VOLUME I

MINERALOGICAL STUDIES OF COPPER, LEAD, ZINC AND COBALT MINERALIZATION IN THE ENGLISH LAKE DISTRICT

(2 volumes)

by

Christopher John Stanley

A thesis submitted for the degree of Doctor of Philosophy

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SUMMARY

Mineralogical studies of copper, lead, zinc and cobalt mineralization in the English Lake District.

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Cobalt, copper and lead - zinc mineralization in the English Lake District occurs as epigenetic infillings, predominantly of normal faults, but also along tear faults and in joints. Host rocks for these deposits are mostly slates and sandstones of the Skiddaw Group and tuffs and lavas of the Eycott and Borrowdale Volcanic Groups of Ordovician age; only minor amounts of mineralization occur in rocks of Upper Palaeozoic and later age. Metalliferous mining in the region reached a peak in the late nineteenth century but there are no cobalt, copper or lead - zinc mines working at the present time.

The mineralogy of the deposits was studied using electron probe microanalysis, X - ray diffraction, and reflected and transmitted light microscope techniques. Two minerals, alloclase and wittichenite, are reported from Great Britain for the first time.

Cobalt mineralization occurs mostly as cobalt - iron sulpharsenides, or as cobalt - iron diarsenides associated with nickel minerals.

Chalcopyrite - pyrite (pyrrhotine) - arsenopyrite is the dominant ore - mineral assemblage for the copper mineralization. Oxidation of these primary minerals has resulted in the formation of copper sulphides and secondary copper minerals.

The lead - zinc mineralization consists of galena and sphalerite with barytes, quartz, minor fluorite and secondary alteration products. Native antimony and antimony sulphosalts occur as inclusions in galena.

Information on the mineral assemblages and parageneses is interpreted, where possible, in terms of phase equilibria and sulphidation data from the literature to estimate some of the conditions of formation of the deposits. Additional information on formation conditions for the lead - zinc mineralization was obtained from a study of fluid inclusions in fluorites and sphalerite.

The Lake District copper, lead, zinc and cobalt mineralization is classified on a mineralogical basis and compared to similar deposits elsewhere. Possible origins for the mineralizing fluids are discussed.

Key words:- English Lake District, base metal mineralization,
ore mineralogy, sulphides, sulphosalts.

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CHAPTER 1

INTRODUCTION

1.1. General

The Lake District is a mountainous area in the northwest of England; an area which includes some of the most outstanding scenery in Britain. This scenery is the result of the effects of the Quaternary glaciation on a variety of bedrock lithologies varying in age from Ordovician to Permo - Triassic. The area has been defined in a number of ways, with some workers including the whole of the Cumbrian peninsular region within the 'Lake District' and others restricting this term so as to apply only to the central area of the region. In this thesis the term Lake District has been taken to include everything within the boundaries of the Lake District National Park, which covers all of the central mountainous region. Its boundaries extend approximately from Caldbeck in the north to Broughton in the south, and from Egremont in the west to Shap in the east; the whole area covering about 2000 square kilometres.

The Lake District copper, lead, zinc and cobalt mineralization occurs as epigenetic fissure infillings cutting Lower Palaeozoic strata, or in veins and joints in the Lower Devonian granites. The main period of tectonic activity affecting the Lake District was the result of earth movements associated with the Caledonian Orogeny, and the area lies in the linear structural belt known as the Southern Caledonides.

1.2 Scope of thesis

The aim of this work has been to investigate the Lake District copper, lead, zinc and cobalt mineralization as a whole, rather than to concentrate on a limited number of mineral veins in some smaller part of the area. The mineralogy of the veins has been studied in thin and polished sections using both transmitted and reflected light microscopy. Mineral species of variable composition or those which could not readily be identified by routine microscopic methods were studied using X - ray diffraction and electron probe microanalysis techniques. Quantitative reflectance and microhardness determinations were made for uncommon mineral species. Fluid inclusions in fluorite and sphalerite were analyzed thermometrically to determine homogenization temperatures and salinities of some of the ore fluids. Details of these analytical techniques are given in Appendix II.

A number of mineral occurrences in the Lake District were not investigated in this work. The haematite veins in the central Lake District were not studied as they appear to have more in common with the West Cumbria haematite mineralization (recently described by Shepherd, 1973) than with the base metal deposits. The Carrock Fell tungsten mineralization was not investigated because it was understood that the mineralogy was already being studied by the Institute of Geological Sciences, London. The Borrowdale Graphite deposit (Strens, 1965) was not examined as it appears to be unique and to be unrelated to the copper, lead, zinc or cobalt mineralization which forms the subject matter of this thesis.

