Hey, 1954) X - shows the Parys Mountain Species





В



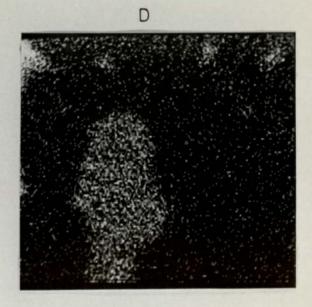


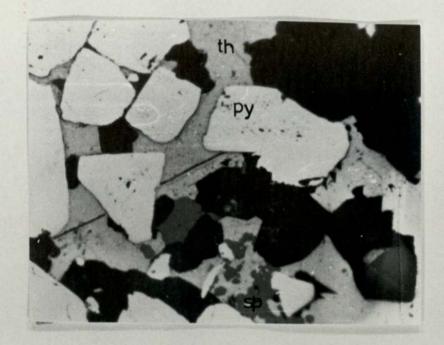
PLATE IV

Plate IV X-ray images

A-B Tetrahedrite in sample 27-145

- A Sb La
- B As K
- C-D Tennantite in sample 27-145
- C As Kx
- D Sb Lx

PLATE III



B

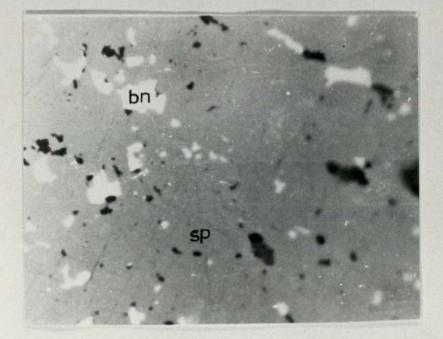
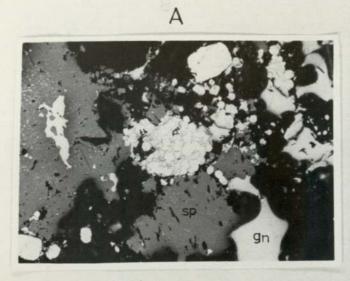
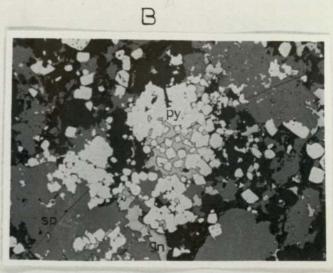


Plate III Photomicrographs

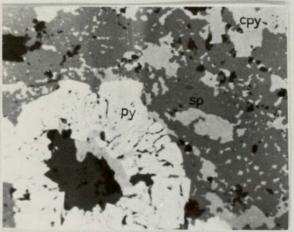
- A Sample from bore hole 27 at 145 feet depth. Tetrahedrite (th) forming the interstitial and fracture infillings of pyrite. 16 x (air)
- B Sample from bore hole H4 at 465 feet depth. Sphalerite (sp) with inclusions/infillings of bournonite (bn). 40 x (oil)

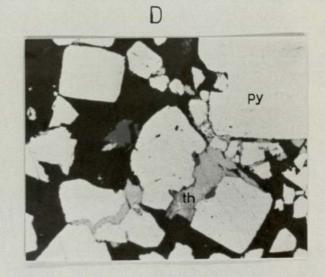
PLATE II













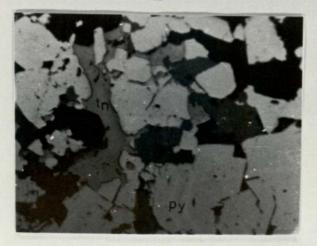
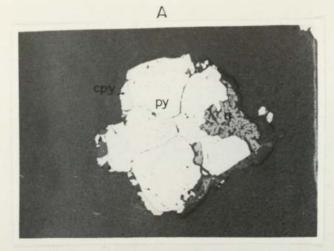


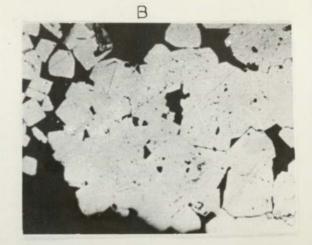
Plate II Photomicrographs

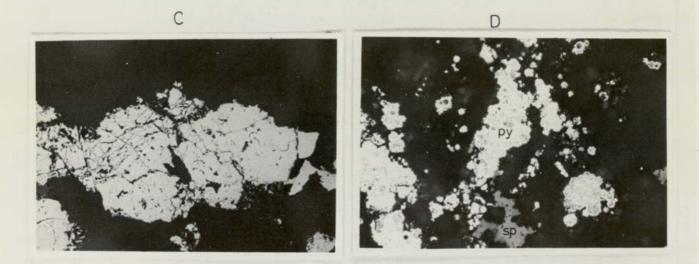
- A-B Sample from bore hole H4 at 474 feet depth. Sphalerites (sp) showing intergrowths with galena (gn). Galena and tetrahedrites forming interstitial matrix for pyrites. $16 \times (oil)$
 - С Sample from bore hole IM6 at 1392 feet depth. Pvrite (py) showing the radiating texture. Chalcopyrite (cpy) and sphalerite (sp) show intergrowth textures. Chalcopyrite is also seen replacing the core of the pyrite and filling in its fractures. 16 x (air)
 - D Sample from bore hole 27 at 145 feet depth. Tetrahedrite (th) forming the interstitial and fracture infillings of pyrite. 16 x (air)
 - E Sample from bore hole 27 at 145 feet depth. Pyrite (bottom centre) showing zoning. Tennantite (tn) is filling in the interstitial spaces of pyrite.

16 x (air)

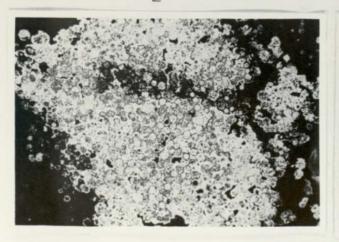
PLATE I

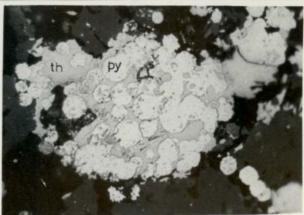






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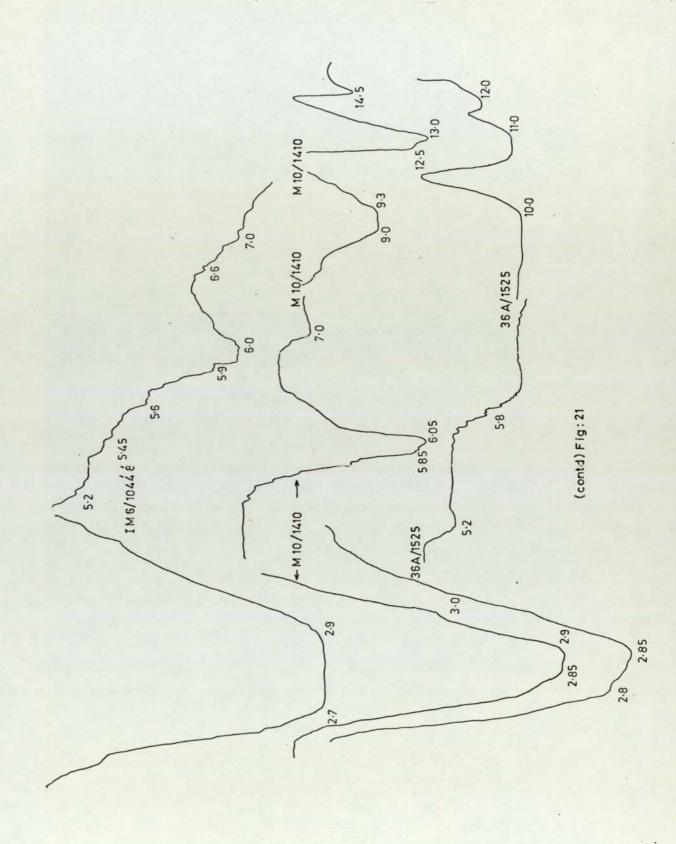


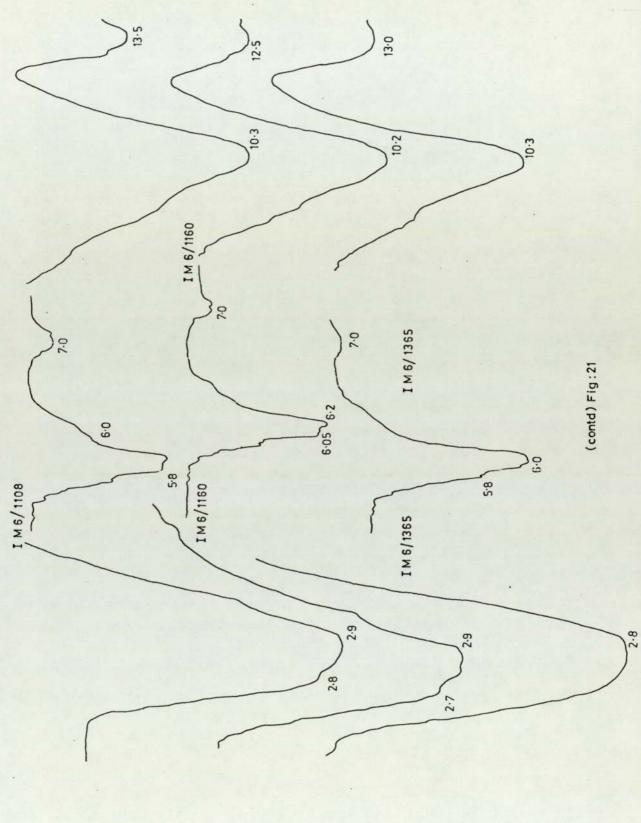


F

Plate I Photomicrographs

- A Sample from bore hole 32 at 1198 feet depth. Pyrite (py) associated with rutile (rt). Chalcopyrite rims pyrite and replaces it at grain boundaries. 4 x (air)
- B Sample from bore hole 27 at 145 feet depth. Aggregate
 of euhedral pyrites homogenised at the centre of the
 aggregate but retaining the cubic outlines at the periphery.
 4 x (air)
- C Sample from bore hole A 15 at 1193 feet depth. Pyrite showing intense fractures developed due to cataclasis. 4 x (air)
- D Sample from bore hole H 4 at 464 feet depth. Framboidal pyrites (py) forming clusters. Sphalerite (sp) is also seen.
 16 x (oil)
- E Sample from bore hole H4 at 464 feet depth. Framboidal pyrites showing atoll textures with tetrahedritetennantite forming the interstitial infillings. 16 x (oil)
- F Sample from bore hole H4 at 474 feet depth. Framboidal pyrites (py) with interstitial infillings of tetrahedrite (th). 16 x (oil)





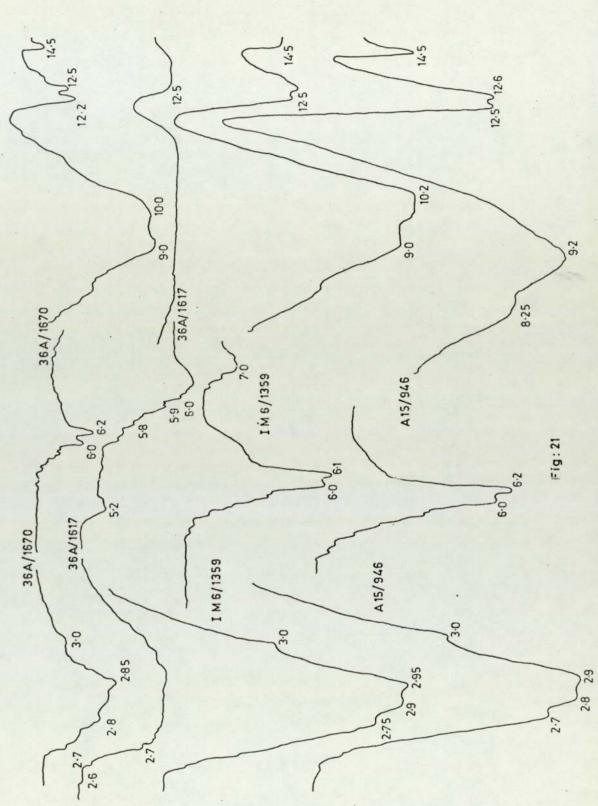


Fig. 21

Infrared spectra of chlorites. 36A/1670, A15/946, M10/1410 Ripidolite 36A/1617, IM6/1044'8" Diabantite IM6/1359, 36A/1525 Chlorite 1b IM6/1365 Aphrosiderite and grochauite IM6/1108, IM6/1160 Chlorites (species not identified)

Sample number is given on top of each spectrum; absorptions in microns wave length are given at the peak portions.

GEOCHEMISTRY OF SOME SULPHIDES AND SULPHO-SALTS FROM PARYS MOUNTAIN, ANGLESEY

by

C. SIVAPRAKASH

A thesis submitted to the University of Aston in Birmingham in partial fulfillment of the requirements for the award of the degree of Master of Philosophy

May, 1977

Geochemistry of some sulphides and sulpho-salts from Parys Mountain, Anglesey.

C. Sivaprakash (Candidate for the M. Phil. degree, May, 1977)

SUMMARY

Sulphide mineralisation occurs at Parys Mountain, Anglesey, associated with Ordovician and Silurian sedimentary and volcanic rocks. Pyrite, chalcopyrite, sphalerite and galena are the sulphide minerals with minor quantities of arsenopyrite and pyrrhotite. Tetrahedritetennantites, and Pb and Bi sulpho-salts also occur as interstitial and fracture infillings in sulphides, mainly in pyrite. Pyritic mineralisation shows conformable features with the host rocks, whereas other sulphides and sulphosalts show epigenetic features.

Sulphides have been analysed for essential and trace elements namely Fe, S, Cu, Pb,Zn,Co, Ni, Ag, As,Sb,Sn,Ba,Mo,Te,Cd,Mn and Bi. Sphalerite and galena are comparatively more enriched in trace elements than pyrite and chalcopyrite. The Co/Ni ratio in pyrites is generally greater than 1.00, suggesting that the deposits are related to volcanism. Substantial quantities of Fe are present in sphalerites in solid solution.

Sulphosalts have been quantitatively identified by electron microprobe analysis to be tetrahedrite-tennantites, bournonites, kobellite, galenobismutite and lead sulpharsenides.

Unit cell edge measurements of sphalerite have been made by X-ray and electron diffraction, and a good linear relationship between mol%/ FeS and unit cell edge is shown. Microhardness, reflectivity, infrared and d.t.a. data for sulphides are given - attempts to correlate the physical-optical characteristics with composition resulted in no significant conclusions, except the relation between microhardness and Fe content in sphalerite.

Diabantite, ripidolite, grochauite, clinochlore and aphrosiderite are the chlorite species occurring in the matrix associated with sulphide minerals; chlorite (1b species) has been identified in the matrix where no sulphide minerals occur.

The mineralogical and chemical results in the present study are interpreted to show that the mineralisation at Parys Mountain is a volcanogenic sedimentary process later enriched by hydrothermal processes.

Key words:

Sulphide mineralogy, composition, trace-elements, sulpho-salts.

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I am indebted to Dr N. F. M. Henry, University of Cambridge for kindly editing the draft during my absence on field work in India, and to Mrs J. Woodman for typing the whole thesis.

> C. Sivaprakash 4 May 1977

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(iv)

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CHAPTER 1

INTRODUCTION

1.1 Geology of Parys Mountain

Parys Mountain lies in the north-east corner of Anglesey (Fig. 1) in North Wales. Situated about 4 km south of Amlwch port it forms a prominent topographical ridge aligned in ENE-WSW direction, rising to over 150m above sea level.

The geology of Parys Mountain has been studied by many investigators for a number of reasons. Structurally and stratigraphically it is a very complex area (Manning, 1959; Bates, 1966) and hence the relationship between its sedimentary and volcanic rocks has been variously interpreted. Its mineral deposits have been compared with other mining fields in the southern Caledonides, such as Avoca (southeastern Ireland), and Coniston (Lake District), because of similar age and comparable tectonic and stratigraphic positions (Williams, 1969; Fitton and Hughes, 1970; Wheatly, 1971a, b). It has a close analogy in its depositional environment to other conformable polymetallic deposits (Wheatly, 1971a), and the close relationship between mineralisation and petrology, especially the volcanic succession of the area, has been well exemplified (Thanasuthipithak, 1974).

The most comprehensive and detailed account of the geology of Parys Mountain was given by Greenly (1919). Later various aspects of its geology, namely stratigraphy, structure, lithology, and mineralisation, were described by Manning (1959), Derry (1961), Bates (1964, 1966), Hawkins (1966) and Wolfenden (1967) - in Thanasuthipithak (1974), Williams (1969), Wheatly (1971a, b) and Thanasuthipithak (1974). A simplified geological map after Thanasuthipithak (1974) is given as Fig. 2.

The general stratigraphic sequence and lithologies proved from the bore holes, and described by Hawkins (1966) and Thanasuthipithak (1974) is given in Table 1.

Parys Mountain is underlain by the Precambrian Mona complex (Fig. 2) which is represented by chlorite schists in the northern and eastern parts of the area, and by micaceous granitoid and quartzitic gneisses in the south. The Ordovician, best exposed in the northern side of the mountain consists entirely of Shales (Table 1). They were named as Parys Green Shales by Greenly (1919), Parys Shales by Hawkins (1966) and 'Slates' by Thanasuthipithak (1974) as they possess a well developed slaty cleavage.

Silurian rocks form the core of the mountain (Fig. 2) and consist of highly cleaved and silicifed shales. Surrounding the core, except to the east, are exposures of highly silicified and sheared rocks forming a hair-pin shaped outcrop. These were called 'Felsites' by Greenly (1919) and were considered by him to be intrusive. Thanasuthipithak (1974) described these felsitic rocks as a succession of extrusive volcanic rocks of Ordovician age consisting of dacitic and rhyolitic volcanic fragmental rocks and some siliceous sinter, a similar conclusion to that of both Hawkins (1966) and Wheatly (1971).

The rocks of the Precambrian Mona Complex are thrust over younger rocks along several low angle thrust faults called the Carmel Head, Corwas, and Nebo Thrusts (Fig. 2).

Although the structural relationship between shales and 'felsitic' rocks and the resultant structure of Parys Mountain has been variously interpreted, it is now generally agreed that the structure is an east-north-easterly trending, single syncline overturned to the north, with shales in the core (Fig. 3) (Thanasuthipithak, 1974).

1.2 Mineralisation

The mineralised belt trends between 060° and 070° following the general strike of the enclosing strata and dips 30-50° to the north. It extends for some 1500 m, and is some 400 m wide and has been worked to a depth of 300 m. The mineralisation occurs as a series of lenticular to tabular ore zones, in the folded sequences of Ordovician and Silurian sedimentary and volcanic rocks. The mineralisation is generally concentrated on both sides of the northern outcrops of the rhyolitic rocks. It is present both in the rhyolitic rocks and in the rocks which are in contact with them, namely the siliceous sinter, parts of the Ordovician slates in the north, and the Silurian slates on the south side of the northern limb (Fig. 4) (Thanasuthipithak, 1974). Based on the host rock and the mineralogy, four types of ores were distinguished by Wolfenden (1967) (in Thanasuthipithak, 1974), and a slightly different division was given by Wheatly (1971a). The former division is made use of in the present study. These ore types are given in Table 2 and the lodes in which they occur are shown in Fig. 4.

The origin of these mineral deposits was regarded by earlier workers to be epigenetic, based on the notion that the 'felsite' was intrusive and probably supplied hydrothermal ore-bearing fluids. Deposition was thought to have been modified by metasomatic pyritization,

chalcopyritization and some lead-zinc metasomatism (Greenly, 1919; Manning, 1959). The controls of ore deposition were thought to be both shear zones and lithological interfaces.

Wheatly (1971a, b) suggested that, at Parys Mountain as well as in other mining fields in the southern Caledonides (Avoca, south-east Ireland; Coniston, Lake District), the conformable lenticular, pyritic zones associated with volcanic sequences, reacted with later hydrothermal fluids to produce the complex galena-sphalerite-pyrite mineralization. He further suggested that the mineralisations in these fields, including Parys Mountain, have a pulsatory metasomatic sequence related to tectono-stratigraphic controls. The ore localisation was thought to have been controlled by suitable structures and the pyritic shale horizons. Thus, Wheatly concluded that the main mineralisation was of an epigenetic hydrothermal enrichment type on a 'prototype' syngenetic mineralisation.

Thanasuthipithak (1974) studied the relationship of mineralisation to petrology and concluded that because there was a close association of ore bodies as lenses and tabular bodies, generally conformable with the Ordovician volcanic host rocks, they could be interpreted to have synsedimentaryexhalative origin. According to him the deposits were later modified by remobilization of some sulphides to produce apparent epigenetic features during the Caledonian orogeny.

1.3 Summary of geological events at Parys Mountain

The main geological events including the mineralisation at Parys Mountain, according to Thanasuthipithak (1974), are a) Deposition of Ordovician sediments in a marine environment with volcanism producing acidic rocks, b) Continued Ordovician sedimentation with some mineralisation, c) Main stage volcanism with some mineralisation, d) Erosion, submergence and deposition of Silurian sediments, e) Deformation of sediments and volcanics during the Caledonian and Variscan orogenies along with remobilization of the sulphides.

1.4 The present investigation

It is hoped that further mineralogical and geochemical studies on sulphide minerals can supplement geochemical information and thus help the various interpretations on the genesis of Parys Mountain mineral deposits. Previous interpretations were based on structural, petrological and mineralogical observations and no investigation of the geochemistry of the ore minerals was made. Similarly no systematic and detailed

investigations of the composition of the ore minerals, trace element distribution patterns, partition behaviour of trace elements, if significant, have been made, and although sulpho-salt minerals were recognised, no quantitative determination of them have been made. Also no previous correlation has been done relating the observed quantitative and qualitative reflected light properties of the opaque minerals with composition.

In fact, there are only a few areas in the British Isles where the major and trace element geochemistry of the ore minerals has been investigated to interpret the metallogenesis. El Shazly (1951), El Shazly et al (1957), Bishara (1966), Kakar (1971) were the few to make systematic investigations on trace elements in sulphide minerals mainly sphalerite and galena. Trace elements in pyrite, chalcopyrite, sphalerite and galena mainly from Avoca and a few from the Parys Mountain, and Coniston areas were studied by Wheatly (1971a) who showed a similarity in trace element in all these areas. The geochemical investigations at Parys Mountain by this author were however not detailed and systematic. He also pointed out that work in progress on the geochemical atlas of Great Britain has delineated an anomalous tin area associated with copper at Parys Mountain, the explanation for which is not properly understood.

The present study was a systematic one of the geochemistry of the ore minerals and some of the physical and optical characteristics of the sulphide minerals. To this end studies were made using electron probe microanalysis, atomic absorption spectrophotometry, X-ray diffraction, electron diffraction, quantitative and qualitative reflected light microscopy, infra-red spectroscopy and differential thermal analysis.

CHAPTER 2

MINERALOGY AND PARAGENESIS

2.1 Introduction

The mineralogy and paragenesis of sulphide and sulpho-salt minerals from Parys Mountain has been described by both Wheatly (1971a) and Thanasuthipithak (1974). A description of the textural and paragenetic features observed in 58 polished sections from bore holes not previously studied (bore hole numbers A15, 27, 19, 36A, 32; mainly of pyritic and Bluestone ore types) is given here in addition to descriptions of those observed in some sections previously studied by Thanasuthipithak (1974). Textural features and optical characters of the opaque minerals were examined in reflected light using a Reichert Zetopan Ore Microscope with a micrometer ocular for grain size measurement.

Pyrite is the most abundant of the sulphides followed by chalcopyrite, sphalerite, galena and minor quantities of microscopically identifiable tetrahedrite-tennantite, arsenopyrite, pyrrhotite, lead and bismuth sulphosalts. Megascopically the specimens studied show 4 or 5 distinct forms. The general features of these forms and the corresponding ore types are summarized in Table 3, and Fig. 5 shows sketches of these forms. 2.2 Microscopic features

Only primary minerals are described here, although some secondary minerals, such as covellite and bornite, have been described by Wheatly (1971a) and Thanasuthipithak (1974). A list of ore minerals present, and their general characters are presented in Table 4. Pyrrhotite, from Parys Mountain, has been described by Wheatly (1971a) and Thanasuthipithak (1974), and arsenopyrite has been described by the latter author, but in the present study only their compositions have been determined and these are given in Chapter 3.

2.2.1 Pyrite

Pyrite is the most abundant of all the sulphides, and is most abundant in the pyritic ore type, being present both in the layered sulphide and in disseminated forms, and is relatively least abundant in the Bluestone Ore type. Pyrite grains show both primary fabrics, representing the original depositional features, and secondary fabrics representing deformational and recrystallised features. Euhedral-subhedral, anhedral and framboidal type pyrite grains comprise the primary type. Colloform pyrite was also described by Thanasuthipithak (1974). Cataclastic, radial and recrystallised textures comprise the secondary type.

2.2.1.1 Euhedral-Subhedral pyrite

This type is mainly associated with black shale and dacite as disseminations through the rock. The following three divisions can be made: a) Isolated simple pyrite euhedra in which the grain size varies from about 0.05 mm to about 2 mm with some chalcopyrite replacement at the margins. Pyrite euhedra are associated with rutile and in some instances are seen to replace it (Plate IA). It is therefore paragenetically later than rutile. b) Spherically arranged aggregates of pyrite cubes forming pseudomorphs after framboidal pyrite. As many as 14 pyrite euhedra are present forming a spherically arranged aggregate of pyrite cubes homogenised at the centre of the aggregate but retaining their cube outlines at the periphery (Plate IB). c) Pyritohedra with intense deformation textures, the pyrite grains being heavily fractured (Plate IC). In most instances the fractures are filled by other sulphides.