A major constraint on the extent and detail of the present study was the amount of representative ore - bearing material which could readily be collected, most of the mines now being either in a dangerous condition or totally inaccessible. Representative specimens were collected from the veins themselves where this was possible, or from adjacent spoil tips. Specimens from the Kingsbury and Russell

Collections (British Museum of Natural History) were used to supplement material collected in the field.

1.3 Layout of thesis

The thesis has been written so that each of the chapters containing data on the mineral deposits (Chapters 3 - 8) is a separate entity, thus enabling individual sections to be easily extracted for publication purposes (those parts already published are contained in Appendix III). This has inevitably led to some repetition, although this has been kept to a minimum. All the Tables, Figures, Plates and Maps are given together in Volume II, with the References and Appendices at the end of Volume I. A list of abbreviations is given in Appendix I.

CHAPTER 2

REVIEW OF LITERATURE

2.1 General geology

2.1.1 Stratigraphy

The Lake District (Map 1) is composed predominantly of folded Lower Palaeozoic rocks which form an inlier, flanked by younger Devonian, Carboniferous and Permo - Triassic strata.

In addition to the Geological Survey memoirs (Ward, 1876; Eastwood et al., 1931; and Eastwood et al., 1968) which only cover a small part of the Lake District, regional studies of much of the metalliferous mining area described in the present work have been undertaken by Mitchell (1940,1963); Hartley (1925,1932,1941); Gough (1963) and Simpson (1967). Although there have been disagreements over the stratigraphic correlation in some areas (for instance between Gough (1963) and Hartley (1941) in the Glenridding area, near Ullswater), the major subjects for debate have been the nature of the Skiddaw Group - Borrowdale Volcanic Group boundary, and of the various periods of deformation associated with the Caledonian Oregeny.

The oldest rocks in the area are the 'Skiddaw Slates' or Skiddaw Group of Arenig age. These rocks consist of several thousand metres of cleaved mudstones, siltstones and 'turbiditic greywacke - sandstones' (Wadge,1978a), the base of which is not seen. Detailed accounts of lithologies and faunas are given by Jackson (1978) along with a comprehensive bibliography. Wadge (1978a) has recently outlined a classification of these and other Lower Ordovician rocks and has given details of the stratigraphic relationships between the Skiddaw Group and the overlying Eycott and Borrowdale Volcanic Groups.

The 'Eycott Volcanic Group' or Eycott Group, which includes all interbedded volcanic and sedimentary sequences which may be correlated with the successions of Eycott Hill and the Caldbeck Fells (Wadge,1978a), was first recognized as being older (Llanvirn) than the main volcanic outcrop (the Borrowdale Volcanic Group of Llandeilo - Caradoc age) by Downie and Soper (1972) on microfossil evidence. It had been previously noticed (Fitton and Hughes,1970; Fitton,1971) that the rocks of the northern outcrop in the Caldbeck Fells and Eycott Hill areas were distinct both petrographically and geochemically to those of the main outcrop to the south. Whereas the volcanic rocks of the Eycott Group have tholeiitic affinities and consist dominantly of basalt and basaltic andesite flows with a limited development of tuffs, the Borrowdale Volcanic Group is dominantly calc - alkaline and consists mostly of andesites and dacites. More detailed accounts of the outcrops and lithologies of the Eycott Group are given by Eastwood et al.(1968) and Millward et al. (1978).

Rocks of the Borrowdale Volcanic Group crop out in the central Lake District and form characteristically rugged fells, compared to the rounded topography typical of the Skiddaw Group. Although the Eycott Group is conformable with the Skiddaw Group, Simpson's (1967) conclusion that the Borrowdale Volcanic Group overlies the Skiddaw Group unconformably in the Buttermere area, is now accepted (Wadge, 1978a) for the whole region. Wadge (1978a) suggested that much of the earlier discussion of the relationship between the Skiddaw Group and the Borrowdale Volcanic Group was based on the recognition of only these two groups (and not the Eycott Group), and did not take into account different types of stratigraphical relationship between widely different parts of the Lower Ordovician sequence.

The Borrowdale Volcanic Group consists of more than 6 km of basaltic, andesitic and dacitic lavas with pyroclastics (including welded ash flow tuffs) and was probably deposited from three or more major eruptive centres (Millward et al., 1978).

During Caradocian and Ashgillian times, erosion of the volcanics took place subsequent to uplift. The Coniston Limestone Group, now exposed in the south Lake District (and represented in the north Lake District by the Drygill Shales) was deposited unconformably on the earlier rocks. Ingham et al.(1978) described and correlated the Upper Ordovician and Silurian strata in the Lake District. These and later strata do not host any significant copper, lead, zinc or cobalt mineralization.

Wadge (1978b) for the Devonian, Mitchell et al.(1978) for the Carboniferous and Arthurton et al.(1978) for the Permo - Triassic gave up to date accounts and listed the relevant literature.

2.1.2 Structure

Reviews of structural aspects of Lake District geology can be found in Hollingworth (1955), Mitchell (1956), Moseley (1972) and Soper and Moseley (1978).

The earliest earth movements which affected the Lower Palaeozoic rocks were those associated with the Caledonian Orogeny. Simpson (1967) suggested that the Skiddaw Slates were deformed in two tectonic episodes and underwent extensive alteration before the onset of Borrowdale volcanicity. The major end - Silurian orogeny, whilst having a marked effect on the Borrowdale Volcanic Group, had only a minor effect on the Skiddaw Slates. Roberts (1977) summarized the periods of deformation as follows :-

Pre - Borrowdale Volcanic Group	D_1 - N - S trending folds in the largely unconsolidated Skiddaw Group; no cleavage production; gravity collapse structures;
End - Silurian	D_2 - Upright E - W trending folds and main cleavage formed by the principal Caledonian earth movements;
	D_3 - Formation of reclined folds and crenulation cleavage as a result of the intrusion of the Lake District granite batholith;
	D_4 - Formation of minor N - S flexures and fracture cleavage, the result of axial shortening.

According to Soper and Moseley (1978), thrust or wrench faults and faults with both thrust and wrench components were associated directly with the Caledonian Orogeny. However, these are largely unfavourable for mineralization and later pressure release fractures are of much greater importance in localizing mineral veins.

During the Hercynian orogenic episode, many of the earlier Caledonian structures (such as the NW - SE wrench faults) underwent further movement as normal faults (Soper and Moseley, 1978). Most Hercynian faults have NW - SE trends with complementary NE - SW faults and are indicative of an E - W stress regime. Post - Hercynian earth movements gave rise to the doming of the Lake District.

Interpretations of Lake District geology in terms of plate tectonics can be found in Fitton and Hughes (1970) and Moseley (1977).

2.1.3 Intrusions

The main exposed igneous intrusions in the Lake District are the Eskdale, Skiddaw and Shap Granites, the Ennerdale Granophyre, the St John's Microgranite (also known as the Threlkeld Microgranite) and the Carrock Fell Igneous Complex (see Map 1).

Bott (1974) postulated from a gravity survey that a composite granite batholith underlies the central and northern Lake District, connecting the exposed granites at depth. He suggested that the roof region of the granite batholith has two granite 'ridges'; one connecting the Eskdale and Shap Granites, the other connecting the Ennerdale Granophyre, the St John's Microgranite and the Skiddaw Granite.

Whole rock K - Ar isotopic ages have been reported by Miller (1961) for the Eskdale (~383 Ma) and Skiddaw (~399 Ma) Granites and by Dodson et al.(1961) for the Shap Granite (~397 Ma). Brown et al. (1964), using a similar method, obtained isotopic ages of ~334 - 370 Ma for the Ennerdale Granophyre, and ~365 Ma for the Carrock Fell Igneous Complex, but suggested that due to evident argon loss these should be regarded as minimum values. Wadge et al.(1974) obtained a Rb/Sr age of ~445 Ma for the St John's Microgranite. Shepherd et al.(1976) using K - Ar techniques on minerals, confirmed the age of the Skiddaw Granite as ~390 Ma. Pidgeon and Aftalion (1978) using U - Pb dating techniques on zircons obtained an age of ~390 Ma for the Shap Granite and found that the Eskdale Granite was significantly older than this. They suggested that the Eskdale zircons have a minor component of inherited zircon and may represent a mixture of deep crustal source material with overlying sediments containing older detrital zircons.

A recent study by Rundle (1979) has shown that many of the intrusions previously thought to be of Devonian age are in fact Ordovician. Rundle (op.cit.) obtained Rb - Sr whole rock and K - Ar whole rock and mineral ages of ~ 428 Ma for the Eskdale Granite and ~420 Ma for the Ennerdale Granophyre. Gabbro from the Carrock Fell Complex was found to be older (~468 Ma) than both the granophyre (~416 Ma) and the Harestones Felsite (~419 Ma).

Firman (1978a) recently reviewed the Lake District intrusions, and, in addition to the granitic intrusions already mentioned, he noted petrological similarities between many of the olivine dolerite dykes and those in the North Pennines which are of similar age to the Whin Sill.