2.2.1.2 Anhedral pyrite

Anhedral pyrite is less abundant than the euhedral/subhedral type. It is generally fine-grained (0.01 mm to 0.05 mm) and forms allotriomorphic granular aggregates commonly enclosing euhedral pyrite which implies a generation gap between the two types. 2.2.1.3 Framboidal pyrite

Framboidal pyrite was seen mainly in the Bluestone ore type associated with galena-sphalerite mineralisation. Generally three kinds of framboids are present:- a) Isolated framboid microcrysts ranging in size from 2 microns to about 40 microns in diameter. Quantitative studies of framboid grain size were made and the distribution is seen to be positively skewed (Fig. 6). The maximum occurs at 30 microns and the majority of the framboids occur within 15 microns diameter. The size distribution is similar in sections from the different bore holes. There is some clustering of framboids and a plot of the number of framboids per cluster against frequency (Fig. 6d) shows an iiregular pattern with the frequency maximum at 10 framboids/cluster. b) The second type has the framboidal grains in the form of a network whose interstices are infilled mainly by sulpho-salts. This feature was described as atoll texture (Thanasuthipithak, 1974) in which the framboidal grains are extensively replaced, enclosed, and cemented by tetrahedrites (Plate I E, F). c) The third type has the form of a recrystallised

aggregate. The framboids form clusters (Plate ID) and lose their form where they are joined. The loss of shape is attributed to the result of growth of later pyrite between the granules (Raybould, 1973).

In some specimens the core of the framboidal cluster is replaced by sphalerite, and in some instances by tetrahedrite. Radiating textures have also developed in some framboidal pyrites (Plate II C).

Some pyrite grains in the types described above are compositionally zoned (Plate II E). The radiating textures (Plate II C) and irregular fracturing (Plate I C) exhibited by some pyrites are interpreted as resulting from cataclasis. In most specimens the fractures are infilled by other minerals namely sphalerite, and tetrahedrite-tennantites. Pyrite is comparatively free from inclusions; however, in some grains, small quantities of chalcopyrite and some gangue material are present as inclusions.

Pyrite occurs in minor quantities as fine-grained anhedral to subhedral grains forming a distinct vein or fracture filling in the matrix. 2.2.2 Chalcopyrite

Chalcopyrite most commonly is anhedral in form. It occurs: a) as a fracture filling in and replacing euhedral to subhedral pyrites; b) as a matrix material enclosing the pyrite grains; c) as mutual intergrowths with sphalerite, galena and pyrite; d) isolated anhedra embedded in rock matrix; and e) as exsolution bodies in sphalerite. Little chalcopyrite is associated with euhedral pyrite with most being associated with other kinds of pyrite and with other sulphides.

Chalcopyrite, where it is associated with pyrite generally replaces it. It is replaced by sphalerite although there is depositional overlap shown by intergrowths with sphalerite and galena.

2.2.3 Sphalerite

Sphalerite most commonly occurs in the fine-grained Bluestone ore type. The grain size varies between 0.02 mm to 0.5 mm. It is present as anhedral and irregular grains intergrown with other sulphides mainly chalcopyrite, and in lesser quantities filling fractures in cataclastic pyrite.

Two types of sphalerites are recognised: a) sphalerite with exsolutions of chalcopyrite and b) sphalerite without exsolutions. The first type is far more abundant than the second. Both the types are intergrown with chalcopyrite. Bournonite is found as inclusions or

infillings in sphalerite. Sphalerite generally shows mutual replacement textures and intergrowths with galena (Plate II A and B) and this is interpreted to indicate co-deposition.

2.2.4 Galena

Galena is present mainly in the Bluestone ore and Copper ore types and is not present in the Pyritic ore type. The grain size varies from 0.05 mm to 0.2 mm. It forms allotriomorphic masses and most commonly is intergrown with sphalerite and chalcopyrite.

Mutual replacements of sphalerite and galena are also present. A little galena, however, clearly replaces sphalerite, and paragenetically is therefore later. Inclusions or infillings of some sulphosalts are present in galena.

2.2.5 Tetrahedrite-tennantite

The tetrahedrite group is the most abundant of the sulpho-salts at Parys Mountain and it is found only in the Bluestone ore type. These minerals occur as a) fracture fillings in pyrite grains (Plate II D); b) an interstitial cementing matrix for some subhedral pyrite grains (Plates II E and III A); c) inclusions in some sphalerites and chalcopyrites along the peripheries of, and extensively replacing, pyrite framboids. The tennantite end member has a lower reflectivity value than that of tetrahedrite. The tetrahedrite has a reflectivity of between 34.3 and 36.5% at 589 nm in air, and tennantite between 29.5 and 31.7%. The microhardness value ranges 279-328 Kg/mm² for both minerals and their grain size varies from 0.005 mm to 0.01 mm. 2.2.6 Bournonite

Bournonite occurs as very small (grain size 30 microns) inclusions in sphalerite (Plate III B). The reflectivity is generally high (38 - 42%) but could not be precisely estimated because of the very small grain size. 2.2.7 Lead Sulpharsenides

These minerals generally are very similar to galena and it is very difficult to distinguish between them optically. They are distinguished from galena only by an absence of cleavages and triangular pits and by anisotropism (seen only in oil immersion). Electron microprobe analysis showed these minerals to be lead sulpharsenides. They are white in colour, have irregular shapes and generally occur replacing sphalerite and galena along with other sulpho-salts. The reflectivity values are similar to those for galena (about 39.3 - 43.5%) and the

microhardness was not determined because of the very small grain size (about 0.05 mm).

2.2.8 Bismuth sulpho-salts

These are very similar in appearance to the lead sulpho-salts; however, they have a more greyish white colour, are more anisotropic, and the reflectivity (34.5 - 37%) is slightly lower than that of the lead sulpharsenides. They were identified, from electron microprobe analyses, as kobellite and galenobismuthite. Grain shapes are anhedral and irregular and they are generally present only as infillings in other sulphides mainly sphalerite and pyrite.

Mutual replacements between the sulpho-salt minerals are absent and it is difficult to infer paragenetic differences between them. The occurrence as inclusions, and as interstitial infillings in sulphides, is interpreted to indicate that they are later than the sulphides.

2.3 Textural features

The textural relationships outlined fall into two distinct categories. To distinguish between them, here they are called: a) Primary fabrics - developed in the original precipitation or depositional processes, and b) Secondary fabrics - developed either superimposed on an original primary fabric (e.g. cataclastic texture in pyrite) or formed due to some epigenetic process (e.g. fracture infilling of sulpho-salts in pyrite). The two types of fabrics are summarized in Table 5.

2.4 Paragenesis

A simplified paragenetic diagram for the ore minerals, based on the textural relationships outlined above, is presented in Table 6. This is in general agreement with that of Wheatly (1971a) and that of Thanasuthipithak (1974). It should be noted that the information on pyrrhotite and arsenopyrite is from Thanasuthipithak (1974). 2.5 Stratiform features of Parys Mountain ores

Stanton (1972) described stratiform ores as those that occur as layers concordant with the stratification of the enclosing rocks. They are thus confined stratigraphically snd occur in preferred horizons. A comparison of mineralogical features of Parys Mountain ores with those of New Brunswick described by Stanton (1959, 1960 Parts I and II) as a typical conformable stratiform deposit brings out the following coincident features:-

- a) Imperfect alignment of ore lenses parallel to the bedding plane or schistosity
- b) Dominance of pyrite as iron sulphide with pyrrhotite being very local and minor
- c) Dominance of sphalerite among non-ferrous minerals
- d) Galena, although important, is subordinate to sphalerite
- e) Presence of trace quantities of minerals such as arsenopyrite, tetrahedrite-tennantite and other sulpho-salts.

Further the close association of the ores with pyroclastic volcanic rocks, tuffs and siliceous sinter as one of the stratiform type characters (Stanton 1960 Part I) can also be demonstrated in case of Parys Mountain ores (Thanasuthipithak, 1974).

Stanton (1964) considered that the textural features observed in stratiform ores are not depositional but result from growth during diagenesis and metamorphism. This is supported by experimental studies (Stanton and Gorman 1968). This hypothesis can explain the isolated uninhibited growths of euhedral and framboidal pyrites and intergrowths of other minerals with mutual boundary configurations. It cannot, however, account for fracture and interstitial infillings because of the fact that availability of mineral matter at such vacant spaces cannot be a coincidence, but it is a depositional feature along the available channel ways.

At Parys Mountain, the association of mineralisation with characteristic acidic volcanic rocks, megascopic conformable characters, mineralogical assemblages, close similarities to well established stratiform deposits such as Avica, all point to the fact that it is a synsedimentary stratiform conformable mineralisation. Replacement fabrics and fracture and interstitial infillings, favour some deposition at a later date superimposed on the original minerals as a later process of epigenesis. Pyrite represents the major conformable mineralisation with a little chalcopyrite. Microscopic evidence suggests that the minor sulphides and sulpho-salts were deposited at a later date as a process of epigenesis.

CHAPTER 3

SULPHIDE INVESTIGATIONS

3.1 Introduction

The essential and trace element contents of the sulphide minerals and their physical and optical characteristics, namely the reflectivity, microhardness, infra-red spectra and differential thermal analysis were determined to see if they could be correlated with composition and/or to compare with the published data. Table 7 lists the techniques employed and the nature of information obtained from the various minerals.

Samples for the present study were obtained from diamond drill cores, and selection and preparation techniques are described in Appendix 1.

Analaysis for essential and trace elements was done by Atomic Absorption Spectrophotometry (A. A. S.) and Electron Probe Microanalysis. Fe, Cu, Zn, Pb, Co, Ni, Mo, Ba, Cd and Te were analysed by A. A. S. This technique was used because of its high sensitivity and minimum interference from other elements for the elements determined (McLaughlin, 1967; Volborth, 1969) and its simplicity and rapidity of operation (Kahn, 1968; Angino and Billings, 1972). A Perkin Elmer model 460 Atomic Absorption Spectrophotometer was used for all analyses. Details of the technique and sample solution preparation method are given in Appendix 2.

Electron Probe Microanalysis was used to analyse the more finely grained sulphides which could not be recovered in the powdered form, and for the quantitative determination of the sulpho-salt minerals. Some 74 analyses were made on various sulphides and sulpho-salts from some 43 polished sections (Tables 8-12) for the elements Fe, S, Cu, Pb, Zn, Co, Ni, As, Sb, Bi, Mo, Sn, Ag, Cd, Mn and Se. Instrumental and analytical details are given in Appendix 2.

Techniques for reflectivity, microhardness measurements, and sample preparation, along with instrumental details of infra-red and differential thermal studies are given in Appendix 2.

3.2 Pyrite

3.2.1 Composition

Pyrite (FeS₂) has a theoretical composition of 46.6 wt% Fe and 53.4 wt% S. Specimens of euhedral, subhedral, anhedral, and

framboidal pyrites were analysed for both essential and trace elements by electron microprobe and atomic absorption spectrophotometry and the values are given in Table 8. S was not determined in the samples analysed by the latter technique. The mean, minimum and maximum values are given in Table 13. The Fe content was found to fall in the range from 43. 16 to 48.25%, with a mean value of 45.01% which is lower than the theoretical one. The S content ranges from 52.35 to 55.38% with a mean of 54.14% which is slightly higher than the theoretical value.

Trace quantities of Cu, Pb, and Zn are present in nearly all the samples analysed. Cu is a common trace element in pyrite, and in the present study the majority of the samples contain less than 2000 ppm of Cu. The high quantities 1.08% and 1.27% of Cu measured in samples H 14/186, and A 15/971 respectively (Table 8) are probably due to some slight contamination by chalcopyrite. Pb and Zn have a similar distribution pattern with mean values close to each other (Mean Pb 482 ppm and mean Zn 528 ppm). The samples analysed by A. A. S. were free from galena and sphalerite and the analysis in the electron microprobe was done only on pure pyrite grains. Therefore Pb and Zn are probably present in solid solution. Zn, however, is not unexpected in pyrite as Fe and Zn commonly substitute for one another in many minerals.

Co and Ni were present in nearly all the samples. Co substitutes for Fe in the pyrite structure (Rankama and Sahama, 1950), and Ni can exist in solid solution in pyrite (Fleischer, 1955). In the present study these two elements were found in almost all the samples analysed by A. A. S., but they were present in quantities below measurable limits in the samples analysed by probe. Analysis by A. A. S. showed the Co content to range from 30 to 2075 ppm (Table 8) with the majority of the samples containing less than 800 ppm. Although the distribution of Ni is irregular it has the comparatively narrow range of 16-696 ppm. The Co content is thus generally higher than that of Ni.

The Co/Ni ratios determined are given in Table 8. The majority of them show Co/Ni ratios to be greater than 1. High Co values and a Co/Ni ratio > 1 were found to be characteristic of pyritic deposits associated with volcanism (Loftus-Hills and Solomon, 1967). Those deposits in which the Co/Ni ratio is < 1 for pyrites are considered to

be sedimentary in origin. Hawley, and Gavelin and Gabrielson, (in Fleischer, 1955) found separately that the Co content and the Co:Ni ratio were generally high in high temperature deposits. Analysis of Parys Mountain pyrites by Wheatly (1971a) showed a high Co content and Co/Ni ratio > 1.00 and so he concluded the deposits to be associated with volcanism. In the present study, since the majority of the samples showed a consistent Co/Ni ratio > 1.00 it is concluded that pyritic mineralisation is related to volcanism at Parys Mountain.

Notable quantities of As have been reported in pyrite (Rankama and Sahama, 1950). However, in the present study probe analyses showed As to be present in quantities below measurable limits except in 3 samples where it is greater than 0.1% (Table 8).

Cd occurs in pyrite in lower concentrations than in sphalerite (Vlasov, 1964). In the present study only about 40% of the samples analysed contain Cd and in quantities generally less than 1000 ppm.

Ba cannot usually substitute for Fe because of its larger ionic radius and is therefore not common in pyrite (Rankama and Sahama, 1950). In the present study, however, Ba was found in most of the samples analysed by A.A.S. although most of the samples contained below 500 ppm (Table 8).

Mo is not a common trace element in pyrite, though it was reported in syngenetic pyrites by El Shazly (1951). In the present study it was found in some 25% of the samples in quantities less than 500 ppm.

Te, because of physical and chemical similarities, commonly substitutes for S, and as much as 0.1% of Te has been reported in pyrites (Vlasov, 1964). In the present study the majority of the samples analysed by A. A. S. contain less than 200 ppm Te (Table 8). Te is relatively more common in pyrite than in other sulphides.

Other elements detected, although present in below measurable quantities by probe analysis, are Ag, Mn, Bi and in a few samples Se. Sb and Sn were looked for but were not detected.

3.2.2 Physical-optical characteristics

3.2.2.1 Microhardness

The microhardness values for the pyrites determined are given in Table 19. For a load of 100 gm Bowie and Taylor (1958) reported values of 1027-1240 kg/mm² for pyrite. Pyrite from Parys Mountain

has a hardness range of 1031-1483 kg/mm². Higher hardness values of 1186-1836 kg/mm² are quoted by Young and Millman (1964). The measurements made in the present study are thus well within this region. The indentations obtained were all fractured as has been observed by other authors. The weight percentages of Fe in pyrites were plotted against microhardness number (Fig. 7a); however, no relationship was found.

3.2.2.2 Reflectivity

Results of reflectivity measurements on pyrites in the wavelength region 400nm - 700nm at intervals of 20nm including 589nm are given in Table 23, and the spectral reflectivity profiles are shown in Fig. 6a. The profiles show a regular pattern generally increasing sharply with wave length until about 520nm and then increasing very gently (Singh, 1965). However, no significant differences could be observed with different types of pyrites namely the framboidal, euhedral, anhedral and subhedral pyrites (Fig. 8a). Reflectivity values at 589nm were plotted against weight percentage Fe in pyrite (Fig. 9a), but no conclusion could be drawn about their relationship.

3.2.2.3 Infrared studies

The infrared spectra produced for pyrite are given in Fig. 10. The pyrites show poor resolution, and this has been previously reported by Hunt et al (1950). The two absorptions shown by pyrite are in the wave length region 2.8-2.9 microns and 6.1-6.2 microns (Fig. 10). It can be seen in the figure that, compared to the sample A 15/924 which has Fe content of 43.98%, the two samples 36A/1617 and 32-1108, which have Fe content of 45.23% and 45.71% respectively, have more prominent absorptions in the wave length region 6.0-6.2 microns. In sample IM 6/1231, which has Fe content of 46.78%, the absorption in the wave length region 6.2 microns although more prominent than sample A 15/924, is less prominent than the other two samples. This probably indicates that variations in composition may have some role in the absorption patterns. 3.2.2.4 Differential thermal analysis (d.t.a.)

The d.t.a curves obtained for 6 pyrite samples are given in Fig. 11. Comparison with the curves obtained by Kopp and Kerr (1957) show that the present curves are in good agreement in that the pyrites show a broad exothermic peak in the region of 400-500°C. The endothermic

reactions are present at about 550°C. Samples studied have Fe content ranging from 43.19 to 46.78% but no significant differences in the exothermic or endothermic behaviour of these pyrites was observed. 3.3 Chalcopyrite

3.3.1 Composition

The theoretical composition of chalcopyrite in wt.percent. is 34.6% Cu, 30.4% Fe, and 35.0% S. In this study 19 samples were analysed and the results are given in Table 9. Out of these, 8 were analysed by A.A.S., and 11 by electron probe. Four samples analysed by the latter technique were also analysed by A.A.S. S was determined only in the probe analyses. The mean values for Cu, Fe and S of 34.53%, 29.62% and 35.78% (Table 14) respectively are close to the theoretical values given above, although there is a considerable range. The maximum frequency of Cu occurs in the range of 34-36%, Fe in the range of 29-31%, and S in the range of 36-37% (Table 9).

Zn was found in all the samples analysed, ranging from 1000 to 5600 ppm, with a mean around 1900 ppm; this is attributed to the closely associated sphalerite, which commonly occurs as small inclusions in chalcopyrite. However, chalcopyrite is structurally similar to sphalerite and some Zn may also be present in solid solution in the chalcopyrite structure.

As and Bi have been reported in chalcopyrite (Fleischer, 1955), and probe analyses in the present study show that most of the samples contain these two elements (Table 9). Three samples contain more than 0.1% As, and another 3 samples contain more than 0.1% Bi (Table 9). These samples are from the ore types in which arsenopyrite and bismuth sulpho-salts occur respectively. None of the samples which have a high As content contain arsenopyrite. The high As content does not result from contamination but probably is due to its presence in the structure of chalcopyrite. Bismuth sulpho-salts are present as very fine-grained minerals (Chapter 4) in some of the sections (H 4/491, IM 9/269) that have a high Bi content. Thus these minerals probably have contributed to the high Bi values in the form of tiny inclusions.

Co and Ni are present in most of the samples analysed. Analysis by A.A.S. showed that Co ranges from 60 to 710 ppm and Ni from 12 to 1060 ppm (Table 9). Trace quantities of Co and Ni are not unexpected

in chalcopyrite although Ni tends to be concentrated in pyrite relative to chalcopyrite (Vaughan 1971).

Cd commonly is present in chalcopyrite, although in lower quantities than in sphalerite, because of the structural similarities between them (Vlasov, 1964). Analysis by A.A.S. showed Cd to be present in the range of 98 to 446 ppm.

Pb was found in most of the samples analysed in the range of 313 to 1045 ppm.

Te was found in only a few samples, ranging from 55 to 192 ppm, probably substituting for S.

Ba (A.A.S. analysis) was found in quantities ranging from 165 to 1653 ppm, with a mean of 737 ppm. It is not a very common trace element in chalcopyrite and its presence in the chalcopyrites at Parys Mountain is difficult to explain.

Mo (A.A.S. analysis) was also found in some 50% of the samples, in quantities ranging from 28 to 510 ppm, with a mean of 217 ppm.

Ag, Mn, Sb, Se and Sn were all below the limits of measurement of the electron probe.

3.3.2 Physical-optical characteristics

3.3.2.1 Microhardness

Microhardness values measured for chalcopyrite are given in Table 20. This hardness range of $171-221 \text{ kg/mm}^2$ with perfect indentations, is in close agreement with that of 186-219 by Bowie and Taylor (1958). Weight %s of Fe in the chalcopyrites were plotted against microhardness number (Fig. 7b), however, as in the case of pyrite, the relationship is not pronounced.

3.3.2.2 Reflectivity

Reflectivity measurements for chalcopyrite in the wave length region 400-700nm including 589nm are given in Table 24. The spectral reflectivity profiles are given in Fig. 8b. Like pyrite, chalcopyrite also has a regular spectral reflectivity profile, generally increasing sharply with wave length until about 520nm and then increasing very gently. Reflectivity values at 589nm plotted against weight % Fe showed no relationship.

3.3.2.3 Infrared studies

The infrared spectra produced for chalcopyrite are given in Fig. 12.

Chalcopyrite has a poor resolution and one sample (A 15/1193) showed absorption in the vicinity of 6 and 7 microns region. In the two samples studied No. A 15/1193 has Cu 35.05%, Fe 32.37% and S 34.20% and the other (M 10/1521) has Cu 34.73%, Fe 27.73% and S 35.96%. The sample A 15/1193 has a very much higher Fe content than the other and this probably is responsible for its having a more pronounced absorption pattern in the region 2.85-2.9 and 6.0 microns regions. 3.3.2.4 Differential thermal analysis (d.t.a.)

The d.t.a. curves obtained for chalcopyrite are given in Fig. 13. The five samples studied showed marked exothermic behaviour in the vicinity of $450-460^{\circ}$ C. as part of a broad exothermic reaction starting at 400° C and continuing up to 500° C. No significant differences in differential thermal behaviour with compositional variations were observed. The sample with a lower Fe content (sample M 10/1521 with Fe content 27.73) than the others (which have Fe contents ranging from 28.55% to 32.37%), has a smoother curve. This is probably because reactions with higher Fe contents become more vigorous than those with lower Fe content. Further detailed investigations are necessary for significant conclusions.

3.4 Sphalerite

3.4.1 Composition

Sphalerite has a theoretical composition of 67.10% Zn and 32.90% S by weight, but in nature this is not found because the sphalerite structure is remarkably tolerant of substitutions by Fe, Cd and Mn for Zn. Nearly all natural sphalerites are diadochic compounds of ZnS with FeS (up to 42%), Cd (up to 2%), and MnS (up to 9%) (Boyle and Jambor, 1963). Both Zn and S can be isomorphously replaced by substantial quantities of other elements (Vaughan, 1971). The Fe content in particular has received a very considerable attention (Kullerud, 1953; Kalliokoski, 1959; Sims and Barton, 1967; Benson, 1960; Barton and Skinner, 1967; Campbell and Ethier, 1974; Williams, 1974). Trace elements in sphalerite have also been studied in greater detail than in any other sulphide.

In all, 22 sphalerite samples were analysed by electron probe and A.A.S. The Zn content was found to range from 51.68% to 64.74% (Table 10), with a mean of 58.46% (Table 15), and the S content ranges

from 32.23% to 38.66% with a mean of 35.29%. The Fe content ranges from 0.67% to 18.32% (Tables 10 and 11) with a mean of 6.42%. In addition to the analyses listed in Table 10, Fe and Cd were also determined using electron probe on 4 samples to enable calculation of the cell edges (discussed later).

There is a good antipathetic relationship between Zn and Fe content (Fig. 14) allowing the interpretation that Fe has substituted for Zn. The Fe content is believed to be present in sphalerite in solid solution and is not due to any contamination because most of the samples analysed were pure grains.

Cd was found in all the samples analysed in quantities ranging from 215 ppm (A.A.S. analysis) to 0.33% (probe analysis) (Tables 10 and 11).

Cu is present in all samples in quantities ranging from less than 0.1% to 2.75% (Table 10) as analysed by probe and A.A.S. The very high Cu contents of some samples can probably be attributed to submicroscopic inclusions or exsolutions of chalcopyrite, though the Cucontent of sphalerite is present in variable quantities (Rankama and Sahama, 1950).

Pb was found in some 11 samples ranging from 286 ppm to 1468 ppm (Table 10). However, this is probably due to intimate admixtures with galena as has been reported elsewhere (Fleischer, 1955).

Co has been reported in sphalerite and in a very few instances Ni also has been reported (Fleischer, 1955). A.A.S. analysis of Parys Mountain sphalerites showed Co to be present in 5 samples ranging from 206 to 967 ppm and one probe analysis showed 0.1% of Co. Ni was found in 3 samples in the range of 340 ppm to 433 ppm.

Sb, As and Bi have been reported from sphalerites although in most instances only qualitatively (Fleischer, 1955). As and Bi are present in trace quantities (below 0.1%) in most of the Parys Mountain sphalerites analysed by probe, although 4 samples contained more than 0.1% As, and another two more than 0.1% Bi (Table 10). Sb was not detected. It is likely that these quantities are from sulpho-salts containing As and Bi admixed in the sphalerites.

Mn is present in most samples but below measurable limits (0.1%) by electron probe, and in only 3 samples was it found to be more than 0.1% (Table 10).

Ba was found in the samples analysed by A.A.S. ranging from 174 to 7222 ppm (Table 10). As in the case of other sulphides its presence is unexplained.

Mo was found in trace quantities and in a few instances more than 0.1% (Table 10).

Ag and Sn were found not to be present by electron probe. 3.4.2 Unit cell edge measurements of sphalerite

In the present study the reason for the measurement of unit cell edges was two-fold: 1) To investigate whether there is a linear relationship between Fe content and measured cell edges of sphalerite by X-ray diffraction; 2) To investigate the possibility of using a single crystal electron diffraction technique to obtain Fe content in the same way as in X-ray diffraction, if confirmed that there is a linear relationship between cell edge and Fe content.