The magmatic events are summarized in Table 2.1.

2.2 Mineralization

Two recent review articles provide useful background information. Ineson (1977) described the mineralization of the Lake District, the North Pennines and North Wales. Firman (1978b) gave a comprehensive review of many aspects of the Lake District mineralization.

The Lake District was first mapped by the Geological Survey in the 1870's; although mining was then active, the resulting memoir by Ward (1876), contained little regarding the mineralization except for vein hades and directions and a simplified mineralogy. Kendall (1884) was the first to discuss the mineralization in scientific terms. He classified the veins according to the dominant metal present and recognized five types; namely, lead, zinc, copper, iron and manganese. In addition to noting the geological distribution he suggested that the veins were not formed before the Devonian. Kendall (op.cit.) was one of the first to disagree with the belief, widely held at that time (e.g. De La Beche, 1839; Geikie, 1882), that the mineral veins were filled fissures, advocating instead that the vein material had been formed in situ by 'metamorphism and substitution', the metallic minerals being deposited by chemical solutions with sulphur coming from the volcanic rocks. Since it has now been accepted (e.g. Eastwood, 1921, and in Dewey and Eastwood, 1925; and Rastall, 1942) that the veins are fissure infillings, the main points for discussion have been the ages of the mineralization, the source, composition and temperature of the mineralizing fluids, the relationship of the mineral veins to local and regional structures and the controls exercised by host rock lithology and the underlying basement.

2.2.1 Mining History

The area has had a long mining history. Postlethwaite (1913) mentioned some of the early sources of information (Close Rolls of Henry III) which refer to the Goldscope copper mine as being worked in the early thirteenth century. Eastwood (in Dewey and Eastwood, 1925),however, suggested that some of the mines were worked in Roman times. Production declined in the early years of this century after reaching a peak in the 1880's.

Postlethwaite (1913) remains the major source work on the mining history and includes an excellent although not exhaustive account of the various mines and their basic mineralogy. Two special reports of the Geological Survey, one (Eastwood, 1921) dealing with the lead - zinc ores, the other (Dewey and Eastwood, 1925) with the copper ores, give details of the mining history and vein descriptions. Eastwood (1959) regarded these earlier reports as reconnaissance surveys to be followed by fuller investigation. This was apparently never carried out.

Shaw (1970) has given a more up to date account of the mines and trials in the Lake District, using his experience as a miner in the

Greenside, Hartsop Hall, Potts Ghyll and Force Crag mines.

At the present time (Oct.1979) only one mine in the Lake District, the Carrock Fell Tungsten Mine is in production. Although development and exploration work took place at Force Crag Mine during 1977 - 1978, this work has now ceased and until further capital is available, there are no immediate prospects of mining being resumed. These two mines were the only ones working when the planning laws were introduced, and with the growth of conservation organizations there is little likelihood of planning permission being granted for the reopening of any other mines in the region.

Little work has been done to predict or explore for further deposits. Cruzat and Meyer (1973) using geological and geochemical parameters combined with statistics produced a highly speculative forecast which recent geochemical stream sediment surveys in the south-west Lake District (Mc Allister W.D.N., personal communication) seem to disprove. Firman (1978b) suggested that Cruzat and Meyer (1973) greatly exaggerated the mining potential of the Lake District.

2.2.2 Mineralogy

Early mineralogical studies concentrated on the abundant and colourful secondary alteration products, particularly well developed in the Caldbeck Fells area. Goodchild (1881,1882,1883) listed many of the minerals and Day (1928), and Kingsbury and Hartley (1955, 1956, 1956a, 1956b, 1957, 1958, 1960) also refer mainly to the alteration products. Davidson and Thompson (1948) listed both primary and secondary minerals from the Caldbeck Fells as well as from other parts of the Lake District.

Small studies of particular primary mineral occurrences rather than general lists of exotic alteration products have been few in number. Russell (1925) recorded 'smaltite' and nickeline from Coniston and native bismuth and bismuthinite from Shap. The Shap mineralization, which occurs mainly along joints in the granite and in the aureole, has also been described in some detail by Firman (1957). Hitchen's (1934) account of the tungsten mineralization at Carrock Fell remains the standard reference, and the hydrothermal alteration in the Grainsgill area was described by Ewart (1962). Clarke (1974) described some bismuth sulphotellurides associated with the tungsten mineralization.