Kullerud (1953) reported that the effect of FeS (and the other common trace impurities MnS and CdS) is to cause an increase in the unit cell dimensions in a linear way. This then allows for accurate measurements of cell dimension to be used as an indicator of Fe content. Skinner (1961) presented an equation for this:

a = 5.4093 + 0.000456 X + 0.00424 Y + 0.00202 Z where X, Y and Z are the contents of FeS, CdS and MnS in mol% and a is the cell edge in angstroms. Krause, and Van Aswegen and Verleger (in Boyle and Jambor, 1963) have, however, reported that Fe content has no increasing effect on unit cell edge and Williams (1965) has argued that the equation is the least squares fit to the experimental data and is therefore subject to possible error. The concept is, however, supported by Boyle and Jambor (1963) and by Evans et al (1968), and is used in this study.

The unit cell dimensions of 17 sphalerite specimens were measured using a Debye-Scherrer Powder Camera (114.59 mm diameter) fitted to a Phillips Norelco X-ray Diffractometer with Ni filtered CuK radiation ($\lambda = 1.5405$ Å). No correction for film shrinkage was applied and the diffraction patterns were measured on a Central Scientific Instruments' Linear Comparator with a vernier having a least count of 0.05 mm (Straumanis' method as described by Zussman, 1967). X-ray diffraction angles (9) calculated by this method were tabulated and the

interplanar spacings were read from tables. Corresponding hkl values were obtained from an X-ray diffraction data file (Berry, 1974), and unit cell edges calculated.

Unit cell edges of sphalerite were also calculated by substituting the mol% values of FeS, MnS and CdS in the equation by Skinner (1961). In general there is a good agreement between measured and calculated cell edges (Table 17) but there is a systematic trend of measured edges being greater than calculated edges, as also noticed by Evans et al (1968); Skinner 1961, found the opposite. A plot of measured cell edges against measured Fe content (mol% FeS) (Fig. 15) shows a good linear relationship between the two. This is interpreted to show that unit cell edge increases with increasing Fe content. The increase in cell edge at lower Fe contents is very pronounced, however, as higher values for Fe content are reached the rate of increase is less pronounced and the curve flattens out slightly. This observation is in agreement with the observations of Boyle and Jambor (1963), although it is a little less pronounced than that found by Evans et al (1968). It is concluded from these results that the accurate measurement of cell edge can be utilised to obtain FeS content. Mol% CdS plotted against cell edge showed no significant relationship (Fig. 16), because the electron probe was notable to measure accurately the trace quantities of Cd present in sphalerite. Mol% Mn was not plotted against cell edge as the data was insufficient.

Cell edge measurements were also made on 12 sphalerite samples by an electron diffraction technique for comparison purposes. Specimens were prepared using the technique described by McConnell (1967) and single crystal electron diffraction patterns were obtained using a Jeol JEM 100 E Transmission Electron Microscope at 100 kV. The diffraction patterns in each case were photographed and the 'd' spacings were calculated using the formula

$$d_{hkl} = c.f.$$

 γ_{hkl}

where d_{hkl} is the lattice interplanar spacing

 \mathbf{v}_{hkl} is the measured distance from origin 000 to spot hkl on the electron diffraction photograph. c.f. is the Camera Factor, a constant

provided (which depends on the camera length (L) and the wave length of the electron beam (λ) (c.f. = λ L).

hkl values were obtained from X-ray powder file and the cell dimensions calculated as in the case of X-ray diffraction.

The cell edges measured are given in Table 18 and it can be seen that all the electron diffraction measurements are higher than those from X-ray diffraction. This is a systematic error in the electron diffraction measurements, probably resulting from an inaccuracy in the assumed Camera Factor. The accuracy could be improved by estimating this Camera Factor at the time of measurement by using an internal standard. Provided an internal standard is used an electron diffraction technique for cell edge measurement has many advantages: 1) It requires less sample than that required by X-ray diffraction; 2) Diffraction patterns can be obtained from several selected spots on a specimen and the Fe content obtained from several measurements might be used to indicate variations in Fe content within a specimen; 3) Diffraction patterns can be readily seen and photographed immediately and thus it is much quicker than X-ray diffraction; 4) Very sharp reflections can be obtained, unlike X-ray powder patterns where measurements are sometimes inaccurate because of obscure reflections and blackening of the film in the back reflection region.

3.4.3 Physical-optical characteristics

3.4.3.1 Microhardness

The microhardness data for sphalerite show it to have a range of 148-240 Kg/mm² (Table 21). The weight % of Fe in sphalerite was plotted against microhardness number (Fig. 7c), because it had been noticed by previous workers that an increase in Fe content of sphalerite increased its microhardness (Young and Millman, 1964; Bishara, 1966; Vaughan, 1971). In the present study, a good linear relationship between Fe content and microhardness was seen (Fig. 7c). 3.4.3.2 Reflectivity

Results of the reflectivity measurements in the wave length region 400 nm-700 nm including 589 nm are given in Table 25, and the spectral reflectivity profiles are shown in Fig. 8c. Sphalerite in this study was seen to have maximum reflectivity in the wave length region 480-500 nm, as has been reported by Gray and Millman (1962) for sphalerites. In many grains little variation was observed with wave length, but generally the values decrease with increase in wave length. Reflectivity values at 589 nm plotted against weight % Fe in sphalerite (Fig. 9b) showed no significant relation.

3.4.3.3 Infrared studies

The infrared spectra for sphalerite are shown in Fig. 17, and compared with other sulphides, show good resolution. All the sphalerites show clearly two absorption peaks in the vicinity of 2.8-3.0 microns wave length. The 5 samples studied had Fe contents ranging from 1.59% to 18.32% (Fig. 17), and unlike pyrite and chalcopyrite, no differences in absorption patterns with varying Fe content were observed.

3.5 Galena

3.5.1 Composition

The theoretical composition of galena is 86.6 wt% Pb and 13.4 wt% S. Twelve samples were analysed, and the Pb content found to range from 80.15% to 87.15% (Table 12), with the majority of the samples containing between 82 and 86% Pb. All galenas analysed except one (A 15/1193) have a lower than theoretical Pb content, and have considerable As and Bi contents. The S content ranges from 13.85 wt% to 15.75 wt% (Probe analysis).

As, Sb and Bi are common trace elements in galena (Rankama and Sahama, 1950) and these elements were looked for in the specimens analysed by electron probe. As was found to range from 0.1wt% to 2.85 wt% with a mean of 1.48 wt%. Bi ranges from 0.27 wt% to 3.49 wt% with a mean of 1.58 wt% (Tables 12 and 16), and more than 0.1 wt% Sb was found in all samples. As and Bi sulpho-salts are present in very fine-grained sizes in most of the sections analysed by probe and high values in these analyses are thus probably due to some submicroscopic admixtures of these minerals with the galena. However, since As, Bi and Sb are common in galena, it is likely that they are also present in solid solution. No further information was gained in this study.

Ag is a common trace element in galena (Fleischer, 1955) and it was detected in all the samples analysed by probe and 4 samples were found to contain more than 0.1 wt% (Table 12). As there are no Ag

sulphides in the specimens analysed, the Ag content is not due to contamination but probably is present in solid solution.

Cu, Fe and Zn are all present generally above 1000 ppm or 0.1 wt% (Table 12). Cu occurs in lower quantities than in sphalerites. Fe and Zn although reported by previous workers in galenas, were probably due to contamination by pyrite and sphalerite (Fleischer, 1955). Most of the samples in the present study contain Fe and Zn (Table 12) (Probe and A.A.S. analysis) above 0.1 wt%.

Cd was found in most of the samples in quantities generally below 1000 ppm (Table 12). In 2 samples it was found to be 0.11 wt%. Goldschmidt (in Vlasov, 1964) suggested that admission of Cd into galena is due to the Cd-Pb isomorphism, and trace quantities of Cd in Parys Mountain galenas are probably present in solid solution.

Co and Ni are present only in trace quantities (Table 12) and in the samples analysed by A.A.S. they were found to be below 500 ppm.

Sn was detected in most probe analyses and 3 samples contain more than 0.1 wt% (Table 12).

Ba was measured by A.A.S. in 3 samples and it was found to be present below 500 ppm (Table 12). Its presence as in the other sulphides is difficult to account for.

Mo was also found in a few samples and 2 probe analyses showed more than 0.1 wt% (Table 12).

Te was measured in 4 samples by A.A.S. and was found to be below 100 ppm (Table 12). It has probably substituted for S. 3.5.2 Physical-optical characteristics

3.5.2.1 Microhardness

The measured values for microhardness of galena have a range of 61.7-107 kg/mm² (Table 22) in contrast to Bowie and Taylor's (1958) measurements of 71-84 kg/mm². The wider range in microhardness of Parys Mountain galenas probably results from the presence of considerable quantities of As and Bi. Weight %s of As and Bi were plotted against microhardness (Figs. 7d, e) and there appears to be slight linear relationship between them, though this needs confirmation by more data.

3.5.2.2 Reflectivity

Reflectivity measurements in the wave length region 400 nm-700 nm,

including 589 nm are given in Table 26, and the spectral reflectivity profiles are shown in Fig. 8d. Galena is a highly reflecting species and it shows irregular spectral profiles as reported by Gray and Millman (1962). Reflectivity % at 589 plotted against weight % As and weight % Bi showed no significant relationship probably because of insufficient data. (Fig. 9c, d).

3.5.2.3 Infrared studies

The infrared spectra produced for galena show poor resolution with broad absorption peaks between 2.8 and 3.0 microns wave length and one absorption peak in the vicinity of 6.0 micron wave length region (Fig. 18). No significant difference in absorption pattern was seen between the two samples studied, although one sample (19-424) contains 2.24% of As and the other (sample H 4/491) has only 0.10%, and both of them have nearly similar quantities of Bi (Table 12). 3.6 Arsenopyrite

Two grains of arsenopyrite were analysed by electron probe and the results are listed in Table 27 along with the theoretical value for the ideal formula FeAsS.

Compared with theoretical composition the Parys Mountain arsenopyrite has less As content but more Fe. Co, Ni, Cu, Pb and Zn are present in trace quantities (below measurable limits by electron probe).

3.7 Pyrrhotite

One pyrrhotite grain was analysed by electron probe and it has the following composition

Fe S Co Ni Cu Pb Zn Total 57.33 M 10/1521 40.91 1.30 tr tr tr 99.55

The high Cu content is difficult to account for from a single analysis and no further information was obtained in the present study. 3.7 Summary and implications of sulphide investigations

Investigations on Parys Mountain sulphide minerals have the following significant features:-

 Analysis by electron probe on inclusion free areas showed the presence of substantial quantities of trace elements probably in solid solution.
 The generalisation could be made that Co is concentrated in pyrite relative to other sulphides. Co and Ni are more common in pyrite and chalcopyrite than in sphalerite and galena.

3) Cd is concentrated in sphalerite relative to other sulphides, and there is a wide range of Fe content in sphalerites.

As, Bi and Ag are concentrated in galena relative to other sulphides.
 Sn is also present in galena but is absent in others.

5) Mo is concentrated more in sphalerite and galena than in pyrite and chalcopyrite. Ba is concentrated in chalcopyrite relative to pyrite. The significance of these two elements is not clear.

6) Correlation of trace element assemblage with the different types of the same mineral are inconclusive, such as between euhedral, anhedral and framboidal types in case of pyrite (Table 8), and in sphalerite grains those with exsolutions and without exsolutions (Table 10).
7) Concentration profiles for essential and trace elements were observed while analysing the sulphides by electron probe. It was noticed that variations of essential and trace elements within the same grain were more pronounced in case of sphalerite and galena than in the case of pyrite and chalcopyrite.

8) The Co/Ni ratio in pyrites (> 1) relates the deposits to volcanism

High quantities of Cu in pyrites have been used by Frenzel and Ottemann (1967) in Fiji deposits to indicate a subvolcanic origin. High quantities of Cu in some Parys Mountain pyrites may be related to volcanism, though in some, contamination by inclusions is likely. 9) High Ag, Sb and Bi in galena indicate high temperature of formation as low quantities of these have been reported only from low temperature deposits (Fleischer, 1955; El Shazly et al 1957). Marshall and Joensuu (1961) also found that galenas having poor trace element assemblage predominantly form at lowest temperatures and vice versa. From this point of view the Parys Mountain galenas may throw some light on temperature of formation. However, it requires more data to draw any conclusions on this.

10) A linear relationship was observed between Fe content and unit cell edges of sphalerite and between microhardness and Fe content in sphalerite.
11) Attempts to correlate composition with some physical and optical characteristics of the sulphides allowed no significant conclusions, although some of this was due to insufficient data.

CHAPTER 4 SULPHO-SALTS

4.1 Introduction

The sulpho-salt minerals are intimately associated with the major sulphides at Parys Mountain. Their optical properties and textural relationships with the sulphides have been discussed elsewhere (Chapter 2). Their physical and optical characteristics are so similar that they are difficult to identify and distinguish optically (Uytenbogaardt and Burke, 1971) and so electron probe microanalysis is the most common method used for their mineralogical determination.

Most of the commonly known sulpho-salts contain one or more of the following elements - Fe, Co, Ni, Cu, Ag, Zn, Hg, Sn, Pb, Mo together with one or more of As, Sb and Bi; S is an essential constituent. These chemically complex sulpho-salts are commonly 'patterned' structurally after the simple sulphides (Ross, 1955) and are modifications of the cubic or hexagonal close packing structures. The sulpho-salt minerals present at Parys Mountain are listed in Table 28 along with their theoretical formulae. In addition to those listed, bismuthinite was reported by Thanasuthipithak (1974).

4.2 Tetrahedrite-tennantite

Many workers do not regard the tetrahedrite-tennantite group of minerals as sulpho-salts and there is considerable disagreement in assigning a chemical formula to them. Springer (1969), from the analyses of world wide material, concluded that the general formula (Cu, Ag, Fe, Zn, Hg)₃ (As, Sb, Bi, Te)S_{3.25} is valid for tetrahedrite although the majority corresponds to (CuAg)_{2.50} (Fe Zn)_{0.50} (As Sb)S_{3.25}. Later Maske and Skinner (1971) proposed a formula $Cu_{12+x}As_{4+y}S_{13}$ where $O \ll x \ll 1.72$ and $O \ll y \ll 0.08$ for tennantite. Skinner et al (1972) proposed $Cu_{12+x}Sb_{4+y}S_{13}$ for tetrahedrite where $O \ll x \ll 1.92$ and $-0.02 \nsim y \gg 0.27$. This complexity is due to extensive substitutions in the structure where Zn, Ag, Hg, Pb, Ni or Co as well as Fe may replace Cu in quantities ranging up to 16% (Vaughan, 1971).

Complex substitutions can occur in tetrahedrite partly because Cu occurs in both mono and divalent states. The first type is tetrahedrally co-ordinated with three S atoms in unusual planar groups (Riley, 1974). Cu in these sites can be replaced by Ag and Hg. In the second type Cu, which is in 3-fold co-ordination in the structure, can be replaced by Zn and Fe (Vaughan, 1971). Other substitutions involve Sb, which can be completely or partly replaced by As and in minor quantities by Bi, Sn and Ge (Ramdohr, 1969). This complexity is well exemplified by the Parys Mountain minerals (Table 29).

Analyses of 6 tetrahedrites and 3 tennantites from Parys Mountain are shown in Table 29, and these represent the average analysis taken from 2 or 3 points in each grain. The atomic proportions (Table 30) were calculated by making the total of Cu + Ag + Fe + Zn equal to 12, Sb + As + Bi equal to 4 and obtaining the relative proportion for S based on the total of these two groups (Petruk et al., 1971). Analyses of tetrahedrites from Parys Mountain and Avoca, reported by Wheatly (1971a) are given in Table 29, for comparison.

Comparison of the compositions determined in the present study with those reported by Wheatly (1971a) (Table 29) shows that Ag content in Parys Mountain minerals in the present study is low, the maximum Ag value being 1. 28 wt% from bore hole H4/491 (Bluestone ore) as compared to Wheatly's maximum Ag value of 5.4 wt%. The Fe content in the present study ranges from 3.16 to 10.18 wt% and is higher than that shown by Wheatly's (1971a) analyses. The zinc content ranges from 1.29 to 8.18 wt% and this range is quite in agreement with the analyses of Wheatly (1971a). All tetrahedrites contain some As and tennantites some Sb (X-ray images in Plate IV). Cu and Sb contents are in good agreement with Wheatly's (1971a) analyses. Bi is observed in both tetrahedrites and tennantites, the maximum content being 1.42 wt% from bore hole 27-145. There is a compositional break between tetrahedrite and tennantite as shown in Fig. 19. Such break was also noticed by Wheatly (1971a) at Avoca.

Deviations from the stoichiometric formula are illustrated by the atomic proportions of S given in Table 30. Such deviations have been noted in analyses elsewhere (Petruk et al., 1971) and are considered to be the result of complex metal substitutions with the whole complex forming an extensive solid solution series.

4.3 Bournonite

The theoretical formula for bournonite is CuPbSbS₃. Analyses of specimens from Parys Mountain, Avoca and Idaho are compared with the theoretical values in Table 31, along with atomic proportions for the analyses in the present study. The compositions and atomic proportions are at variance with the stoichiometric values. This is especially true of specimen 2 (sample M 10/1548) which contains appreciable quantities of Bi, Fe and Zn and has a Cu content very much higher than the theoretical value. The analysis of specimen (H4/465) however is in good agreement with the theoretical values and with the analyses of Avoca minerals (Wheatly 1971a). Analyses of specimens from Parys Mountain show As to be present in considerable quantities probably substituting for Sb. A solid solution series exists between Sb end member (Bournonite) and the As end member seligmannite (CuPbAsS₃) and this is considered to account for the As content in Parys Mountain analyses. 4.4 Bismuth sulpho-salts

Kobellite $(Pb(Bi, Sb)_2S_5)$ and galenobismuthite $PbBi_2S_4$ were identified at Parys Mountain in the Bluestone ore type. Kobellite is a disordered Bi-Sb-Pb sulpho-salt of composition $Pb_{6-x}(Bi, Sb)_{7+x}$ (Fe, Cu)S_{17.5} with $O \leq x \leq 1$ (Weunsch, 1974). Weight percentages and atomic proportions for kobellite and galenobismuthite are given in Tables 32 and 33 along with theoretical values and some comparative analyses.

Comparison with theoretical composition shows the analytical data on Parys Mountain kobellite to be in good agreement with theoretical compositions. As is present substituting for Sb, and appreciable quantities of Cu and Fe are also present in the Parys Mountain kobellites. The deviation in composition from the theoretical composition of Parys Mountain galenobismuthite is due to a high Zn content which is probably present in solid solution.

4.5 Lead sulpharsenides

Mineral grains optically very similar to galena with high As values are classed here as lead sulpharsenide minerals. Analyses of these and calculated atomic proportions are presented in Table 34.

Chang and Bever (1973) have outlined the various disagreements on formulae for the lead sulpharsenide group of minerals. The calculated atomic proportions (Table 34) roughly correspond to jordanite which has a formula Pb₁₄As₇S₂₃ or Pb₁₃As₇S₂₃. However, since there is no standard and accepted formula for jordanite, Parys Mountain minerals are classed as lead sulpharsenides only, rather than comparing them to any of the theoretical formulae.

4.6 Implications of sulpho-salt geochemistry

The complexity and uncertainty of the sulpho-salt geochemistry at Parys Mountain is due to the extremely local and minor abundance of these minerals and their fine grain size. Textural relationships with the major sulphides as outlined in Chapter 2 suggest that they are later than the conformable pyritic mineralisation. There is no geochemical evidence from sulpho-salt studies to assign any environment or temperature of formation for the Parys Mountain mineralisation.

Experimental studies by Maske and Skinner (1971) showed that the ideal composition for tennantite $Cu_{12}As_4S_{13}$ is probable only at lower temperature, i.e. below 300°C, and above this temperature, it deviates. Chang and Bever (1973) pointed out that lead sulpho-salt minerals are essentially restricted to hypogene deposits, particularly in the mesothermal intensity range. Minerals such as galenobismuthite have been described as occurring in high temperature areas (550 - 610°C) of volcanic fumaroles in the Lipari Islands (Palache et al., 1944 in Craig, 1967). Czemanske and Hall (1975) have reported that the Darwin lead-zinc-Silver deposit where lead sulpho-salts occur, is a high temperature deposit.

If comparisons are made with Parys Mountain minerals, then a high temperature, at least a relatively higher temperature phase than earlier conformable pyritic mineralisation has to be assigned for the Parys Mountain sulpho-salts. Nevertheless, strong similarities in mineralogy, host rock geology and sulpho-salt assemblage exist between Parys Mountain deposits and the Kuroko deposits of Japan (Lambert and Sato, 1974) which are not considered to be of high temperature mineralisation.

CHAPTER 5

WALL ROCK STUDIES

5.1 Introduction

Despite the widespread occurrence of chlorite associated with mineralisation areas, little use has been made of its development in mapping metal distributions (Tuddenham and Lyon, 1959), and zoning in mineral deposits. In the present study 12 chlorites from wall rocks in mineralised sections, and 6 from non-mineralised sections, were studied, using X-ray diffraction techniques to identify them and to determine any differences which might be present between the different sections. Eight of the chlorites from the mineralised sections and 3 from non-mineralised ones were also subjected to infra-red absorption spectroscopy to discover any differences that might be present. Of the chlorites from mineralised sections 11 were largely from materials associated with pyritic and chalcopyritic mineralisation and in one case with sphaleritic mineralisation (sample IM 9/269).

5.2 X-ray diffraction studies

Powder samples used were either obtained from rock chips which were ground in a tungsten carbide mill or directly from the core samples using a vibrating needle.

Diffraction patterns were obtained on a Phillips Norelco X-ray diffractometer, with Ni filtered CuK radiation, and quartz as an The measured 'd' spacings of the chlorites are internal standard. given in Tables 35 to 40. It was noticed that, while there is a variation in chlorite species from place to place in the case of the mineralised sections, in general there was no variation in specimens from the nonmineralised sections. A variation in chlorite species was also noticed in mineralised sections from the same bore hole (bore holes 36A and IM 6) (Tables 35, 36 & 38 to 40). Diabantite, clinochlore and grochauite varieties of chlorite were found mainly associated with pyritic mineralisation with some chalcopyrite and sphalerite. Ripidolite was found associated with pyrite and chalcopyrite, and aphrosiderite with pyrite. Chlorite 1b species was found in all the non-mineralised sections Comparison of the chlorites at Parys Mountain with the studied. classification of the chlorites given by Hey (1954) as in Fig. 20 shows

that they are closely related varieties in terms of Si, total iron and Fe /(Fe + Mg). These different varieties of chlorites which have slightly different compositions probably are the result of the wall rock alteration associated with epigenetically formed sulphides. The differences may have been caused by the proposed secondary hydrothermal sulphide mineralisation rather than by the early sedimentary pyrite mineralisation. Determination of composition of chlorites in terms of major and trace elements and the identification of the species by X-ray study on a greater number of samples would be a useful investigation to find whether the above observation is localized or whether it is a general feature with the mineral deposits at Parys This is particularly important in establishing the Mountain. relative ages of mineralisation and metamorphism because premetamorphism chlorites would likely be destroyed.

5.3 Infra-red studies

Specimens used were 11 chlorites directly recovered from core samples and free from other minerals such as quartz. These were subjected to infra-red absorption spectroscopy, using the technique described in Chapter 3, and the spectra obtained were compared with those obtained by Tuddenham and Lyon (1959). They all fall under group 1 of the classification proposed by the above authors in that each spectrum has one strong absorption band in the wave length region between 9.3 and 11.0 microns and two to three clearly visible absorption bands between 2.6 and 3.0 microns (Fig. 21). It was, however, not possible to distinguish the chlorites from mineralised and nonmineralised sections because no significant differences in absorption patterns were seen.

CHAPTER 6

DISCUSSION AND CONCLUSIONS

6.1 Discussion

The mineralogical, textural and geochemical features discussed in the previous chapters can be used to add to discussion of the metallogenesis of these sulphide minerals. Interpretations of mineralisation should account for (a) Source and availability of various essential and trace elements, (b) Mode of transportation and availability of sites for precipitation or deposition (environment of formation), (c) Genetic relationship with the host rocks, (d) Post depositional characteristics. These are discussed below for Parys Mountain in the light of information derived in this study.

6. 1. 1 Source and availability of elements

As outlined in Chapter 2, the Parys Mountain deposits can be considered as stratiform type based on field, megascopic and mineralogical characteristics. These stratiform deposits, because of a close association with a volcanic succession, and generally having a Co:Ni ratio of > 1, are thought to be related to volcanism. Hutchinson (1973) defined volcanogenic sulphide deposits as strata bound lenticular bodies of massive pyrite mineralisation, containing variable amounts of chalcopyrite, sphalerite and galena in layered volcanic rocks. They are believed to have been formed subsequently by volcanic fumarolic activity which occurred periodically during volcanism. The Parys Mountain deposits have close similarities to the Type II of Hutchinson (1973), in metals, volcanic rocks, volcanic activity, tectonic position and geological age.

Hutchinson Classification Type II is as follows :-

Type II	Pb-Zn-Cu Pyrite
Associated volcanics	Intermediate to felsic, calc-alkaline volcanic suites; andesite, dacite-rhyolite tuff etc.
Type of volcanism	Felsix centres of explosive, Pyroclastic and ignimbritic activity. Subaqueous to subaerial.
Associated sediments	Epiclastic predominates
Tectonic position	Later eugeosynclinal orogenic stage
Examples	Mt. Isa (Proterozoic) New Brunswick (Ordovician)

Petrological studies by Thanasuthipithak (1974) has established the presence of all these characteristics at Parys Mountain and that the volcanics belong to an orogenic-calcalkaline magma series formed in a continental margin/ island arc environment.

That many of the world's economically workable sulphide deposits have been derived from volcanic processes is firmly established by many workers throughout the world. Detailed discussions of individual deposits are given in Stanton (1960), (1965), Hutchinson (1965), Krauskopf (1967), Schermerchorn (1970), Ferguson and Lambert (1972), Lusk (1972), Goosens (1972), Constantinove and Govett (1973), Sillitoe (1973), Strauss and Madel (1973), Roberts (1975), Thurlow et al., (1975), Spence and Spence (1975), Spence (1975), Jenks (1975) and Angus and Davis (1976).

6.1.2 Environment of formation

Many of the volcanogenic deposits quoted above, though related to volcanism are thought to have been formed by an interplay of volcanic-sedimentary or volcanic-hydrothermal processes. It has to be postulated that there existed a sedimentary volcanic basin at Parys Mountain in which thick volcanic products accumulated. The sulphide metallic phases, mainly iron sulphide from volcanic emanations, were also deposited along with the volcanic successions within certain restricted environments. Thanasuthipithak (1974) called such a process 'synsedimentary-exhalative'. However, as pointed out by Anderson and Nash (1972) the word 'exhalative' implies vapour transport and there is no evidence at Parys Mountain that the metals were carried in the vapour phase. Alternative terms given by Anderson and Nash (1972) are volcanogene-sedimentaire, volcano-sedimentaire, and submarine volcanic sedimentary. The term volcanogenic-sedimentary (Ilavsky 1976) is perhaps the most suitable for the Parys Mountain mineralisation.

However, microscopic features discussed in Chapter 2 suggest that the mineralisation at Parys Mountain was not a single simple episode. Although much of the copper ore has been removed by previous mining operations, its paragenesis is clear and it is only the pyritic mineralisation that has obvious conformable or syngenetic features. The leadzinc sulphides and sulpho-salts are later and they apparently show features of deposition from a multi-component hydrothermal system, though they could have resulted as complex substitutions in other sulphides. Where

deposition has occurred from such a system the mobility of ore metals is in decreasing order as experimentally given by Barnes and Czemanske (1967) Pb-Cu-Zn-Sn-Ni-Fe-Co; (this coincides with the general paragenesis). All these epigenetic minerals were formed in fractures, and interstitial infillings and replacements of the earlier pyritic mineralisation.

6.1.3 Relationship with the host rocks

As outlined above the pyritic mineralisation is reported to be conformable and syngenetic with the host volcanic succession. Epigenetic mineralisation though, complex mineralogically, shows some crosscutting features consistent with later formation or remobilisation, presumably during metamorphism.

6.1.4 Post depositional characteristics

The earlier pyritic mineralisation shows post depositional charactieristics mainly the evidence of deformation and remobilisation. These are the cataclastic textures, fracturing recrystallisation of framboid pyrites, etc. which became vacant sites for the subsequent epigenetic mineralisation. Either both these phases, or the earlier pyritic mineralisation, were remobilised during the Caledonian orogeny (Thanasuthipithak, 1974).

Both in the earlier syngenetic mineralisation and later hydrothermal deposition the source for the metallic sulphide is believed to have been volcanic. This repetition of ore formation is not uncommon in volcanogenic sulphide deposits.

It can therefore be concluded that the Parys Mountain mineralisation is consistent with a volcanogenic-sedimentary deposit of a stratiform type later enriched by hydrothermal processes. This deposit was later remobilised during the Caledonian orogeny to produce many of the crosscutting features.

6.2 Summary of conclusions

In the present study of mineralogy and geochemistry of Parys Mountain sulphides and sulpho-salt minerals, the following conclusions are reached:

1) The mineralogy, paragenesis and association with a volcanic succession of rocks allow the interpretation that the deposit is both stratiform and conformable associated with volcanism. An earlier synsedimentary pyritic mineralisation has been enriched by an epigenetic

complex sulphide and sulpho-salt mineralisation.

2) The deviations in composition of the major sulphide minerals pyrite, chalcopyrite, sphalerite and galena from their stoichiometry are interpreted as due to presence of appreciable quantities of trace elements and complex substitutions.

3) Pyrite and chalcopyrite have relatively low trace element content and they mainly contain Co, Ni, Ba, As, Pb, Zn, also Cu in pyrite. The Co/Ni ratio in pyrites is generally > 1. This is interpreted to indicate that the deposits are related to volcanism.

4) Sphalerite and galena are rich in As, Ag, Bi, Sb contained in solid solutions.

5) The iron content in sphalerite varies widely, and this is interpreteted as being due to solid solution.

6) Measurements of cell edge of sphalerites, using both electron diffraction and X-ray diffraction techniques, showed it to vary linearly with iron content. Electron diffraction is thus an alternative method for measuring the iron content of sphalerites.

7) There is a good relationship between iron content and microhardness in sphalerite. However, this was found not to apply to the other sulphides, namely pyrite and chalcopyrite.

8) The chlorite group minerals, diabantite, ripidolite, grochauite, and aphrosiderite were formed in wall rocks at the contacts of the mineralisation. Chlorite 1b species was found in non-mineralised sections.

APPENDIX I

SAMPLE SELECTION AND PREPARATION

All the sulphide samples studies were taken from the diamond drill cores including some previously studied by Thanasuthipithak (1974), and only fresh looking material was selected. Two types of samples were required: a) sections of mineralised parts for polishing (reflected light microscopy, reflectivity, microhardness, and electron probe measurements); b) powdered sulphide minerals for chemical analyses, infrared and differential thermal studies. In the latter case, only mineral grains which were sufficiently coarse (average size >about one mm) to be liberated with considerable amount of purity were selected. More finely grained minerals were analysed by electron probe on polished sections.

Sulphide mineral grains were liberated directly from the core specimen using an electrically vibrating needle. They were then thoroughly washed using acetone and distilled water and dried. They were examined under a binocular microscope and impurities were removed by hand. In some instances a heavy-liquid technique was used (Muller, 1967) to separate less coarse grained sulphides from fine grained gangue. In some cases the core chip was polished on a coarse grade abrasive paper to allow grain boundaries to be clearly seen before the grain was liberated. Most of the sphalerite samples were recovered in this way.

A certain amount of mineral impurity was, however, unavoidable. This was especially true of sphalerites and pyrites with some chalcopyrite exsolutions. Also some very fine grained gangue inclusions in sulphide minerals could not be separated.

APPENDIX 2

LABORATORY METHODS

2.1 Atomic Absorption Spectrophotometry (A.A.S.)

Solutions for A.A.S. were prepared by dissolving the sulphide samples in concentrated Hcl and concentrated HNO3 (Strasheim et al. 1960; in Angino and Billings, 1972). About 200 mg of powder was weighed accurately into a conical flask and 8 to 10 ml of concentrated Hcl was added. This was allowed to stand for approximately one hour for the initial reaction to take place before adding 8 to 10 ml of concentrated HNO3. This method was used in preference to direct use of aquaregia to prevent basic nitrates being formed on the surface of the sulphide grains (Dolezal et al. 1968, in Ghosh, 1972). After adding HNO, some 3 hours were allowed for a clear solution to form. The solutions were stirred and then transferred to 150 or 250 ml volumetric flasks, made up to volume with double distilled water, and quickly transferred to polythene bottles. The solutions were analysed within three days of preparation because elements present in low concentrations are lost by absorption on to the sides of the bottle, if stored for longer periods.

Standards were prepared from stock solutions containing 1000 ppm of the element in each case. These stock solutions, except Mo were supplied from BDH Chemicals Limited. The Mo standard was prepared by dissolving 1.840g of ammonium paramolybdate ($(NH_4)_6 Mo_7O_{24} 4H_2O$)) in 1 litre of 1% ammonium hydroxide (NH_4OH), for 1000 ppm concentration.

Analyses for Cd, Co, Cu, Fe, Ni, Pb, Te and Zn were done using an air acetylene flame, and Mo and Ba were determined using a nitrous oxide acetylene flame. An integrated period of 0.5 seconds was allowed for each aspiration. At the beginning of each run, standard solutions were aspirated starting from lower concentration to higher concentration, followed by the sample solution. At least 4 readings were taken for each sample solution. The mean of these concentrations was taken and from it the weight % in the sample was calculated. 2.2 Electron probe microanalysis

Analyses were done on carbon coated polished sections and in some instances on the sections mounted in conducting bakelite. The standards used were either pure metals/elements or compounds (Table 41).

Analyses were done using a Cambridge Microscan V with a constant accelerating potential of 15 kV, a sample current of 0.3 mA and a beam current of 0.05 mA. The crystals used were PET (Pentaerythritol) and LiF (Lithium fluoride). Both crystals were used because readings were obtained simultaneously in two separate channels thus allowing two elements to be determined simultaneously. Counting rates were measured for intervals of 10 seconds. Peak intensities for various elements determined in each grain were read at least twice, and the mean taken. Similarly background readings also were taken at least twice.

A dead time correction was applied for counts more than 2000/ second, though for count rates below 10,000 counts /second, the error is considered to be less than 1% (Adler, 1970). Dead counts were read from the graph supplied and were added to the measured counts. The concentration after applying dead time was calculated using the formula

 $Wt \% = \frac{Peak-Background + Dead time (counts/second) of specimen x C}{Peak-Background + Dead time (counts/second) of standard}$ where C is the weight percentage of the element in the standard.

The measured concentrations were subjected to corrections described by Long (1967), Adler (1970). Corrections for Atomic Number (Z), Fluorescence and Absorbance, were made using a computer programme produced in the Department of Metallurgy, University of Aston. 2.3 Reflectivity

Measurements of reflectivity were made on a Reichert Zetopan Ore Microscope equipped with a reflex microphotometer (Singh, 1965). Comparative quantitative measurements were made against Tungsten Titanium Carbide (WTiC) and silicon carbide (SiC), standards with reflectivity being calculated from the formula

 $R \sim \%$ of Mineral = $\frac{\text{Deflection Value of Mineral}}{\text{Deflection Value of Standard}} \times K$

where K = calibrated reflectivity % of standard

 λ = monochromatic wave length

R% = Reflectivity percentage

All measurements unless otherwise specified were made at a wave length of 589 nm in air. A glare correction was applied before calculating R% to compensate for reflections from the back of the objective (Bowie and Henry, 1964).

2.4 Indentation microhardness

Measurements of microhardness were made with a Leitz Durimet Microscope with an attached indenter. Varying loads of 50, 200 and 300 gm were applied to obtain a sharp indentation and an indentation time of 30 seconds was allowed for each specimen. The diagonals of the projected impression on the polished surface were measured using a travelling micrometer ocular. The hardness number was calculated using the formula

$$VHN = \frac{1854.4 \text{ x L}}{d^2}$$

where VHN =' Vickers microhardness number in kg/mm²

L = Load applied

d = Indentation diagonal

2.5 Infrared Absorption Spectroscopy

Samples for infrared studies were prepared by potassium bromide pellet method (Tuddenham and Lyon, 1959; and Lyon, 1967). Spectra were obtained on a Perkin-Elmer 237 Grating Infra red Spectrophtometer in the wave number region 600-4000 cm⁻¹. 2.6 Differential Thermal Analysis

Analyses were made on samples of pyrite and chalcopyrite on a Dupont-900 Differential Analyser using a sample preparation technique described by McLaughlin (1967). Glass beads were used as standard. A heating rate of 50°C/minute was applied, with the scale for chart paper of 100°/inch.

Sulphides contain corrosive elements such as S and As (Kopp and Kerr, 1957). Special techniques of diluting the samples with alumina to avoid corrosion by S or As were not employed because the maximum temperature reached was only 600°C.

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e 1 Stratigraphic sequence at Parys Mountain

	(Hawkins, 1966)		(Thana suthipithak,	1974)
Age	Lithology	Thickness	Lithology	Thicknes
Silurian	Grey shales with graptolites		Dark-grey to black slates	
Ordovician	Fine-grained sediments with a few occurrences	600 ft	unconformity ?	
	of tuff in felsitic zone of silicification		Rhyolitic volcanic rocks	200m
			Grey to greenish-grey slates	600m
	Parys shales	720 ft		
	Black shales * Grey shales weather- ing to brown and green			
	Grey micaceous shales with beds of sedimen- tary breccia	1200 ft		
	Carmel I	Head Thru	st	
Pre- Cambrian	Amlwch beds Pale-green phyllites		Chlorite schists, micaceous and granitoid gneisses, quartzitic gneisses.	

* Note: These are the Parys Green Shales of Greenly

Table 1

Table 2. Classification of Ore Types.

Author	Mineralisation Type	Host rock or matrix	Minera Major	logy Minor	Example	
Wolfenden (1967) (in Thanasu- thipithak 1974)	Copper ore	Northern rhyolites and its contacts	Pyrite Chalco- pyrite	Sphalerite Galena	Great ore Opencast lode, Hill Side open case, Black rock lode	
	Bluestone ore	Dacite, silicified silurian slates and in rhyolites in contact with Ordovician slates	Argent- iferous galena, Sphalerite	Chalco- pyrite Pyrite e	Clay shaft lode Black rock lode	
	Pyritic ore	Within rhyolitic rocks	Pyrite	Chalco- pyrite	Golden venture lode Carreg-y-doll lode, Middle lode, South branch lode North dis- covery lode	
	Low grade Galena-Sphalerite ore	Disseminated in Orodovician slates	Calena Sphalerit	e	Not mined be- cause of low grade	
Wheatly 1971a	Pyritic zone	Black shale (Ordovician slates)	Pyrite Chalco- pyrite	Pyrrhotite Sphalerite Galena	Disseminated in shale units	
	Siliceous zone	Shales and tuffs (silicified Silurian slates and rhyolitic tuffs + siliceous sinter)	Pyrite Chalco- pyrite Sphaler- ite Galena	Pyrrhotite Tetra- hedrite Bismuth- inite Native Bismuth	Carreg-y-doll, Golden Venture lode Charlotte lode, North discovery lode.	
	Lead-zinc zone	Shales and tuffs	Sphaler- ite Galena Pyrite Chalco- pyrite	Tetra- hedrite Bournon- ite	Morfa-dee and Black rock lodes, clay shaft lodes (Bluestone)	
	Veins	Shales, tuffs and lavas	Galena, Sphaler- ite Chalco- pyrite	Tetra- hedrite	Great cross Cowis Carreg-y-doll lode.	

Ore Type		Form	Description	Miner Major		Grain size/ dmsns	Matrix/ host matrix
		Layered sulphide form Continuous and dis- continuous layers conformable with the quartz and chloritic matrix parallel to foliation of the host rock. Some layers have a lenticular shape, major lens made up of smaller lenses giving rise to en- echelon arrangement		Pyrite Sphal- chal- erite copyrite		Thick- ness of the layer 2mm- l cm.	Quartz- chlor- itic rocks
	b)	Disseminated form	Well developed euhedral and sub- hedral pyrite grains disseminated in host rock.	Pyrite	Chal- co- pyrite	0. 3mm -2 mm	
Copper ore	a)	Massive form	Irregular, coarse granular inter- growths	Pyrite Chal- co- pyrite	Sphal- erite Galena	0.5cm to even 2cm in case of pyrite	Quartz is the main matrix
	ь)	Vein and stockwork form	Intersecting con- tinuous and dis- continuous veins of chalcopyrite	Chal- co- pyrite	Pyrite	Aver- age width of the vein about 5 mm	Sili- ceous rocks
Blue- stone ore	Fi	ine-grained	Microscopic gran- ular intergrowths	Sphal- erite Galena Chal- co- pyrite Pyrite	Sulpho salts	- Aver- age size ∠ l mm	Shales and tuffs (Sili- ceous/ sinter)

Table 3 Summary of some mineral forms at Parys Mountain

	Microhardness range (Kg/mm ²)	Reflectivity % range at 589nm (air)	Special association
Euhedral, subhedral anhedral and fram- boidal	1027 - 1483	45.9 - 56.5	Euhedral pyrite with rutile
Anhedral, allotrio- morphic	174 - 221	38.2 - 42.6	
Anhedral, rounded and as intergrowths with chalcopyrite	148 - 240	16.3 - 22.1	
Anhedral, sometimes intergrows with sphalerite	61 - 201	37.3 - 41.3	
Euhedral to subhedral	in the life	1	
Anhedral, irregular	- 10	-	
Fracture and interstitial infillings mainly in pyrite	279- 328	34.3 - 36.5 (Tetra- hedrite) 29.5 - 31.7 (Tennan- tite)	Pyrite
Inclusions - white in colour and anisotropic	-	-	Sphalerite
		39.3 - 43.5	Sphalerite and galena
Interstitial infillings in pyrite, sphalerite	-	-	
	anhedral and fram- boidal Anhedral, allotrio- morphic Anhedral, rounded and as intergrowths with chalcopyrite Anhedral, sometimes intergrows with sphalerite Euhedral to subhedral Anhedral, irregular Fracture and interstitial infillings mainly in pyrite Inclusions - white in colour and anisotropic Inclusions and intergrowth with mainly sphalerite and galena Interstitial infillings in	Euhedral, subhedral anhedral and fram- boidal1027 - 1483Anhedral, allotrio- morphic174 - 221Anhedral, rounded and as intergrowths with chalcopyrite148 - 240Anhedral, sometimes intergrows with sphalerite61 - 201Euhedral to subhedral-Anhedral, irregular-Fracture and interstitial pyrite279- 328Inclusions - white in colour and anisotropic-Inclusions and intergrowths with mainly sphalerite and galena-Interstitial infillings in-	Euhedral, subhedral anhedral and fram- boidal1027 - 148345.9 - 56.5Anhedral, allotrio- morphic174 - 22138.2 - 42.6Anhedral, rounded and as intergrowths with chalcopyrite148 - 24016.3 - 22.1Anhedral, sometimes intergrows with sphalerite61 - 20137.3 - 41.3Euhedral to subhedral infillings mainly in pyriteFracture and interstitial pyrite279- 32834.3 - 36.5 (Tetra- hedrite) 29.5 - 31.7 (Tennan- tite)Inclusions - white in colour and anisotropicInclusions and intergrowths with mainly sphalerite and galenaInterstitial infillings in a

Table 4	Table	showing	the	ore	minerals	at	Pary	s Mountain
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P	rimary			Secondary	
Texture	Description	Mineral/s	Texture	Description	Mineral/s
1) Panidio- morphic	Euhedral grains	Pyrite	1) Cataclastic	Fractures and other deform- ative features are present	Pyrite
2) Framboid- al	A spherical or subspherical aggregate of pyrite granules or microcrysts	Pyrite	2) Vein filling	A distinct and narrow filling of pyrite in the matrix in the form of a vein	Pyrite
3) Allotrio- morphic granular	Irregular and anhedral grains	Pyrite Chalco- pyrite Sphaler- ite Galena & sulpho- salts	3) Inter- stitial fillings	Later formed minerals are present in the interstitial spaces of the previously formed grains	Sphaler- ite in Pyrite Tetra- hedrite - Tennan- tite in Pyrite
 Mutual intergrowths 	The two minerals are usually inter- grown with no distinct boundary between them		4) Replace- ment	Later formed minerals re- place previously formed minerals along peripheries	Chalco- pyrite replaces pyrite
			5) Recryst- allisation and homo- genisation	An aggregate of framboidal or euhedral grains homo- genised at the centre, retaining their respective out- lines at the periphery	Pyrites

Table 5 Summary of Textures shown by ore minerals at Parys Mountain

Table 6 Simplified Paragenetic diagram of Primary Sulphides and Sulpho-salts at Parys Mountain

Time		\longrightarrow
Rutile		
Euhedral Pyrite	-	
Anhedral, framboidal Pyrite Vein-filling Pyrite		
Pyrrhotite		
Arsenopyrite		
Chalcopyrite		
Sphalerite -		
Galena		
Tetrahedrite - Tennantite Bournonite		
Lead sulpharsenides		
Bismuth sulpho-salts		

Name of the No. technique samp			Minerals		Information
Reflected Light Microscopy	58		Sulphides and Sulpho-salts		Identification, Des- cription and Paragenesis
Reflectivity	71 grains	a)	Sulphides	a)	Plotting of spectral reflectivity profiles.
		Ъ)	Sulpho- salts	b)	For identification
Microhardness	56 grains		Sulphides		Quantitative measurement
X-ray diffraction (Powder Camera)	17		Sphalerite		Unit cell measurement
Electron diffraction	12		Sphalerite		Unit cell measurement
Atomic Absorption spectrophotometry	55		Sulphides		Major and trace element analysis
Electron Probe Microanalysis	74		Sulphides and Sulpho-salts		Major and trace element analysis
Infra-red absorption spectroscopy	13		Sulphides		To compare with published data and to see if related to composition
Differential thermal analysis	11		Pyrite, Chalcopyrite		To compare with published data and to see if related to composition

Table to show the techniques employed and the nature of information obtained

Table 7

Explanation for Tables 8 - 12

A. A. S.	Atomic Absorption Spectrophotometry
ЕРМА	Electron Probe Microanalysis
A	Anhedral
F	Framboidal
Е	Euhedral
S	Subhedral
х	Not determined
XX	Looked for but not detected
tr	traces

Results of EPMA are quoted in %

Results of A. A. S. are quoted in % for essential elements, and in parts per million for trace elements. Where EPMA and AAS analyses have both been done on the same sample, the analyses for essential elements are those done by EPMA and the trace elements unless quoted in % are those analysed by A.A.S.

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Zn Co/ Ni	414 -	502 1.43			22 14.53		71 0.79	874 1.30			08 0 84	210 7.47			204 0.84		325 9.74			518 -	-	
12.18			1													-						
Te	7 49			8 133						68		5 31			24				-			
Pb	107				429	-			411			595			536				XX	XX	361	
Ni	XX	46	400	37	47	349	158	253	16	26	541	62	208	84	969	556	50	XX	XX	XX	59	14-15-15-15-15-15-15-15-15-15-15-15-15-15-
Mo	xx	xx	XX	XX	xx	XX	46	37	193	241.	256	39		13	19	168	xx	442	xx	xx	xx	
. Cu	2873	1025	300	335	760	650	12715	454	348	137	380	540	2575	120	568	957	479	2487	2875	1563	340	
°	39	66	1900	222	683	742	125	340	206	xx	455	590	143	105	583	958	487	262	36	66	269	
Cd	xx	xx	xx	128	216	xx	105	16	76	хх	XX	хх	xx	xx	33	XX	xx	45	XX	xx	275	
Ba	xx	386	235	645	761	хх	171	108	150	349	148	205	103	xx	267	105	112	хх	394	268	827	
As	×	×	0.16	x	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	
Total																						
S	×	×	54.65	×	х,	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	
Fе	44.56	43.16	43.98	46.93	44.32	43.73	43.36	44.84	43.55	45.56	44.97	44.64	47.15	46.33	45.57	44.96	46.78	44.19	44.88	45.23	45.71	
Type of grain	A	A	ы	ſ4	A	Ŀц	A	E	A	ы	S	S	S	S	S	Α.	s	A	A	A	ы	4
fethod	AAS	:	EPMA & AAS	AAS	=	=	=	-	:	=	=	=	:	=	:	=	=		=	=	:	
Sample Method Number	A15/911	A15/916	A15/924	A15/928	A15/935	A15/953	A15/971	A15/980	A15/1193	IM6/516' 6"	IM6/770	IM6/1044' 8"	IM6/1101	IM6/1108	IM6/1160	IM6/1179	IM6/1231	IM6/1393	36A/1611	36A/1617	32-1108	0011 00
SI. S No. P	1 4	2 4	3 4	4	5 A	6 A	7 A	8 A		10 IN	11 IN	12 IN	13 IN	14 IN	15 IN	16 IN	17 IN	18 IN	19 36	20 36	21 32	cc cc

n Co/ Ni	1.02	-	1.89		0.48				0.15			0.17											
Zn	629	125	17	3280	202	0.28	ħ	tr	148	380	Ħ	260	tr	ţŗ	ţ	ħ	ħ	ħ	XX	ħ	XX	ţ	хх
Чe	XX	XX	62		XX	×	×	×	39	36	×	169	×	×	×	×	×	×	×	×	×	×	×
РЪ	269	804	490	305	152	ħ	1300	5	156	589	F	440	ţŗ	ħ	ħ	ħ	t	xx	xx	xx	ħ	xx	tr
Ni	133	50	19	185	563	tr	ħ	ħ	552	276	Ħ	410	ħ	tr	ţ	tr	tr	tı	xx	xx	xx	xx	хх
Mo	120	xx	xx	xx	xx	tr	tr	ħ	230	68	ħ	100	ħ	5	xx	xx	XX	xx	xx	xx	xx	xx	tr
Cu	200	210	9767	2075 10800	tr	ħ	0.12	0.10	2875	1260	0.11	ħ	0.12	ţ	ħ	5	ţ	ħ	ħ	tr	ţ	ţ	tr
°C	136	789	36	2075	268	ħ	H	ħ	83	160	H	69	ħ	tr	Ħ	ţ	ţ	0.12	ħ	H	F	H	H
Cd	xx	хх	xx	xx	320	tr	xx	5	260	249	Ħ	180	0.10	0.13	0.11	tr	0.10	ħ	5	ħ	ħ	5	tr
Ba	хх	130	xx	125	xx	×	×	×	хх	×	×	195	×	×	×	×	×	×	×	×	×	×	×
As	×	×	×	×	0.21	0.11	5	ħ	×	ħ	tr	×	tr	tr	tr	tr	tr	tr	tr	tr	ħ	ħ	xx
Total				98.61	98.98	99.44	98.50	98.92		98.16	98.43		98.64	99.70	98.07	98.17	99.19	99.07	100.44	98.06	98.43	100.64	99.56
S	×	×	×	53.97	55.38	52.88	53.61	54.62	×	54.97	54.82	×	54.53	54.17	53.34	53.28	52.35	54.69	55.07	53.34	53.66	54.68	54.37
ъ	48.25	47.65	45.91	44.64	43.60	46.56	44.89	44.30	43.75	43.19	43.61	44.85	44.11	45.53	44.73	44.89	46.84	44.38	45.37	44.72	44.77	45.96	45.19
Type of grain	A	A	s	¥	A	S	A	A	A	A	A	S	A	A	A	A	A	A	Ŀ	ы	£4	ц	A
Method Type of grain	AAS		=	EP MA & AAS		EPMA	-		AAS	EPMA & AAS	EPMA	AAS	EPMA	EPMA	-	=	=	-		=	=	:	-
Sample Number	HMA/1510	H ₄ 3A/1837	A14/1534	H14/186	H14/265	IM9/264	IM9/269	IM9/285	IM9/288	1M9/292'	IM9/294' 6''	IM9/364' 6"	M10/1512	M10/1540	M10/1548	M10/1589	M10/1599	M10/1608	H4/456	H4/464	H4/465	H4/474	C4/960
SI No.	23 1	24 1	25	26]	27	28]	29 1	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45

	Table 9	Table showing the essential and trace element composition of Chalcopyrite	ng the es	sential	and trac	e elemen	t com	positio	n of C	halcop	yrite						
SI. No.	Sample Number	Method	Ğ	ъ	S	Total	As	Ba	Bi	Cd	°C	Mo	Ni	Рb	Te	Zn	1111 121
1	A15/920	AAS	34.37	31.16	×		×	924	×	xx	133	28	41	XX	XX	680	100
2	A15/965	AAS	36.11	29.36	×		×	276	×	xx	60	140	12	325	62	395	
3	A15/1193	EPMA & AAS	35.05	32.37	34.20	101.62	ħ	576	x	250	405	510	500	155	55	2140	
4	M10/1410	AAS	34.59	29.92	×		×	1653	×	xx	440	260	690	410	xx	1790	
5	M10/1521	EPMA & AAS	34.73	27.73	35.96	93.42	0.27	1385	x	1	710	ħ	726	xx	74	1895	
9	M10/1589	EPMA	35.81	28.15	36.15	100.11	t	×	0.13	tr	ţ	xx	5	tr	×	tr	
2	A14/1534	AAS	33.87	30.98	×		×	260	×	180	275	405	122	820	192	1388	
80	IM6/762		33.70	30.12	×		×	742	×	235	344	280	215	285	xx	969	
6	IM6/1392		32.40	30.34	×		×	210	×	446	486	85	190	1045	xx	851	
10	IM6/1393	EPMA	33.66	31.19	34.85	99.70	0.12	×	хх	tt	tr	tr	ħ	ħ	x	tr	
=	H4/464	EPMA & AAS	34.64	30. 15	36.58	101.37	0.11	xx	5	211	410	300	510	5	X	345	
12	H4/465	EPMA	34.72	25.80	36.49	97.01	ţ	×	tr	H	tr	tr	ħ	tr	×	2100	
13	H4/491	EPMA & AAS	34.54	27.75	36.61	93.90	4	165	0.24	198	625	Ħ	446	656	xx	911	
14	H4/581	EPMA	35.19	32.12	33.29	100.60	ħ	×	t	tr	tr	хх	ħ	ţ	×	0.38	
15	IM9/264		32.07	29.25	36.93	98.25	t	×	ħ	xx	tr	XX	ħ	Ħ	×	0.27	
16	IM9/269		37.09	28.76	35.61	101.46	ţŗ	×	0.13	xx	5	XX	H	ħ	×	0.56	
17	H14/171	AAS	32.27	30.69	×		×	368	×	98	290	xx	1060	316	xx	1100	
18	H14/186	EPMA	35.25	32.81	32.81	100.54	xx	x	хх		ħ	xx	5	ħ	×	0.47	
19	H43A/855	AAS	35.25	28.55	x		×	1526	×	xx	236	x	xx	313	x	1295	

	Sample Method Zn number	1100	Zn		Fe	S	Total	As	Ba	Bi	Cd	S	Cu	Mn	Mo	Ni	Pb	Te	Type
	H4/456 EPMA & 58.99 4.21 35.27 AAS	58.99		4.21 35.27	35.27		98.47	0.12	2189	Ħ	0.17	206	2980	Ħ	X	xx	1468	105	Exsolutions of Chalco- pyrite present
\mathbf{x} 1393 \mathbf{x} 876 967 3157 \mathbf{x} \mathbf{xx} 315 315 11 57 \mathbf{x} \mathbf{xx} \mathbf{xx} \mathbf{xx} \mathbf{xx} \mathbf{xx} \mathbf{xy}	H4/460 " 64.74 1.12 34.63	64.74			34.63		100.49	0.10	7222	ţŢ	0.12	668	15360	Ħ	285	433	1286	xx	
	H4/467 AAS 53.01 13.77 x	53.01 13.77	13.77	13.77				×	1383	×	876	967	3157	×	хх	385	315	16	
	H4/473 EPMA 61.70 1.16 35.59	61.70		1.16 35.59	35.59		98.45	tr	×	xx	0.15	ħ	0.33	хх	хх	xx	0.11	×	н
	H4/474 " 54.87 12.47 32.23	54.87		12.47 32.23	32.23		99.57	tr	×	xx	0.13	tr	2.28	0.10	0.12	xx	0.14	×	=
	H4/481 " 56.12 9.12 35.83	56.12 9.12 35.83	9.12 35.83				101.07	tr	×	0.14	0.13	tr	0.26	xx	0.12	хх	xx	×	
	H4/491 EPMA & 51.68 14.21 35.28 1 AAS	51.68 14.21 35.28	14.21 35.28			-	101.17	Ħ	174	0.11	0.28	ħ	4600	5	2100	5	286	149	-
26 tr x tr 0.11 tr 0.30 tr tr tr tr x 37 tr 1088 tr 388 tr 2870 tr tr tr tr x 44 0.12 x tr tr xx 0.18 tr tr x tr x 46 0.12 x tr xx 0.18 tr xx tr x x 90 tr 569 tr 215 135 1088 xx 565 340 85 260 75 xx 515 tr 0.12 xx 0.23 tr x x x 75 xx 0.11 0.10 0.13 tr x x x x x x x x x 75 xx 0.11 0.10 0.13 tr x 0.12 x	IM9/283 EPMA 64.31 1.65 34.33 10	64.31 1.65 34.33	1.65 34.33			10	100.29	ħ	×	цг.	tr	tr	0.65	ħ	tr	tr	0.12	×	
37 tr 1088 tr 388 tr 2870 tr tr </td <td>IM9/285 " 60.43 2.75 37.08 10</td> <td>60.43 2.75 37.08</td> <td>2.75 37.08</td> <td></td> <td></td> <td>10</td> <td>100.26</td> <td>tt</td> <td>×</td> <td>ħ</td> <td>0.11</td> <td>ħ</td> <td>0.30</td> <td>ħ</td> <td>ţŗ</td> <td>ţŗ</td> <td>ħ</td> <td>×</td> <td></td>	IM9/285 " 60.43 2.75 37.08 10	60.43 2.75 37.08	2.75 37.08			10	100.26	tt	×	ħ	0.11	ħ	0.30	ħ	ţŗ	ţŗ	ħ	×	
	IM9/285'2" EPMA & 61.84 2.86 35.67 100. AAS	EPMA & 61.84 2.86 35.67 AAS	2.86 35.67	35.67	35.67	10	0.37	ħ	1088	5	388	H	2870	ħ	5	ħ	Ħ	×	=
	IM9/292'6" EPMA 62.66 1.59 35.19 99.	EPMA 62.66 1.59 35.19	1.59 35.19			66	. 44	0.12	×	tr	tr	xx	0.18	ħ	хх	хх	tr	×	
98 tr 569 tr 215 135 1088 xx 565 340 85 260 75 xx x xx 0.12 xx 0.22 tr xx 0.12 x 92 tr x xx 0.12 xx 0.22 tr xx 0.12 x 48 0.37 x xx 0.11 0.10 0.13 tr tr tr x 60 tr x 0.11 0.10 0.13 tr tr tr x 61 tr x 0.11 0.10 tr tr tr x 61 tr tr 1.08 0.13 tr tr x x 61 tr tr 1.08 0.13 tr tr x x 61 tr tr 1.08 0.13 tr tr x x <t< td=""><td>IM9/294' " 62.07 5.09 33.94 101.</td><td>62.07 5.09 33.94</td><td>5.09 33.94</td><td></td><td></td><td>101</td><td>. 10</td><td>ţ</td><td>×</td><td>Ħ</td><td>t</td><td>хх</td><td>0.40</td><td>ħ</td><td>xx</td><td>хх</td><td>tr</td><td>×</td><td></td></t<>	IM9/294' " 62.07 5.09 33.94 101.	62.07 5.09 33.94	5.09 33.94			101	. 10	ţ	×	Ħ	t	хх	0.40	ħ	xx	хх	tr	×	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	IM9/294'6" EPMA & 61.87 2.96 36.15 100. AAS	EPMA & 61.87 2.96 36.15 AAS	2.96 36.15	36.15	36.15	100	. 98	ħ	5 69	5	215	135	1088	xx	565	340	85	260	:
92 tr x xx xx xx xx tr xx 48 0.37 x xx 0.14 tr 0.10 tr tr tr xx 69 tr x tr 0.11 0.10 0.13 tr tr tr x 69 tr x tr tr 2.75 tr tr tr x 61 tr tr 1.08 0.13 tr x tr x 61 tr tr tr 1.08 0.13 tr x tr x 61 tr tr tr 1.08 0.13 tr x tr x 61 tr tr tr 1.08 0.13 tr x tr x x 168 3.0 x 384 x 190 53 x $tr tr tr 0.477 tr tr x tr x$	IM6/1160 EPMA 54.56 11.58 35.61 101.	54.56 11.58 35.61				101.		XX	×	xx	0.12	хх	0.22	tr	хх	хх	0.12	×	No exsolution
48 0.37 x xx 0.11 0.10 0.13 tr tr tr tr xx xx 69 tr x tr 0.12 tr 2.75 tr tr xx tr xx 95 tr xx tr 1.08 0.13 tr xx tr xx 61 tr xx tr tr tr tr xx tr xx 61 tr xx tr tr tr tr xx tr xx 61 tr xx tr tr tr tr xx tr xx 61 tr tr tr tr tr tr tr xx tr xx xx 168 xx tr tr tr xx tr xx xx tr tr tr tr tr tr xx tr xx xx tr tr tr tr tr tr	IM6/1392 EPMA 52.11 10.65 38.16 100.	52.11 10.65 38.16	10.65 38.16	10.65 38.16		100.	. 92	tr	×	хх	0.14	ħ	0.10	ħ	xx	хх	ħ	×	
69 tr x tr 0.12 tr 2.75 tr tr xx tr xx 95 tr x tr tr tr tr 1.03 tr xx tr xx 61 tr x tr tr tr tr tr xx tr xx 61 tr x tr tr tr tr xx tr xx x 168 x 228 886 330 xx 384 xx 190 53 x x tr tr 0.47 tr tr xy tr xx x 413 tr 1600 tr 4020 0.10 tr 990 xx	M10/1548 " 62.78 3.73 32.97 99.	62.78 3.73 32.97	3. 73 32. 97	32.97	32.97	66		0.37	×	xx	0.11	0.10	0.13	ħ	ţ	Ħ	Ħ	×	Exsolutions present
95 tr x tr tr<	M10/1589 " 52.91 10.87 36.91. 100.	52.91 10.87 36.91.				100	. 69	Ħ	×	ħ	0.12	tr	2.75	ħ	ţ	хх	ħ	×	
61 tr x tr tr tr tr tr x tr x x x x x x x 168 x 228 886 330 x 384 xx 190 53 02 tr x tr tr tr tr tr x x x 33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	A15/971 " 53.81 12.56 35.58 101.	53.81 12.56 35.58	12.56 35.58	12.56 35.58		101	. 95	tr	×	ħ	tr	tr	1.08	0.13	ţ	xx	ħ	×	
x 168 x 228 886 330 x 384 xx 190 53 02 tr x tr tr tr tr tr xx tr xx	A15/1193 " 58.56 2.39 38.66 99.	58.56 2.39 38.66	2.39 38.66	2.39 38.66		6		tr	×	tr	tr	tr	tr	ħ	ħ	хх	tr	×	No exsolutions
02 tr x tr tr 0.47 tr tr xx tr x 33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	A15/1194 AAS 57.91 2.19 x	57.91 2.19	2.19					×	168	×	228	886	330	×	384	xx	190	53	-
33 tr 413 tr 1600 tr 4020 0.10 tr tr 990 x	27-145 EPMA 55.26 11.78 32.98 10	55.26 11.78 32.98	11.78 32.98	11.78 32.98		1	100.02	tr	×	ħ	tr	t	0.47	ħ	ţ	xx	ţ	×	Exsolns pre-
	H14/265 EPMA & 63.82 2.77 33.74 10	63.82 2.77 33.74	2.77 33.74			10	100.33	tr	413	t	1600	tr	4020	0.10	tr	t	066	×	sent

1 0 Table

Table 10

Sample	Fe%	Cd%	
H 4/581	2.03	∠ 0.1	
IM 9/269	18.32	0.33	
IM 6/1044'8"	8.77	0.11	
M 10/1512	1.69	0.18	

Table 11 Fe and Cd contents of Sphalerites

Table 12. Table showing the essential and trace element composition of Galena

$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Sample Number	Method	Pb	S	Total	Ag	As	Ba	Bi	Cd	°C	Cu	ъ	Mo	Ni	Sb	Sn	Te	Zn
" 83.88 15.75 99.63 0.11 1.78 x 0.34 tr tr 0.10 0.12 tr 0.11 tr xx EPMA 83.12 15.65 98.77 tr 0.10 233 0.27 xx xx 0.29 0.12 6.80 tr 0.10 tr xx xx AAS 89.15 15.13 95.28 tr 0.37 tr tr 0.38 tr 0.38 tr xx xx <td></td> <td>EPMA</td> <td>81.61</td> <td>14.87</td> <td></td> <td>0.12</td> <td>2.33</td> <td>×</td> <td>1.18</td> <td>0.11</td> <td>xx</td> <td>1.17</td> <td>0.39</td> <td>0.11</td> <td>XX</td> <td>0.21</td> <td>t:</td> <td>×</td> <td>0.29</td>		EPMA	81.61	14.87		0.12	2.33	×	1.18	0.11	xx	1.17	0.39	0.11	XX	0.21	t:	×	0.29
EPMA & 83.12 15.65 98.77 tr 0.10 233 0.27 xx xx 0.29 0.12 6.80 tr 0.10 tr xx AAS 89.15 15.13 95.28 tr 0.38 tr xx tr 0.15 tr x xx AAS 84.77 x xx xx 238 487 xx xx xx xx x		-	83.88	15.75		0.11	1.78	×	0.34	Ħ	t	0.10	0.12	0.12	ħ	0.11	tr	×	0.21
EPMA 80.15 15.13 95.28 tr 2.85 x 0.37 tr tr 0.18 tr 0.15 tr x </td <td></td> <td>EPMA</td> <td></td> <td>15. 65</td> <td></td> <td>Ħ</td> <td>0.10</td> <td>233</td> <td>0.27</td> <td>xx</td> <td>xx</td> <td>0.29</td> <td>0.12</td> <td>6.80</td> <td>ħ</td> <td>0.10</td> <td>ţ</td> <td>xx</td> <td>0.59</td>		EPMA		15. 65		Ħ	0.10	233	0.27	xx	xx	0.29	0.12	6.80	ħ	0.10	ţ	xx	0.59
AAS 84.77 x x xx x		EPMA	80.15	15.13		5	2.85	×	0.37	ħ	ħ	0.38	ħ	xx	tr	0.15	ħ	×	0.54
AAS 85.14 x x x 775 xx 5680 1025 xx xx x x 69 " EPMA & 85.19 14.60 99.83 0.28 1.26 xx 0.98 683 497 6100 913 386 145 0.19 0.13 15 2 AAS 85.28 14.87 97.15 0.15 0.17 x 3.49 tr tr 0.11 xx xx 0.37 tr x 14 x 15 15 2 PMA 82.28 14.81 97.15 0.17 x 3.49 tr tr 0.11 xx xx 0.37 tr x " 83.68 14.81 98.49 tr 2.24 x 0.38 tr tr tr tr tr tr tr 0.16 tr x 19 x x 19 AAS 87.75 x x 336 xr 11 tr 11 tr tr 14 tr t	1000	AAS	84.77			×	×	xx	×	xx	238	359	487	xx	xx	×	×		3188
" EPMA & 85.19 14.60 99.83 0.28 1.26 xx 0.98 683 497 6100 913 386 145 0.19 0.13 15 3 AAS B2.28 14.87 97.15 0.15 0.17 x 3.49 tr tr tr 0.11 xx 0.37 tr x " 83.68 14.81 98.49 tr 2.24 x 0.38 tr tr 0.14 tr tr 0.16 tr x x 19 x x 19 19 x x 19 x x 19 x 19 17 x 14 11 tr 11 x x 19 x 19 19 19 19 19 15 19 11 11 11 14 11 <		AAS	85.14	×		×	×	455	×	775	xx	5680	1025	xx	xx	×	×	69	1164
EPMA 82.28 14.87 97.15 0.15 0.17 x 3.49 tr tr tr 0.11 xx xx 0.37 tr x x " 83.68 14.81 98.49 tr 2.24 x 0.38 tr tr 0.14 tr tr 0.16 tr x x AAS 87.75 x x 396 x 412 xx 933 1236 xr 210 x x 19 EPMA 81.25 13.85 95.10 tr 1.18 x 3.17 0.11 tr 1.65 tr tr xx 0.14 0.13 xx 19 " 83.19 14.67 97.86 tr x 1.07 tr xx 0.14 tr xx 0.41 0.11 x	-	16" EPMA AAS		14.60		0.28	1.26	x	0.98	683	497	6100	913	386	145	0.19	0.13		2200
" 83.68 14.81 98.49 tr 2.24 x 0.38 tr tr 0.14 tr tr 0.16 tr x AAS 87.75 x x 396 x 412 xx 933 1236 xx 210 x x 19 EPMA 81.25 13.85 95.10 tr 1.18 x 3.17 0.11 tr 1.65 tr xx 0.14 0.13 x " 83.19 14.67 97.86 tr x 1.07 tr xx 0.14 tr xx 0.41 0.11 x	10		82.28	14.87		0.15	0.17	×	3.49	t	t		0.11	xx	xx	0.37	ħ	×	0.18
AAS 87.75 x x 396 x 412 xx 933 1236 xx 210 x x 19 EPMA 81.25 13.85 95.10 tr 1.18 x 3.17 0.11 tr 1.65 tr tr xx 0.14 0.13 x " 83.19 14.67 97.86 tr tr x 1.07 tr xx 0.14 tr tr tr xx 0.41 0.11 x		=	83.68	14.81		ţ	2.24	×	0.38	Ħ	ħ	0.14	tr	tr	tr	0.16	tr	×	0.15
EPMA 81.25 13.85 95.10 tr 1.18 x 3.17 0.11 tr 1.65 tr tr xx 0.14 0.13 x " 83.19 14.67 97.86 tr tr x 1.07 tr xx 0.14 tr xx 0.41 0.11 x	6		87.75	×		×	×	396	×	412	хх	933	1236	XX	210	×	×	19	2130
" 83.19 14.67 97.86 tr tr x 1.07 tr xx 0.14 tr xx 0.41 0.11 x	00		81.25	13.85		ţ	1.18	×		0.11	tr	1.65	ħ	tr	xx		0.13	×	0.26
	00	6	83.19	14.67			Ħ	×	1.07	H	xx	0.14	ţ	xx	хх		0.11	×	0.12

Table 13. Table showing the statistical data of Pyrite (in p. p. m. & %)

4	Fe%	S%	As	Ыа	Cd	S	n,	MO	IN	04	Te	TT I
Mean 45.0	-	54.14		314	395	523	1946	138	264	482	78	528
Minimum 42.	42.83	52.35	1	103	33	30	120	13	16	38	15	17
	48.25	55.38	•	827	1300	2075	1.271	442	969	1300	230	3280

Table 14. Table showing the statistical data of Cha.copyrite (in p. p. m. & %)

	Cu%	Fe%	S%	As	Ba	Bi	Cd	ပိ	Mo	Ni	Pb	Te	Zn
Aean	34.50	29.85	35.38		737	0.16%	231	401	217	410	481	95	1907
Minimum	32.40	25.80	32.48	•	165	1000	•	60	28	12	1000	55	1000
Aaximum	37.09	32.81	36.93	•	1653	0.24%	446	710	510	1060	1045	192	5600

Table 15. Table showing the statistical data of Sphalerite (in p.p.m. & %)

Cu %	Fe%	S%₀ .	As	Ba	Bi	Cd	Co	Cu	Mn	Mo	Ni	Pb	Te
	58.46 6.43	35.29	0.17%	1651	0.12%	1190	588	9665	1157	951	382	874	116
	51.68 1.12	32. 23	1000	168	1000	215	206	3.30%	1000	285	340	190	16
	18.32	38.66	0.37%	7222	0.13%	2780	1000	2.75%	1300	2100	433	1468	260

Table showing the statistical data for Galena (in p. p. m. & %) Table 16

	Zn	2674	1164	5860	
	Te	33	15	69	
	Sn	0.12%	1000	0.12%	
	Sb	0.20%	0.10%	0.37%	
	Ni	202	145	260	
	Mo	841	386	1200	
	Fе	1378	487	3900	
	Cu	4310	359	1.65% 3900	
	Co	367	238	497	
	Cd	820	412	1130	
	Bi	361 1.25%	0.27%	3.49%	
	Ba	361	233	455	
	As	14.91 16.50 1.48%	1000 1.68%	2.85%	
and the second second	Ag	16.50	1000	2800	
and the second se	S(%)	14.91	13.85	15.75	
	Pb(%) S(%)	83.50	80.15	87.75	
		Mean	Minimum	Maximum	

Sl. No.	Sample: Number	Measured edge in Å	Calculated edge Å	Difference Å
1	H4/456	5.4146	5.4135	-0.0011
2	H4/460	5.4113	5.4107	-0.0006
3	H4/467	5.4221	5.4211	-0.0010
4	H4/473	5.4120	5.4108	-0.0012
5	H4/474	5.4194	5.4202	+0.0008
6	H4/481	5.4162	5.4172	+0.0010
7	H4/491	5.4201	5.4220	+0.0019
8	H4/581	5.4135	5.4109	-0.0026
9	IM6/1044'8"	5.4206	5.4169	-0.0037
10	IM6/1160 .	5.4198	5.4193	-0.0005
11	IM9/269	5.4249	5.4259	+0.0010
12	'IM9/283	5.4118	5.4107	-0.0011
13	IM9/285'2"	5.4125	5.4118	-0.0007
14	IM9/292'6"	5.4114	5.4106	-0.0008
15	IM9/294'6"	5.4127	5.4118	-0.0009
16	M10/1512	5.4106	5.4114	+0.0008
17	H14/265	5.4152	5.4124	-0.0028

Table 17 Table showing the measured and calculated cell edges of Sphalerite

S1, No.	Sample number	X-ray diffraction Å	Electron diffraction Å	Difference Å
1	H4/456	5.4146	5.4284	0.0138
2	H4/460	5.4113	5.4226	0.0113
3	H4/491	5.4171	5.4248	0.0077
4	IM9/269	5.4249	5.4367	0.0118
5	IM9/283	5.4118	5.4320	0.0202
6	IM9/285'2"	5.4125	5.4177	0.0052
7	IM9/292'6"	5.4114	5.4236	0.0122
8	IM9/294'6"	5.4127	5.4381	0.0254
9	H14/265	5.4202	5.4207	0.0005
10	M10/1512	5.4106	5.4242	0.0136
11	19-424	* 5.4240	5.4196	0.0044
12	A15/1193	* 5.4115	5.4224	0.0109

Table 18Table showing the differences in measured cell edges of Sphalerite
by X-ray diffraction and electron diffraction

* calculated edges

51. No.	Sample number	VHN kg/mm ²	Sl. No.	Sample number	VHN kg/mm ²
1	A15/916	1031	9	M10/1548	1097
2	A15/924	1037	10	M10/1589	1123
3	A15/971	1052	11	H14/186	1118
4	· IM6/1044'8"	1063	12	M10/1599	1155
5	IM6/1160	1185	13	C4/960	1110
6	36A/1617	1123	14	H4/464	1168
7	H43A/1837'	1483	15	H14/265	1107
8	M10/1540	1089	16	32-1108	1063

Table 19 Microhardness values of Pyrite

Table 20 Microhardness values of Chalcopyrite

S1.	Sample number	VHN -	Sl. No.	Sample number	VHN
No.	bampre number	kg/mm ²	0111101	cumpre numer	kg/mm ²
1	A15/920	203	7	IM9/264	221
2	A15/1193	210	8	M10/1548	197
3	A14/1534	201	9	M10/1589	187
4	M10/1521	201	10	H4/465	174
5	M10/1512	187	11	H4/491	194
6	H14/186	194	12	H4/171	210

S1. No.	Sample number	VHN kg/mm ²	S1. No.	Sample number	VHN kg/mm ²
1	A15/971	230	11	IM9/288	206
2	IM6/1160	215	12	M10/1589	195
3	IM9/269	237	13	H4/465	148
4	19-424	203	14	M10/1548	175
5	M10/1512	161	15	H4/481	190
6	A15/1194	172	16	H4/474	210
7	H4/474	195	17	IM9/294'6"	172
8	H4/491	240	18	IM9/285	186
9	IM9/285'2"	168	19	H4/456	203
10	M10/1584	198			

Table 21 Microhardness values of Sphalerite

Table 22 Microhardness values of Galena

S1. No.	Sample number	VHN kg/mm ²	Sl. No.	Sample number	VHN kg/mm ²
1	19-424	61.7	5	H4/491	67.7
2	H4/464	107	6	M10/1584	201
3	H4/474	104	7	IM9/283	96.5
4	A15/1194	77.9	8	H14/265	87.8

Continu		-	Table 23		able sh	owing t	the spec	ctral r	eflectiv	Table showing the spectral reflectivity values of Pyrite (R% air)	es of Py	rite (R	% air)				
No.	400	420	440	460	480	500	520	540	560	580	589	600	620	640	660	680	200
A15/924	41.05	46.1	47.5	50.05	51.8	52.0	52.7	55.0	55.15	56.23	56.45	57.8	56.2	57.3	57.6	57.8	57.7
A15/980	42.5	45.20 45.5	45.5	45.18	47.5	48.2	49.3	49.6	49.8	50. 25	52.1	52.5	52.6	53.8	53.9	53.8	53.7
A15/971	35.05	36.8	37.9	40.10	42.5	43.2	45.05	46.8	47.5	49.0	49.8	50.15	51.2	52.5	54.1	54.6	55.3
A14/1534	36.10		39.8	42.5	43.6	46.0	47.5	49.0	49.65	49.75	51.38	52.1	53.4	55.6	55.2	55.3	55. 25
27-145	42.5		47.0	48.3	49.5	50.25	50.05	51.2	52.1	52.1	52.3	52.1	52.5	53.2	53.8	54.0	54.8
H43A/1855	34.8	36.7	37.2	38.3	41.8	42.9	45.5	47.5	48.3	50.6	52.1	52.35	53.68	54.8	54.95	55.0	54.86
32-1108	34.3		40.15	41.6	42.65	45.73	46.35	46.65	46.75	46.89	47.5	50.05	50.10	50.10	5.05	50.05	51.00
32-1198	36.0		39.8	42.5	45.05	47.8	48.5	50.05	50.10	50.5	52.01	52.25	52.20	51.85	51.80	51.8	50.75
H14/265	32.5		37.3	39.4	40.03	41.6	42.5	43.6	45.80	47.2	47.8	48.3	49.6	49.5	49.9	50.05	50.20
H4/456	36.2		42.6	43.2	45.05	46.7	47.5	48.3	50.15	52.6	53.9	54.8	55.05	55.10	55.20	55.15	55.20
H14/	36.25	37.5	37.8	40.16	41.68	42.5	43.6	45.2	46.25	46.8	47.6	47.8	49.3	50.2	52.6	52.3	52.2
19-424	38.12	40.10	42.3	42.7	44.3	45.6	46.2	47.6	48.3	48.9	49.2	50.12	50.15	49.8	50.2	49.5	50.05
A15/953	42.5	43.4 47.5 4	47.5	48.2	51.6	52.6	54.8	55.1	55.2	56.2	56.3	56.8	56.4	52.5	57.2	57.6	57.3
A15/950	37.0	37.5	39.5	40.25	45.06	46.3	47.5	49.3	47.25	50.15	50.30	52.2	55.0	55.25	55.6	55.3	55.75
A15/	34.8	35.2	36.8	36.9	37.5	40.2	41.5	42.2	43.8	45.0	46.3	49.8	51.3	52.6	52.7	52.6	53.9
32-1269	33.6	37.6	39.5	42.5	45.0	47.5	50.2	51.8	52.5	52.8	53.6	54.9	55.2	55.1	55.3	55.6	55.4
IM6/1101	35.0	37.8	41.8	44.8	47.5	47,8	51.3	51.85	52.6	53.6	52.8	55.05	55.61	55.3	55.4	55.6	55.0
A15/1193	32.6	34.6	39.6	42.5	45.0	47.2	49.6	49.8	50.1	51.2	51.8	52.5	52.6	52.7	52.9	54.0	55.0
IM6/1160	32.5	35.6	40.04	42.6	45.10	47.5	49.8	50.1	50.25	52.5	52.7	54.0	55.0	55.2	55.05	55.10	55.2
A15/941	36.8	37.5	39.8	42.3	42.8	46.8	47.9	50.0	50.10	50.15	51.28	52.20	52.5	52.8	52.4	52.3	52.0
IM6/231	34.3	35.0	36.2	37.2.	40.02	40.35	42.5	42.6	44.8	46.35	47.21	47.75	48.3	48.4	48.2	48.3	49.5
A15/916	38.35	40.05 44.3	44.3	47.5	48.3	50.1	50.2	52.5	52.7	53.6	54.8	55.0	55.6	55.2	54.9	54.8	54.6
IM6/1392	34.8	35.0	40.35	42.6	46.3	46.2	47.5	47.8	47.9	50.25	50.20	53.2	52.5	53.2	53.1	53.6	53.78
H4/474	33.6		36.2	37.8	38.3	40.5	42.5	45.0	45.8	46.9	46.92	46.85	47.25	47.05	46.55	47.2	47.4
A15/935	33.8	36.8	38.6	42.6	47.5	48.9	51.6	52.6	53.78	54.2	53.98	54.5	55.2	55.1	52.8	52.3	52.6

200	52.6	50.3	53.2	51.2	49.8	53.6	55.4	53.5	
680	52.3	50.2	53.6	50.15	49.5	53.78	55.2	53.2	
660	52.8	50.2	54.8	50.25	48.4	53.65 53.78	55.0	53.8	
640	52.7	49.6	53.4	52.3	47.3	53.8	55.3	54.6	
620	52.5	48.4	52.6	51.2	45.8	53.6	55.2	54.8	
600	51.26	47.8	52.5	50.2	45.6	52.5 53.6 53.8 5	54.7	52.2	
589	50.53	47.6				51.6			
580	50.6	46.8	50.2	45.7	44.5	50.5	54.6	50.2	
560	49.35	45.6	49.5	45.2	42.75	48.4	52.6	48.6	
540	49.3	45.7	47.5	45.6	42.6	47.5	51.8		
520	48.6	44.6	47.8	44.2	41.8	45.5 47.5	50.2		
500	47.5	42.5	45.6	43.6	39.6 46.1	42.6 44.2	47.5	46.8	
480	45.1	41.9	45.2	42.5	39.6	42.6	46.8	42.5	
460	42.5	39.8	42.5	40.2	38.2	41.5	42.6	39.8	
440	40.2	37.3					40.2	37.5	
420	37.5 40.2	34.68 37.3	37.39 40.15	35.7 37.8	35.2	35.0	34.6	35.0	
400	34.85	32.15	36.18	33.5	32.3	32.2	34.8	32.6	
	1M6/779	IM 9/364'2"	M10/1548	A15/965	36.A/1611	H4/491	M10/1610	11W9/2921611	

. Table 24 Table showing the spectral reflectivity values of Chalcopyrite (R% air)

	~	3		10	-							00
700	38.73	35.93	34.2	35.85	36.31	36.8	35.2	36.9	39.7	39.3	39.3	40.38
680	38.66	36.03	34.75	36.2	37.5	38.58	36.12	38.05	39.68	39. 65	40.2	41.85
660	39.45	36.65	36.2	36.5	37.61	39.32	36.62	38.86	40.38	40.2	40.4	42.65
640	39.68	36.8	36.65	36.8	39.58	39.68	38.31	39.8	41.4	40.4	40.6	42.83
620	31.71 34.58 37.11 38.23 39.45 40.05 40.25 41.33 41.39 40.66 39.68 39.45 38.66	33.44 35.40 36.49 37.44 37.79 38.81 39.12 40.36 39.60 38.31 36.8 36.65	38.21 38.66 37.81	41.18 38.31	30.10 34.76 35.68 36.61 37.31 38.25 38.65 39.30 40.31 39.58 37.61 37.5	39.47 40.69 39.68	27.81 30.44 32.38 33.98 34.39 36.35 37.12 38.88 38.56 37.34 38.31 36.62 36.12	32. 67 34. 73 36. 01 37. 28 37. 92 39. 13 40. 62 39. 47 40. 31 39. 8	39.47 40.31	40.75	41.37 40.31 40.6 40.4	29.80 30.34 33.76 36.29 33.94 39.92 40.15 42.61 43.85 43.05 42.83 42.65
600	41.39	39.60	38.66		39.30		38.56	39.47		40.44	41.37	43.85
589	41.33	40.36	38.21	32.7 34.10 35.71 37.19 33.14 38.37 39.83 40.36	38.65	38.34	38.88	40.62	33.51 35.91 37.53 38.62 40.55	39.6 41.35	30. 16 31. 35 33. 69 34. 85 32. 83 39. 65 41. 02	42.61
580	40.25	39.12	34.56 36.15	39.83	38.25	36.24	37.12	39.13	38.62	39.6	39.65	40.15
540 560	40.05	38.81	34.56	38.37	37.31	35.86 36.16	36.35	37.92	37.53	29.81 30.34 33.76 35.29 36.94 37.92	32.83	39.92
	39.45	37.79	33.38	33.14	36.61	35.86	3.1.39	37.28	35.91	36.94	3.4.85	33.94
520	38.23	37.44	31.32	37.19	35.68	35.29	33.98	36.01	33.51	35.29	33.69	36.29
500	37.11	36.49	29.91 31.13	35.71	34.76	32.36	32.38	34.73	32.75	33.76	31.35	33.76
480	34.58	35.40		34.10	30.10	30.31 31.15	30.44		31.29	30.34	30.16	30.34
460	31.71		28.54	32.7	27.45	30.31	27.81	31.38	30.35	29.81	29.30	29.80
440	29.04	31.00	26.28	31.8	21.91 22.95 24.60	29.9	20.40 22.56 25.08	28.15 29.28 30.36	23.53 28.01 29.36	27.35 28.45 28.86	28.71	26.8
420	27.54	28.85	24.26	29.10	22.95	25.10 28.78 29.9	22.56	29.28	28.01	28.45	27.36	24.2
400	24.48	25.92	22.75	28.7	21.91	25.10	20.40	28.15	23.53	27.35	26.16 27.36 28.71	23.6
Section 400 420 440 No.	32-1198 24.48 27.54 29.04	A15/1193 25.92 28.85 31.00	IM6/1393 22.75 24.26 26.28	A15/924 28.7 29.10 31.8	A15/943	H14/186	A15/965	1779 MI	H4/456	H43A/ 1855	H4/491	M10/1410 23.6 24.2 26.8

Table 25Table showing the spectral reflectivity values of Sphalerite (R% in air)

14.89 13.53 19.6 20.6 19.3 19.3 13.3 19.4 18.9 17.6 700 700 19.46 15.63 19.6 19.87 13.6 19.6 13.53 20.3 19.6 17.6 680 680 15.87 14.53 14.83 15.33 19.8 20.32 13.53 16.47 17.15 20.3 19.8 20.3 17.37 17.25 17.60 18.85 18.64 18.32 18.8 660 660 19.32 15.87 14.83 15.87 14.53 18.13 19.23 23.07 17.01 17.55 17.42 17.96 17.53 17.55 17.00 17.25 17.05 19.57 18.36 20.3 20.3 640 640 air) 18.13 16.87 22.67 16.32 17.8 620 620 Table showing the spectral reflectivity values of Galena (R % 17.08 19.65 17.94 17.65 17.08 17.28 23.92 600 600 17.83 17.72 17.89 15.92 15.66 16.78 15.92 15.66 16.35 22.13 16.95 16.98 17.72 17.92 17.65 17.43 17.35 15.81 16.35 17.7 589 589 22.25 580 580 18.79 16.50 16.07 22.29 560 560 18.62 18.78 17.53 17.6 17.83 17.79 16.52 16.32 15.89 17.79 17.74 22.04 18.28 15.86 17.63 15.25 15.4 540 540 22.31 16.40 15.21 17.35 17.93 520 520 15.84 14.85 14.86 17.65 16.58 16.11 16.66 16.11 21.87 18.80 17.89 500 500 18.62 18.07 18.72 19.91 21.95 16.78 16.4 18.6 480 480 22.04 18.6 18.9 460 460 17.85 22.16 16.85 16.73 16.15 18.68 16.85 16.76 16.64 18.8 19.05 17.4 18.8 440 Table 26 440 18.80 19.25 22.20 19.15 19.03 18.2 18.3 16.85 16.9 18.9 420 420 18.85 18.35 19.31 22.24 19.2 18.4 400 400 IM6/1393 A15/1193 IM9/294' IM9/2851 A15/980 H14/265 32-1198 -9 H4/456 511 Section 27-145 Section 19-424 No.

36.68 44.83 40.5 33.2 31.2 45.63 41.2 33.2 37.2 35.57 34.2 36.5 45.8 36.35 40.8 34.42 32. 15 32. 00 31. 92 32. 38 34. 16 35. 86 37. 31 37. 31 38. 15 37. 7 41.39 41.08 40.68 41.32 42.36 43.06 46.0 37.39 41.4 36.13 36.8 33. 22 41.18 39.6 32.74 32.47 31.87 41.71 40.57 39.45 40.25 42.66 40.65 38.85 39.29 38.91 38.37 37.83 38.3 32.73 32.79 43.95 42.38 41.96 41.35 33.26 35.69 45.05 45.24 35.19 42.64 42.84 32.8 36.09 32.95 33.45 32.80 43.31 43.15 43.05 45, 15 43.35 38.3 45.92 45.24 43.65 38. 65 43.93 38.75 A15/1193 M10/1584 A14/456 19-424 H4/491

Table 27

Composition of Arsenopyrite

	M 10/1599 %	M 10/1608 %	Theoretical composition %
Fe	36.06	37.11	34.30
As	42.78	43.23	46.01
Co	tr	tr	
Ni	tr	tr	
Cu	tr	tr	
Pb	tr	. tr	
Zn	tr	tr	
S	20.76	21.25	19.69
Total	99.60	101.59	100.00

Table 28 List of Sulpho-salts found at Parys Mountain

General classification	Name	Theoretical formula
Copper Sulpho-salts	Tetrahedrite-Tennantite	(Cu Fe Zn Hg) ₁₂ (Sb As) ₄ S ₁₃
Copper-Lead Sulpho- salt	Bournonite	Pb Cu Sb S ₃
Lead Bismuth Sulpho- salts	Galenobismuthite Kobellite	Pb Bi ₂ S ₄ Pb (Bi, Sb) ₂ S ₅
Lead Sulpharsenides	Lead Sulpharsenide	Pb-As-S (varying)

Table 29 Composition of Tetrahedrite - Tennantites

2.6 3.9 2.5 29.8 0.8 99.2 34.9 24.7 13 25.0 34.4 9.66 1.8 2.6 29.8 1.1 4.9 12 24.5 32.6 98.9 5.4 6.1 28.2 0.8 1.3 11 34.7 25.2 98.2 3.1 1.7 5.7 25.1 2.7 10 H4/473 H4/464 H4/456a H4/456b 27-145 H4/474 27-145 H4/491 M10/1548 28.78 3.16 100.04 1.29 0.12 41.57 25.12 XX XX 6 31.61 1.28 8.31 5.15 1.38 0.87 24.63 97.52 24.29 8 37.88 0.23 1.42 27.47 7.04 4.69 22.16 100.91 ~ 井 32.39 4.31 8.18 23.67 3. 28 26.66 98.49 хх tr 9 0.55 6.05 39.67 4.24 22. 12 1.18 97.75 23. 32 XX ŝ 36.31 2.23 22.85 4.48 25.03 9.61 100.51 ţŗ 4 33.76 0.31 5.36 10.18 23.35 26.18 0.67 101.91 2.1 3 36.12 8.42 98.69 0.89 23.25 1.29 28.52 3.2 tr 2 9.54 2.38 24.77 0.32 25.45 99.01 34.35 0.1 2.1 -Fe Element Cu Ag Zn Sb. As Sample No. Bi S Total

tr - traces xx not detected

1 - 6 Parys Mountain Tetrahedrites (Present Study)

7 - 9 Parys Mountain Tennantites (Present Study)

Parys Mountain Tetrahedrite Hill Side open cast, Bluestone adit dump (Analyst: Wheatly 1971a) 10

11 Parys Mountain Tetrahedrite, Morfa-du Ida Shaft dump (Analyst: Wheatly 1971a)

12 West Avoca Tetrahedrite, South Lode. (Analyst: Wheatly 1971a)

13 East Avoca Tetrahedrite (Analyst: Wheatly 1971a).

Table giving the atomic proportions for Tetrahedrites-Tennantites (Present Study) Table 30

Tetrahedritee

ß	M10/1548	12		~			-	-	-
t i t e	M10	10.27	•	1. 28	0.45	'	3.99	0.00	11.50
Tennantite	H4/491	8.10	0.19	2.42	1. 28	0.13	3.82	0.05	11.42
Ч	27-145	8.99	0.03	1. 90	1.08	0.00	3.90	0.09	12.48
					·				
	H4/474	8.59	1	1.30	2.10	3.26	0.74	•	13.90
r i t e s	27-145	9.33	0.07	1. 62	0.97	3. 53	0.47	•	11.54
a h e d	H4/456b	10.59		1.05	0.37	3.03	0.97	•	13. 95
Tetr	H4/456a	7.99	0.04	2.74	1. 23	3.44	0.50	0.06	12.79
	H4/464	9.23		2.44	0.32		0.61	0.06	11.37
	H4/473	8.66	0.01	2.73	0.58	3.49	0.48	0.02	12.93
		Cu	Ag	Fе	Zn	Sb	As	Bi	S

		Co	mposi	tion			Atomic Prop	portions
	1	2	3	4	5	6	1	2
Cu	15.22	20.72	13.0	13.6	14.2	12.3	1.37	• 1.58
РЪ	39.81	43.86	42.4	44.6	43.8	42.9	1.10	1.03
Sb	22.84	16.17	24.9	22.7	22.7	25.3	1.07	0.64
As	2.49	3.67	-	-			0.19	0.24
Bi	0.12	0.22	-	-			0.00	0.00
Fe	xx	0.25	-	-			- 1994 The -	0.02
Zn	0.16	0.14	-	-			0.01	0.01
S	18.17	15.62	19.7	19.3	20.5	19.6	3.25	2.46
Total	98.81	100.65	100.0	100.2	101.2	100, 1		

Table 31 Composition and atomic proportions of Bournonite

Parys Mountain, H4/465 (Present Study) 1.

Parys Mountain, M10/1548 (Present Study) 2.

Theoretical Composition 3.

1

East Avoca, Tigroney (Analyst: Wheatly, 1971a) 4.

No. 1A, draw point, Avoca (Analyst: Wheatly, 1971a) 5.

Wood river Lead Silver deposit, Idaho (Analysts: Hall and Czemanske, 1972) 6.

	Composition				Atomic Proportions	
РЪ	1 40.26	2 43.18	3 44.4	4 47.1	1 5.51	2 8.77
Cu	2.86	2.19		0.9	1.27	1.45
Bi	30.22	32.15	29.9	32.1	4.10	6.47
Sb	6.12	4.23	8.6	4.5	1.43	1.46
Fe	3.12	1.29	-	-	0.65	0.97
As	1.31	0.88	-	-	0.05	0.00
5	17.18	16.19	17.2	15.7	15.20	21.25
Total	101.07	100.11	100.1	100.3		

Table 32 Composition and atomic proportions of Kobellite

1. Parys Mountain H4/474

1 .

2. Parys Mountain M10/1548

3. Theoretical Composition

4. West Avoca (Analyst: Wheatly, 1971a)

Table 33 Composition and atomic proportions of Galenobismuthite

	Composition				Atomic Proportions	
Bi	1 43.16	2 55.5	3 54.69	4 58.0	1 1.47	
Cu	3.18	-			0.36	
РЪ	26.47	27.5	27.65	24.7	0.83	
Zn	10.12				1.10	
Fe	0.39				· 0.00	
s	13.78	17.0	17.35	17.0	3.06	
	97.10	100.0	99.69	99.7		

1. Parys Mountain H4/474

2. Theoretical Composition

3. Type Material (Analyst: Sjogren (1878) in Berry, 1940)

4. Bally Coog, Avoca (Analyst: Wheatly, 1971a)

Tabl	e 34 Com	position and atomi	c proportions of Lead Sulp	harsenides	
	Compo	sition	Atomic Proportions		
	1	2	1	2	
Cu	0.18	0.28	0.03	0.06	
Pb	69.68	68.18	3.17	4.21	
Sb	0.13	0.05	0.01	0.00	
As	13.24	15.37	1.66	2.63	
Fe	0.16	0.38	0.03	0.09	
Zn	1.88	0.19	0.27	0.04	
Bi	xx	xx			
S	13.82	14.38	4.06	5.75	
Total	99.09	98.83			

1. Parys Mountain 19-424

2. Parys Mountain M10/1589

dÅ (from Tables 7-171)	hkl	d & measured	
7.08	002	7.081	
3.541	004	3.541	
2.458	132, 203	2.458	
2.271	132, 204	2.276	
1.829	136, 205	1.829	
1.550	331, 060	1.542	
1.360	334, 065, 336	1.368	

Table 35 X-ray Powder diffraction data for Diabantite

Table 36X-ray Powder diffraction data for Ripidolite

dÅ (from Tables 7-76)	hkl	dÅ measured	
14.1	001	14.119	
7.07	002	7.076	
4.724	003	4.720	
3.537	004	3.534	
2.599	(131, 202)	2.600	
2.450	132, 203	2.452	
1.826	136, 205	1.826	
1.665	137, 206	1.666	
1.547	331,060	1.546	

dAfrom Tables 19-749	hkl .	d A measured
14.3	001	14.348
7.12	002	7.115
3.56	004	3.559
2. 435	132	2.438
2.255	133	2.256
1.535	245,060	1.536

Table 37 X-ray Powder diffraction data for Clinochlore

Table 38 X-ray Powder diffraction data for Aphrosiderite

dÅ from Tables 2-243	hkl	d Å measured
7.05	002	7.047
3.52	004	3.527
2.83	005	2.822
2.67	200	2.672
1.559	060	1.559

Table 39 X-ray Powder diffraction data for Grochauite

dÅfrom Tables 7-165	hkl	d Å measured	
14.0	001	14.029	
7.08	002	7.081	
3.545	004	3.545	
2.543	132, 201	2.544	
2.842	005	2.844	

Table 40 X-ray powder data for Chlorite 1b

hkl	d Å measured	
001	14.392	
002	7.155	
203	2. 470	
204	2. 287	
060	1.549	
	001 002 203 204	001 14.392 002 7.155 203 2.470 204 2.287

35	36A/1617 (Pyrite with little chalcopyrite), IM6/1044'8" (Pyrite), 36A/1611 (Pyrite)
36	36A/1670 (Pyrite), M10/1630 (Pyrite), A15/941 (Pyrite with little chalcopyrite), M10/1410 (Chalcopyrite with some pyrite)
37	IM9/269 (Sphalerite with some pyrite), 32-1198 (Pyrite with little sphalerite)
38, 39	IM6/1231 (Pyrite), IM6/1365 (Pyrite, Chalcopyrite with little sphalerite; in this section only grochauite is present)
40	IM6/1359, 36A/1525, 6-527, H17A/1510, H43A/1845 (non-

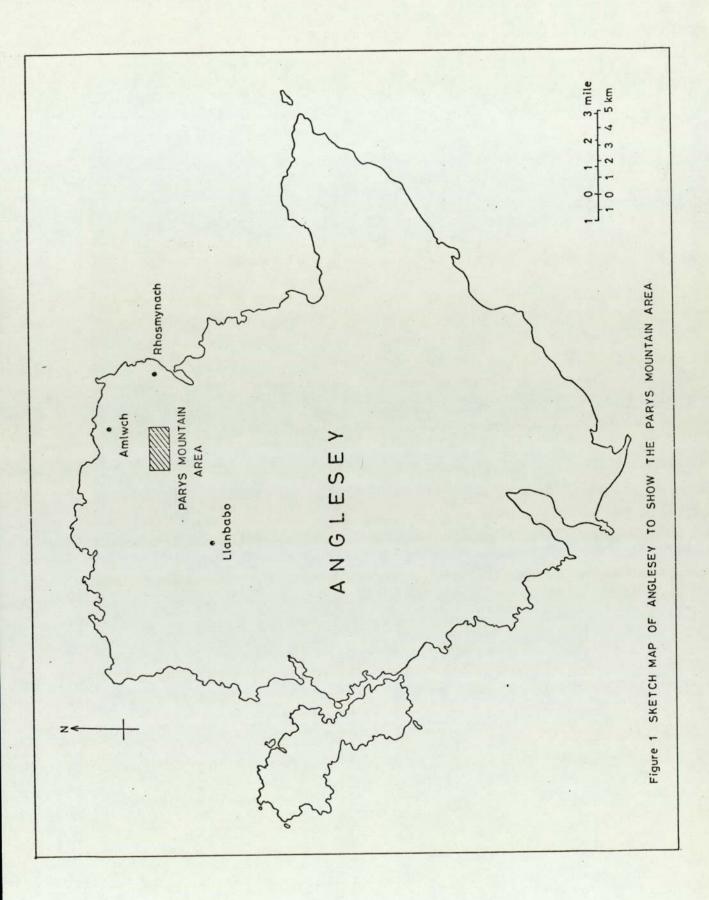
mineralised sections).

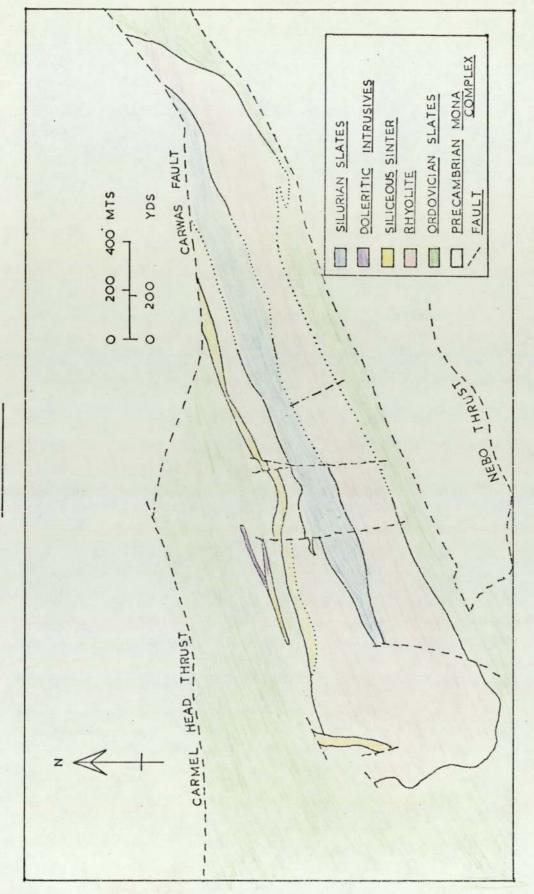
T	ab	le	4	1

Standards used for Microprobe Analysis

Element	Standar	d	Radiation
Ag	Pure Metal		Ag K _X
As	Pure Element		As K
Bi	Pure Metal		Bi L _x
Cd	Pure Metal		Cd L
Co	Pure Metal		Co Kox
Cu	Pure Metal		Cu K
Fe	FeS2	46.55% Fe	Fe K _X
Mn	Pure Metal		Mn K _K
Мо	Pure Metal		Mo Lo
Ni	Pure Metal		Ni K _{ol}
Pb	PbS	86.62% Pb	Рь М 🗙
S	FeS2	53.45% S	SKX
Sb	Pure Element		SbL
Se	No Standard available		
Sn	Pure Metal		Sn K _K
Zn	Pure Metal		Zn K _K

.





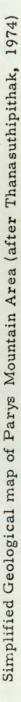
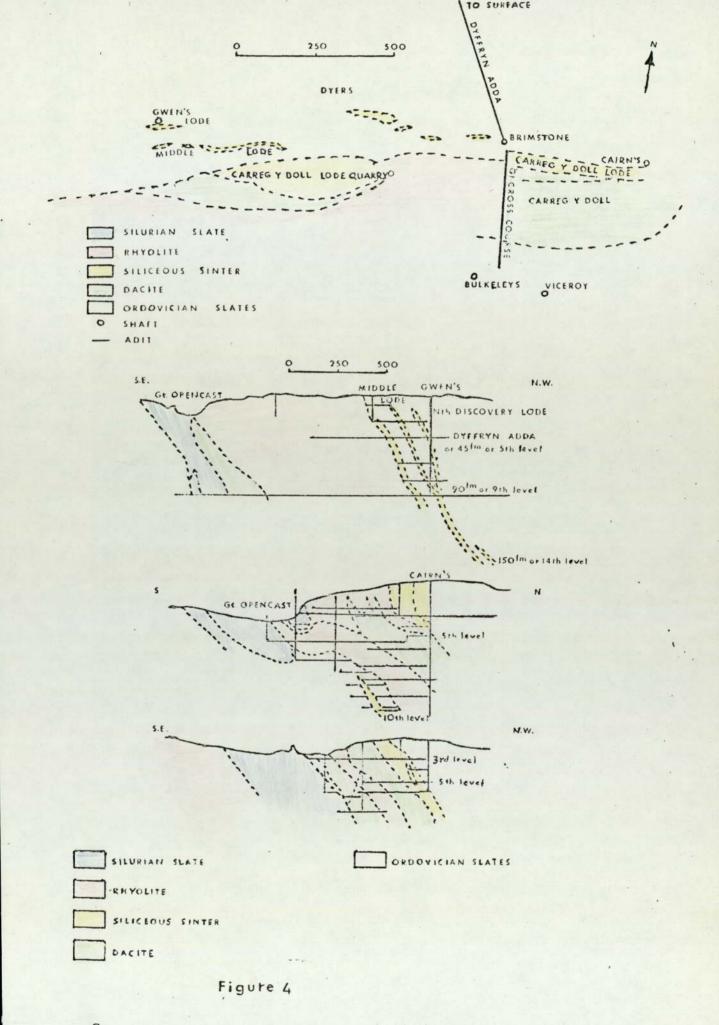


FIGURE 2

. FLGURE 3

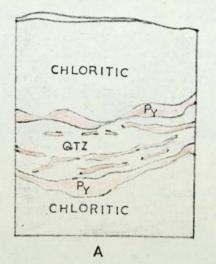
	OF PARTS MOUNTAIN
0	14
CARMEL HEAD THRUSI	RHWNC THRUST NEBO
RHWNC THRUST	400 YDS
	- CARMEL HEAD
(2)	THRUST I III
0 440 HORIZONTAL AND VERTICAL SCAL	30011
	7777 300 FT
	1000 FT 0
SECTION THROUGH THE CENTRAL	PART OF PARYS MOUNTAIN (AFTER GREENLY 1919)
2 SECTION THROUGH THE WESTER	N END OF PARYS MOUNTAIN (AFTER GREENLY 1919)
3 SECTION THROUGH THE CENTRAL	PART OF PARTS MOUNTAIN (ÅFTER MANNING 1959)
(4) SECTION THROUGH THE CENTRAL	L PART OF PARTS MOUNTAIN AFTER THANASUTHIPITHAK 1974 cf. WHEATLEY, 1971)
SILURIAN SLATE	SILICEOUS SINTER
DACITE .	ORDOVICIAN SLATE
RHYOLITE .	PRECAMBRIAN MONA COMPLEX

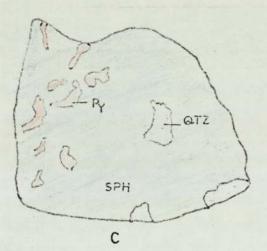
CROSS SECTIONS ILLUSTRATING THE STRUCTURAL INTERPRETATIONS OF PARYS MOUNTAIN



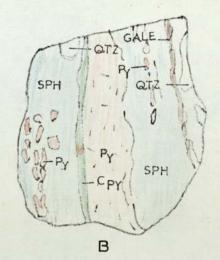
Sections illustrating the various lodes (after Manning, 1959)

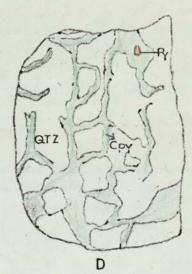
FIGURE 5

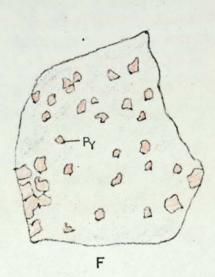






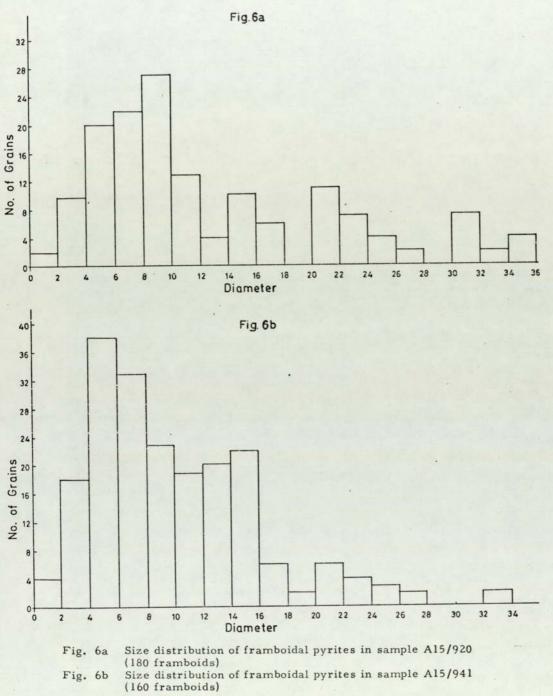


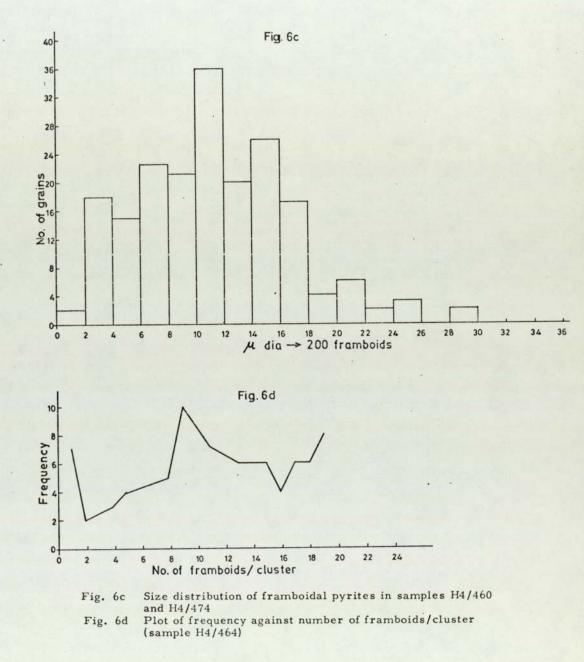


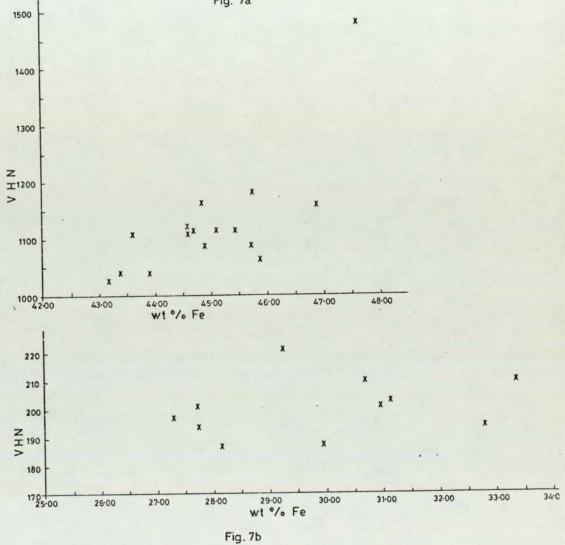


I CM

+







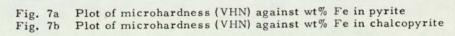
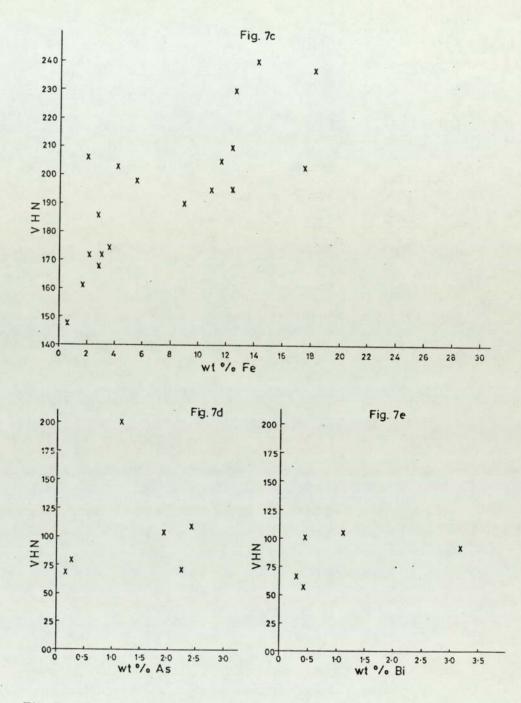
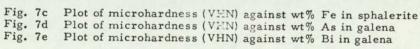
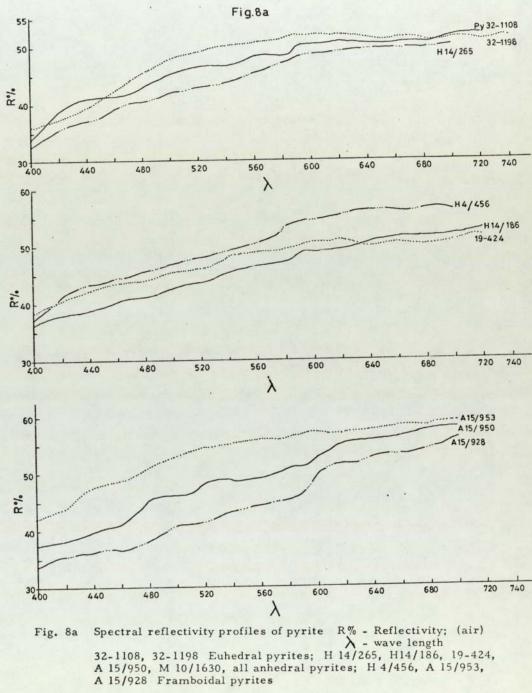
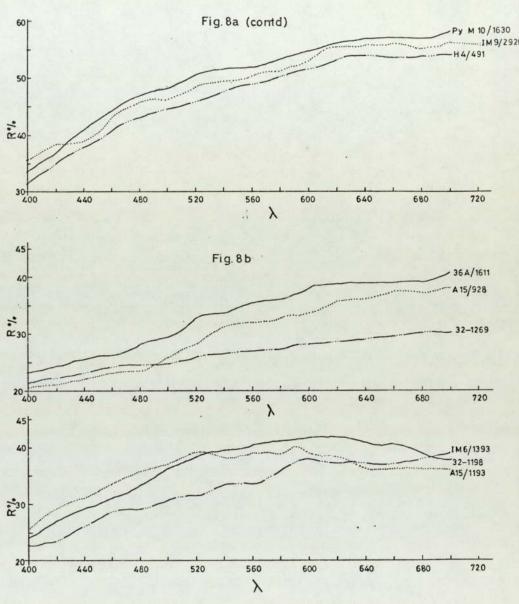


Fig. 7a

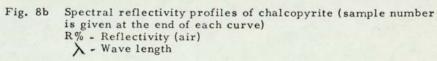


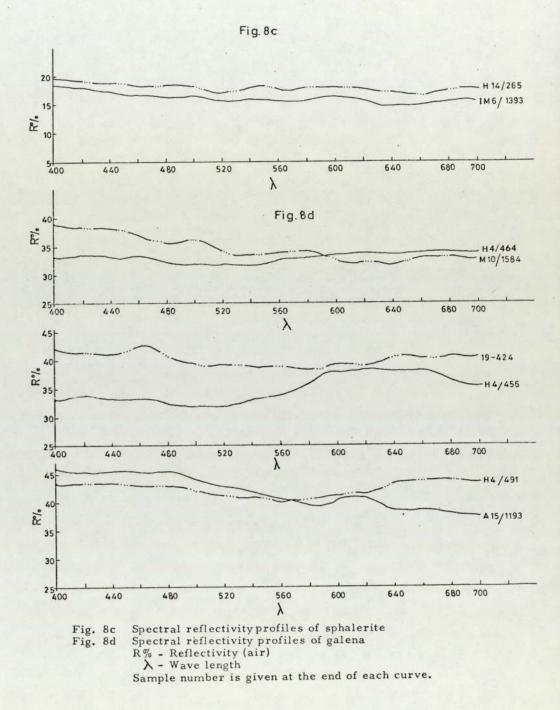


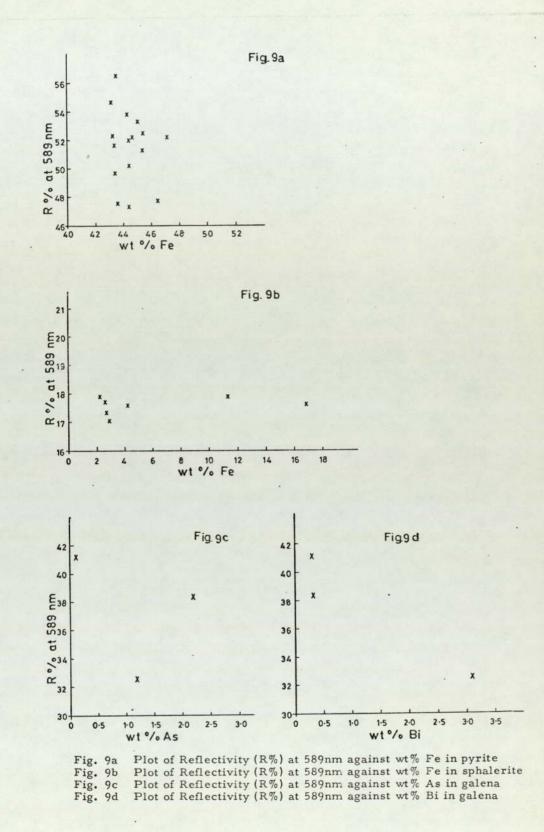


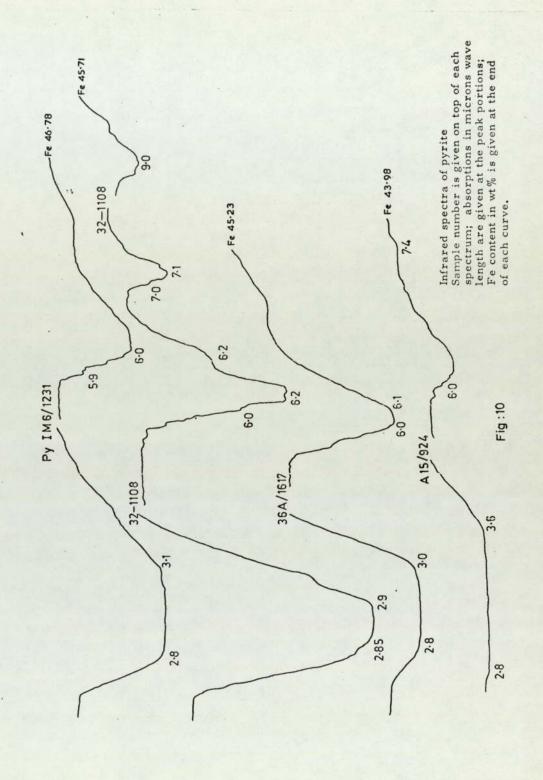


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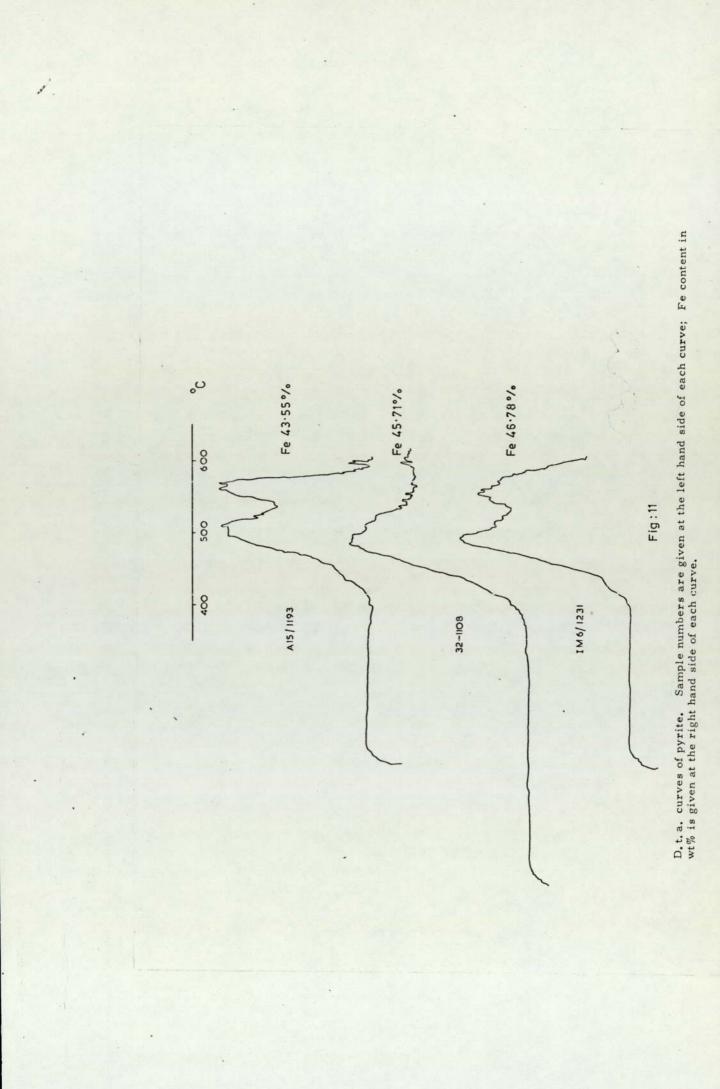


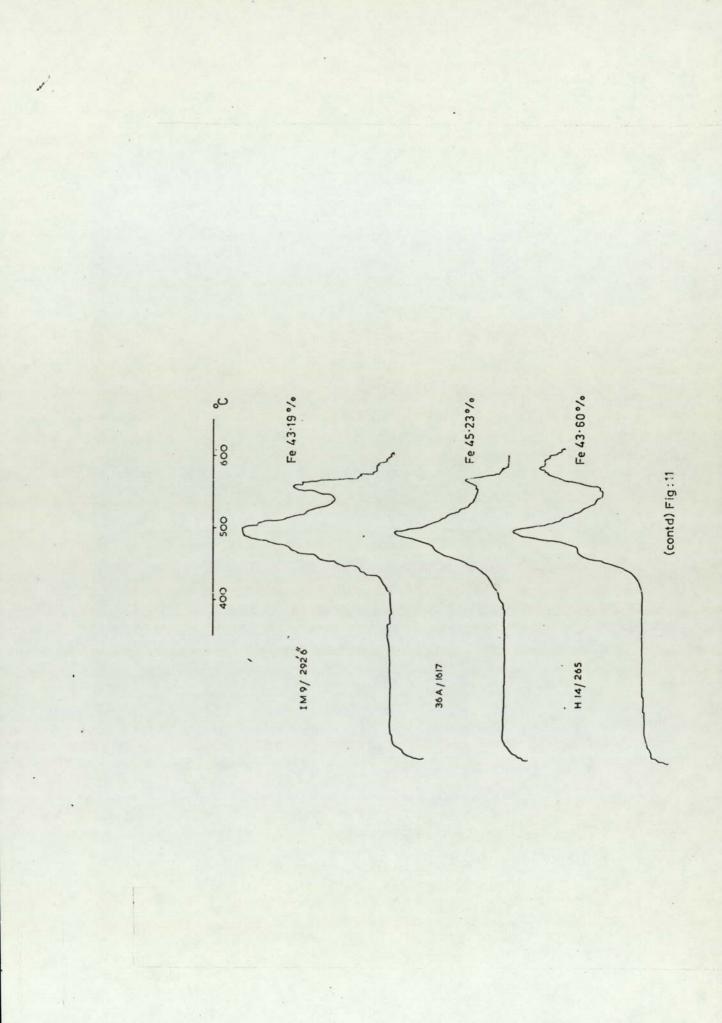


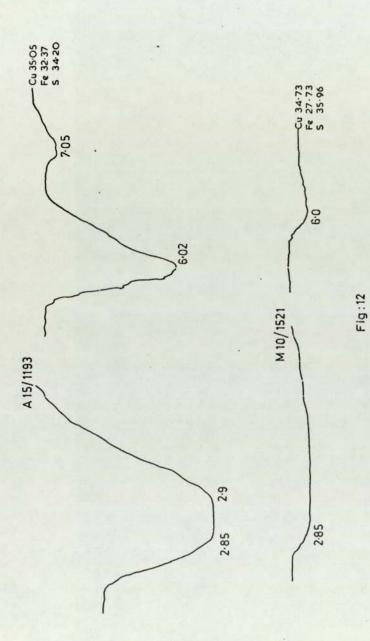




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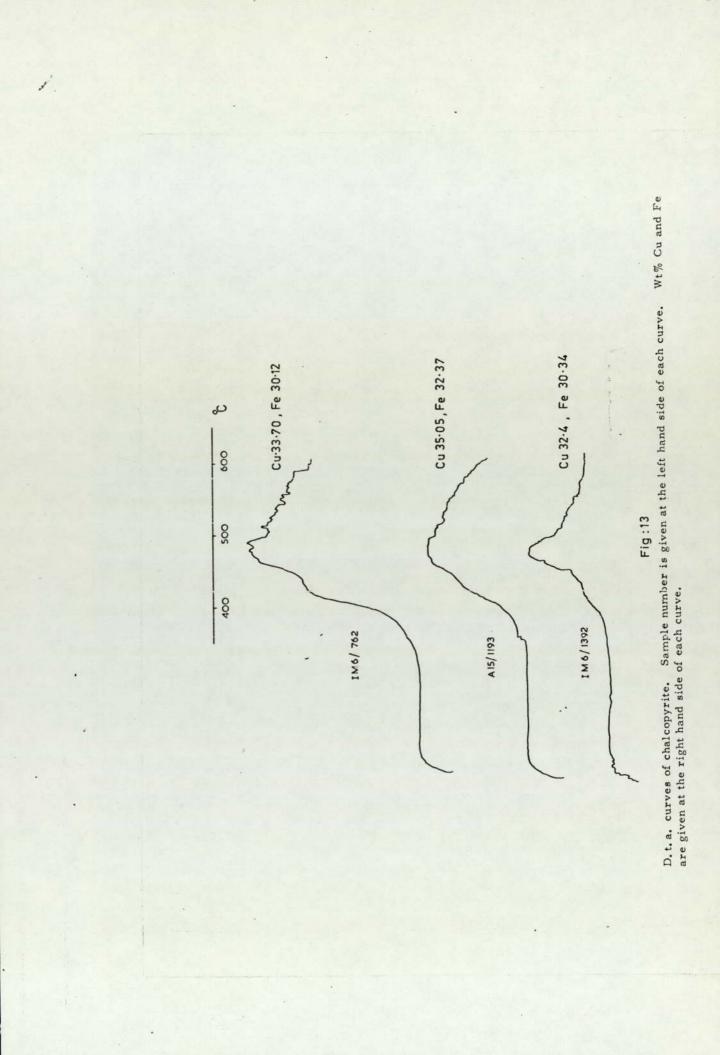


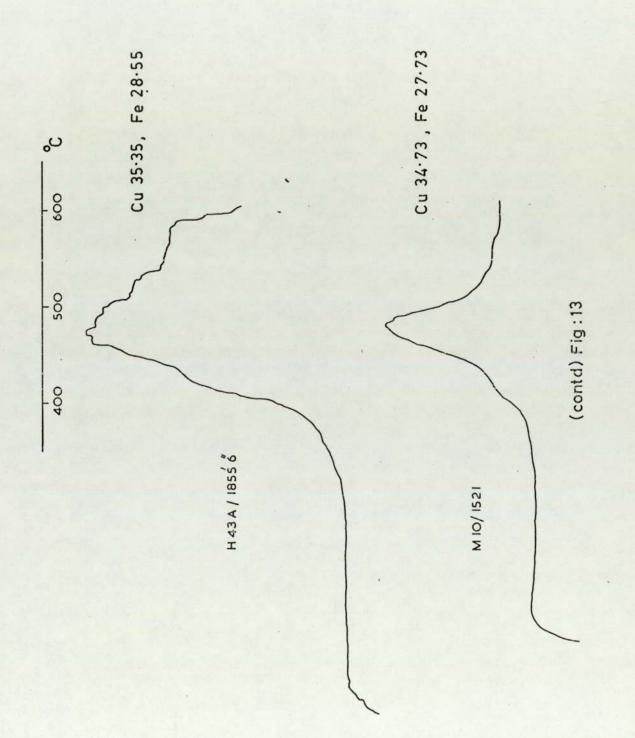


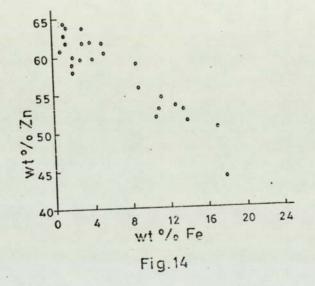


Infrared spectra of chalcopyrite. Sample number is given on top of each spectrum. Absorptions in microns wave length are given at peak portions. Composition in wt% is given at the end of each spectrum.

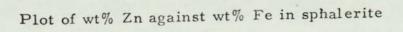
1

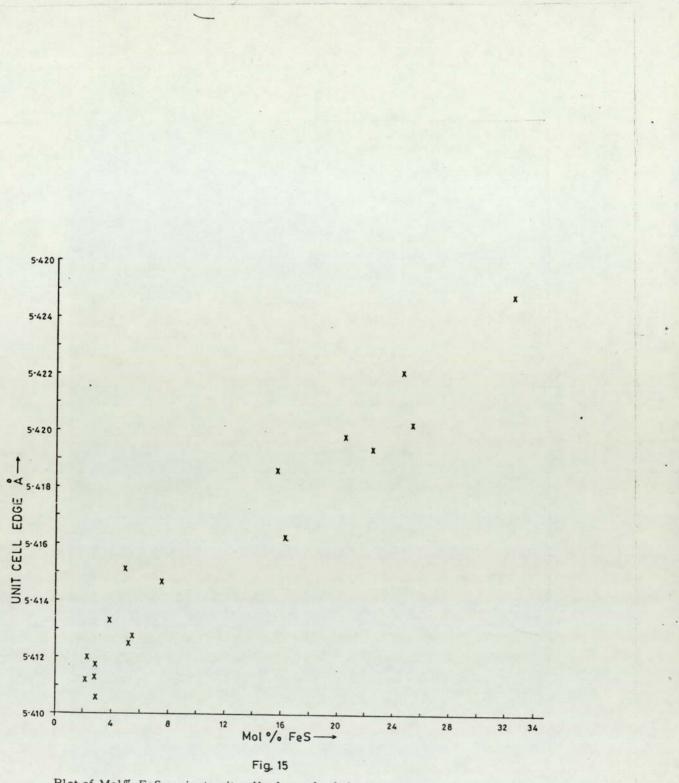






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ä

Plot of Mol% FeS against unit cell edges of sphalerite

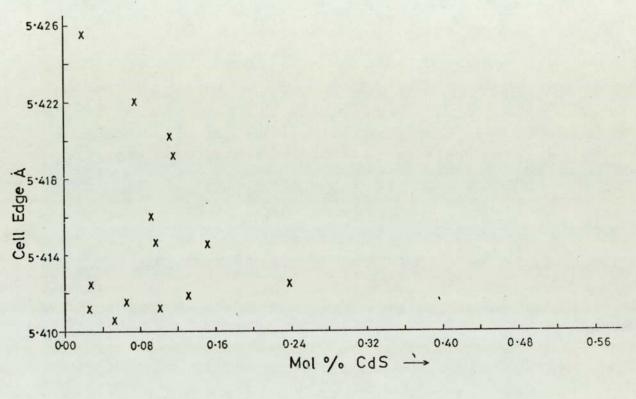
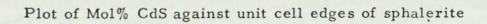
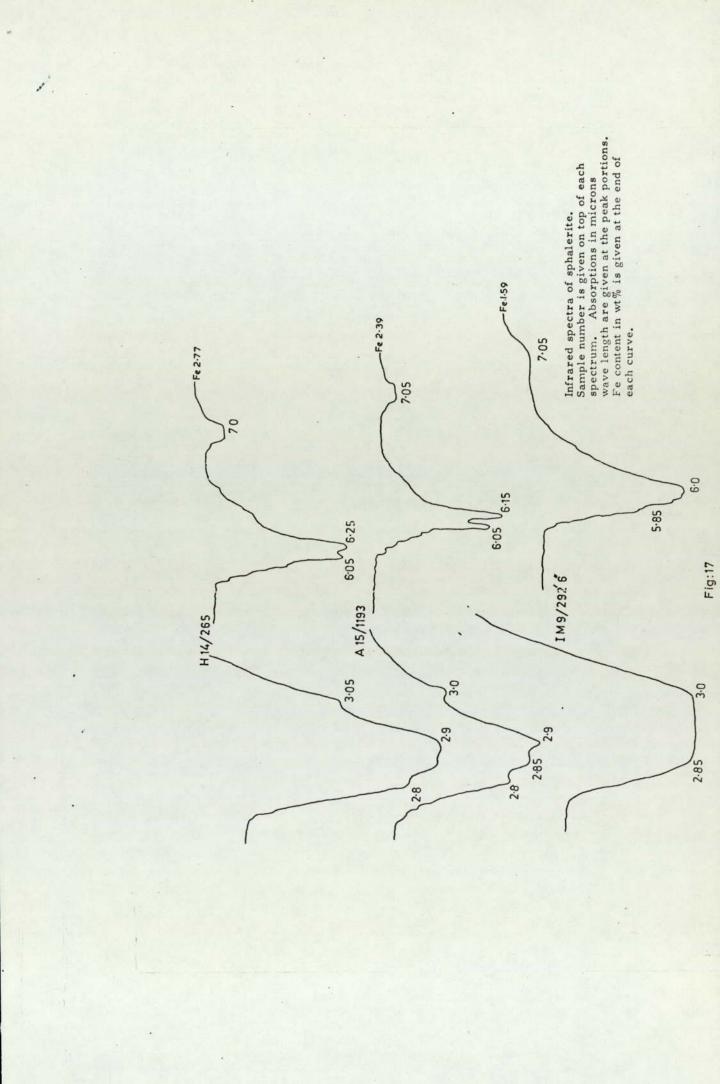
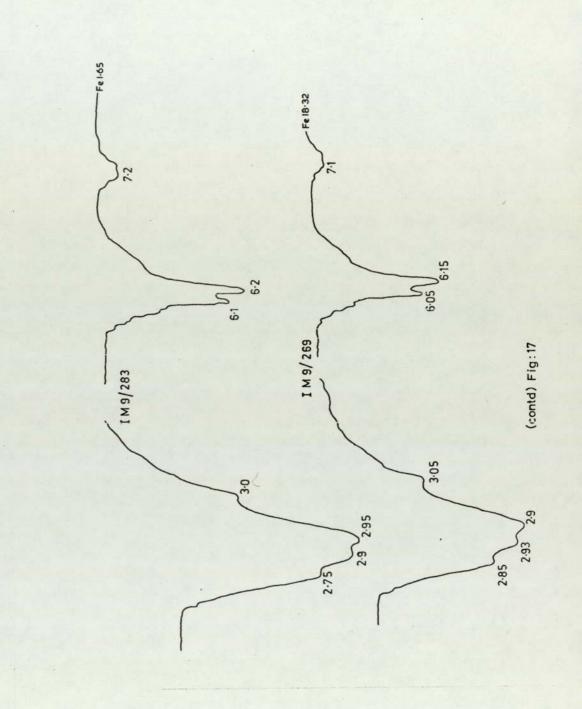


Fig. 16

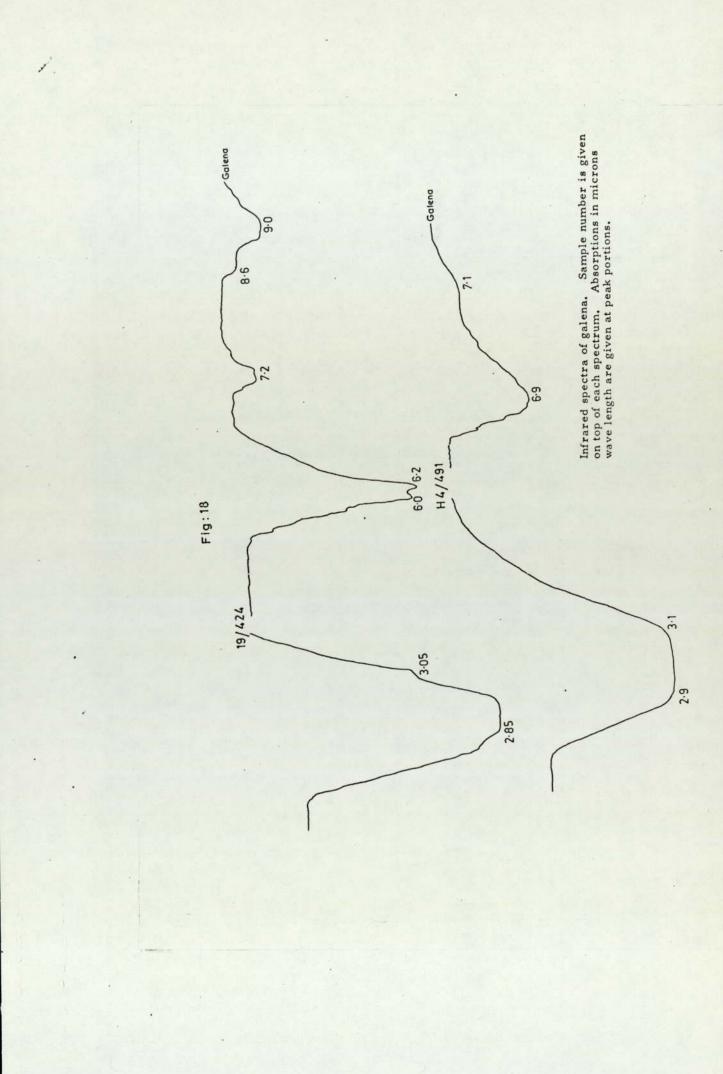


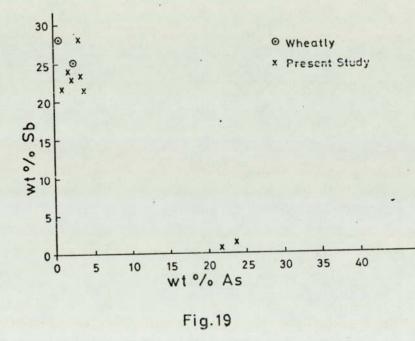
3.



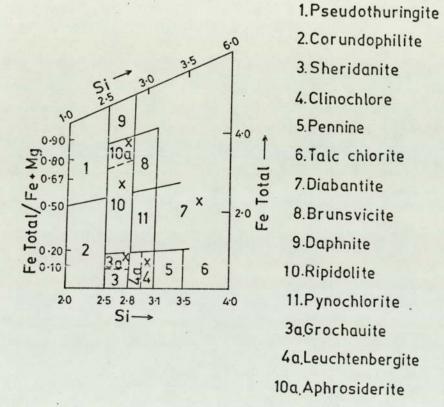


1.



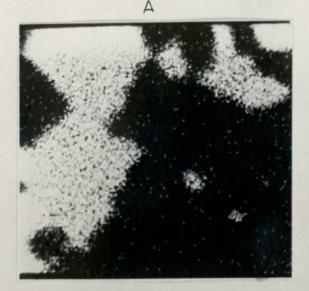


Plot of wt% Sb against wt% As in tetrahedrite-tennantites showing the compositional break.

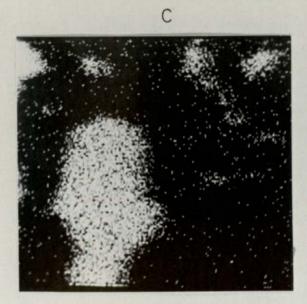


Orthochlorites showing the species and variety boundaries (after Hey, 1954) X - shows the Parys Mountain Species





В



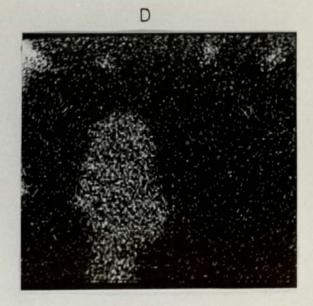


PLATE IV

Plate IV X-ray images

A-B Tetrahedrite in sample 27-145

- A Sb La
- B As K
- C-D Tennantite in sample 27-145
- C As Kx
- D Sb Lx

PLATE III

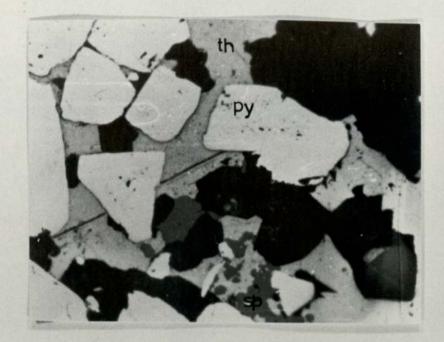


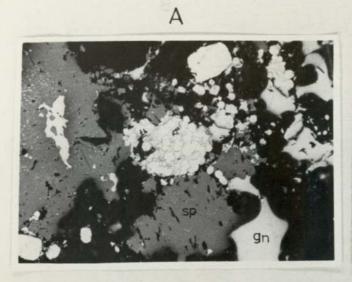


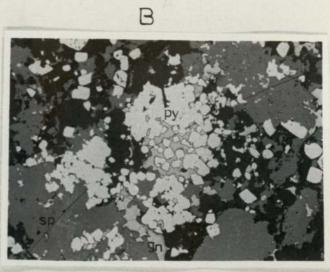


Plate III Photomicrographs

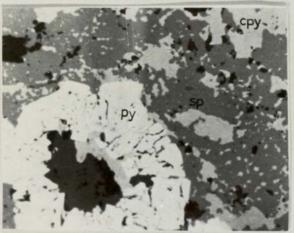
- A Sample from bore hole 27 at 145 feet depth. Tetrahedrite (th) forming the interstitial and fracture infillings of pyrite. 16 x (air)
- B Sample from bore hole H4 at 465 feet depth. Sphalerite (sp) with inclusions/infillings of bournonite (bn). 40 x (oil)

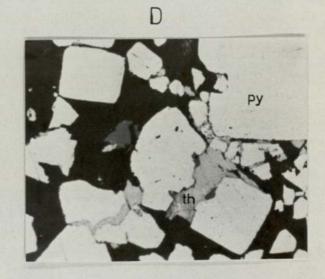
PLATE II













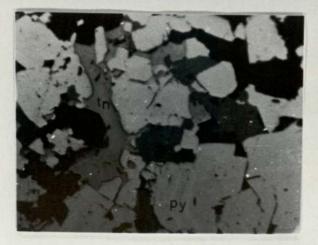
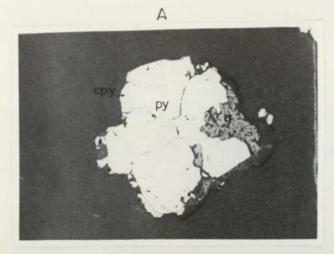


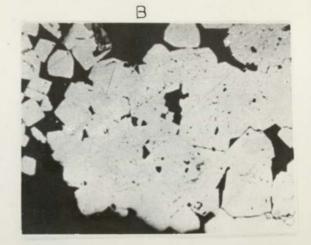
Plate II Photomicrographs

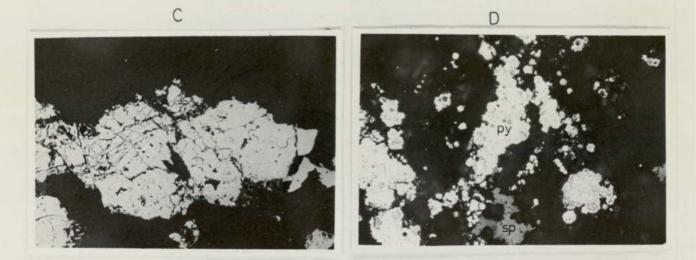
- A-B Sample from bore hole H4 at 474 feet depth. Sphalerites (sp) showing intergrowths with galena (gn). Galena and tetrahedrites forming interstitial matrix for pyrites. $16 \times (oil)$
 - C Sample from bore hole IM6 at 1392 feet depth. Pvrite (py) showing the radiating texture. Chalcopyrite (cpy) and sphalerite (sp) show intergrowth textures. Chalcopyrite is also seen replacing the core of the pyrite and filling in its fractures. 16 x (air)
 - D Sample from bore hole 27 at 145 feet depth. Tetrahedrite (th) forming the interstitial and fracture infillings of pyrite. 16 x (air)
 - E Sample from bore hole 27 at 145 feet depth. Pyrite (bottom centre) showing zoning. Tennantite (tn) is filling in the interstitial spaces of pyrite.

16 x (air)

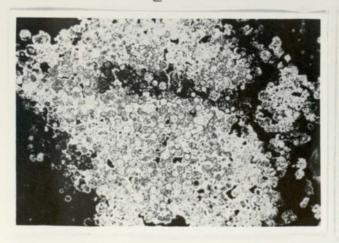
PLATE I

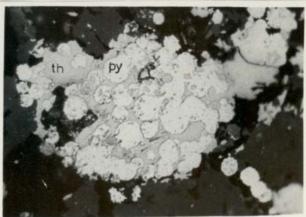






Ε

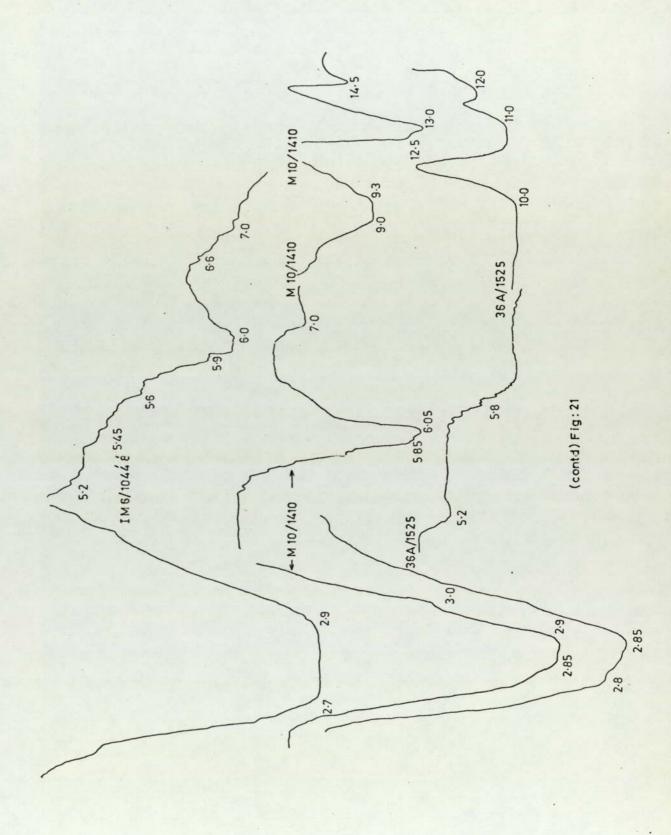


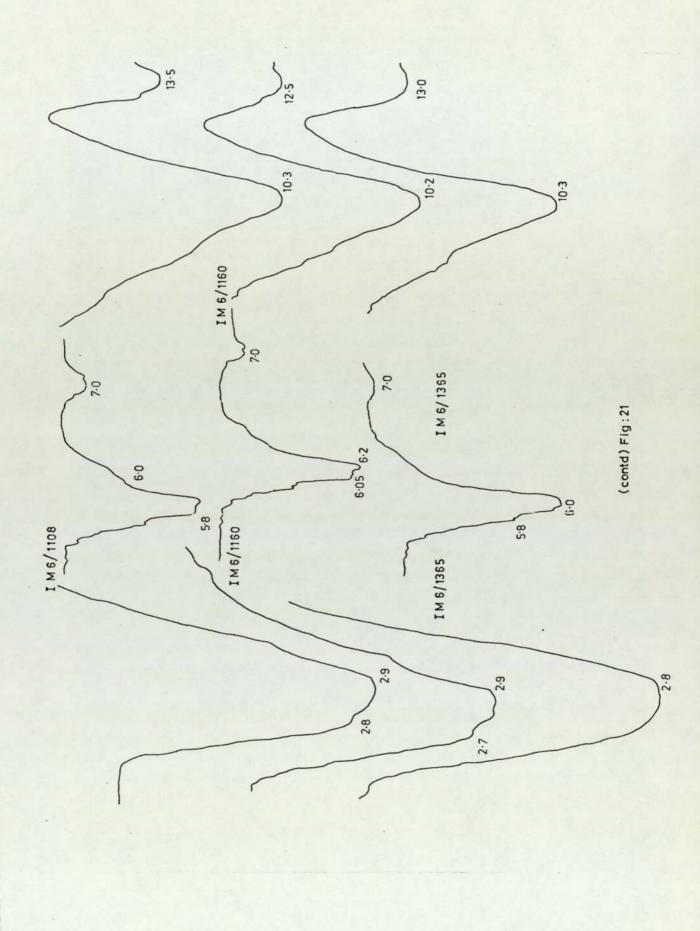


F

Plate I Photomicrographs

- A Sample from bore hole 32 at 1198 feet depth. Pyrite (py) associated with rutile (rt). Chalcopyrite rims pyrite and replaces it at grain boundaries. 4 x (air)
- B Sample from bore hole 27 at 145 feet depth. Aggregate
 of euhedral pyrites homogenised at the centre of the
 aggregate but retaining the cubic outlines at the periphery.
 4 x (air)
- C Sample from bore hole A 15 at 1193 feet depth. Pyrite showing intense fractures developed due to cataclasis. 4 x (air)
- D Sample from bore hole H 4 at 464 feet depth. Framboidal pyrites (py) forming clusters. Sphalerite (sp) is also seen.
 16 x (oil)
- E Sample from bore hole H4 at 464 feet depth. Framboidal pyrites showing atoll textures with tetrahedritetennantite forming the interstitial infillings. 16 x (oil)
- F Sample from bore hole H4 at 474 feet depth. Framboidal pyrites (py) with interstitial infillings of tetrahedrite (th). 16 x (oil)





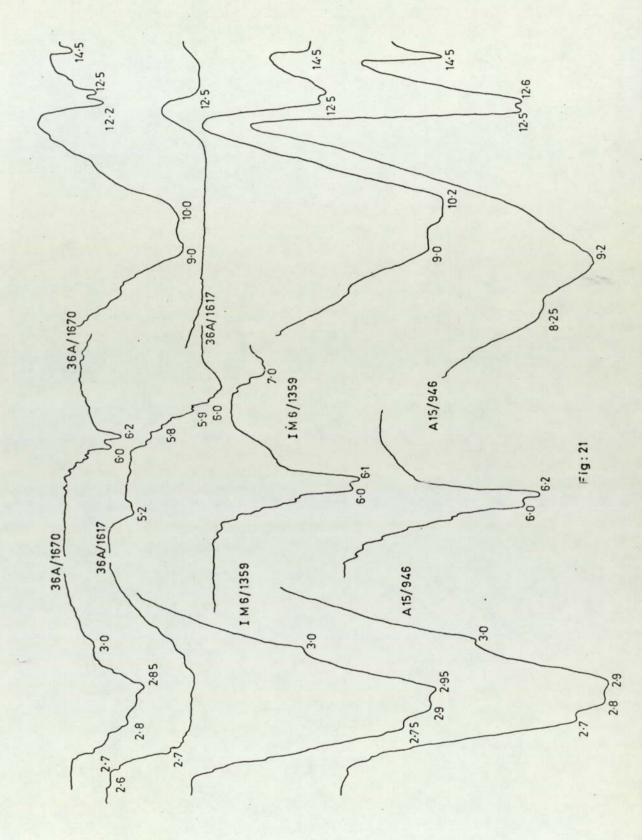


Fig. 21

Infrared spectra of chlorites. 36A/1670, A15/946, M10/1410 Ripidolite 36A/1617, IM6/1044'8" Diabantite IM6/1359, 36A/1525 Chlorite 1b IM6/1365 Aphrosiderite and grochauite IM6/1108, IM6/1160 Chlorites (species not identified)

Sample number is given on top of each spectrum; absorptions in microns wave length are given at the peak portions.