2.2.3 Age of mineralization

Eastwood (1921) considered that there were at least two and possibly three periods of mineralization. Earlier, Finlayson (1910) had regarded the lead - zinc and copper veins as Hercynian and the tungsten veins (at Carrock Mine) as Caledonian. Dixon (1928) and Trotter (1944) suggested that the presumed Tertiary haematite deposits of West Cumbria represented the outer zone of the Lake District non - ferrous orefield and that the latter was therefore Tertiary in age. Rastall (1942) on the other hand assigned a Caledonian age to all the mineral veins. More recently, Strens (1962) suggested four periods of mineralization based on a study of the mineralization in the Newlands - Borrowdale area:-

I	Pre - Bala	graphite - pyrite - chalcopyrite ;
II	Caledonian	chalcopyrite - arsenopyrite - pyrite ;
III	Hercynian	(i) galena - sphalerite ,
		(ii) galena - barytes ;
IV	Tertiary	haematite.

Gough (1963) in a study based on the Greenside lead vein, proposed three major periods of mineralization with five basic assemblages:-

I Caledonian (i) chalcopyrite - pyrite - arsenopyrite;

(ii) wolframite - scheelite;

II Hercynian (i) quartz - barytes - galena - sphalerite - chalcopyrite;

(ii) barytes;

III Post - Triassic haematite - quartz - calcite - dolomite.

Dating of the mineralization by isotopic methods has not resolved any of the problems. Moorbath (1962) obtained lead isotope data from galenas from a number of Lake District localities and concluded:- (i) that the greater part of the Lake District mineralization is not directly connected with the known Caledonian intrusions; (ii) that there is no evidence for Tertiary mineralization in the Lake District; (iii) that there were two major periods of mineralization with respective mean model ages of 210 ± 40 Ma and 320 ± 30 Ma. Ineson and Mitchell (1974) suggested that the single - stage evolution criterion might not be satisfied for the lead isotope data, or that galena may have been contaminated by older lead from the country rocks.

In their own K - Ar isotopic study using clay mineral concentrates from vein gouges and altered wallrock, Ineson and Mitchell (1974) came to the conclusion that mineralization commenced in the early Devonian with the emplacement of copper ores at about 390 Ma, and that late Devonian metasomatism resulted in a large suite of N - S trending lead - zinc veins. Emplacement continued into Namurian/Westphalian times, with evidence that the deposits marginal to the central area are younger in age. Finally, they concluded that the deposits of the Caldbeck Fells are quite distinct geochronologically and mineralogically from the main loci and illustrate a significantly younger, possibly epicyclic, mineralization.

Ineson and Mitchell's (1974) work fails to take into account the fact that many of the veins show evidence of more than one period of mineralization. Without knowing which of these mineralizations their data refer to, they have possibly drawn some erroneous conclusions, particularly in respect of the ages of the lead - zinc deposits and also their distinction of the Caldbeck Fells mineralization. Argon loss may also have led to significant errors. In addition, Shepherd et al. (1976) remarked that their observed unreliability of chlorite as a precise geochronometer cast doubts on the illite - chlorite ages reported by Ineson and Mitchell (op.cit.).

2.2.4 Origins of mineralization

Kendall (1884) was the first to propose an origin for the mineralization, and suggested that the ores were deposited from aqueous solutions. Melmore (1920) correlated the mineralization of the Caldbeck Fells with hydrothermal metamorphism at the margin of the Carrock Fell Igneous Complex and related the sulphide ores to the alteration of these rocks.

More recently, Wheatley (1971, 1972), Shepherd et al.(1976), Dagger (1977) and Firman (1978b) have all suggested mechanisms involving deep circulating mineralizing fluids controlled to some extent by the granite bodies underlying the Lake District. These ideas are further discussed in Chapter 9.

CHAPTER 3

COBALT MINERALIZATION AT SCAR CRAG, WEST OF KESWICK

3.1 General

Arsenopyrite and a variety of cobalt - iron - sulpharsenide minerals occur in a quartz - chlorite - apatite vein known either as the Scar Crag or the Cobalt Vein. The main cobalt - bearing mineral in the vein is alloclase, and this is the first recorded occurrence of the species in Great Britain (also noted in Ixer, Stanley and Vaughan, 1979 - see Appendix III).

Cobalt mineralization in the Lake District is not common and, although minor amounts of cobalt and nickel minerals have been found at Coniston (Russell, 1925; see also Ch.8) and at Dale Head (see Ch.4), these occurrences are associated with chalcopyrite - pyrite - arsenopyrite - pyrrhotine assemblages. The Scar Crag occurrence therefore appears to be unique.

The vein crops out (Plate 1) above the footpath from Braithwaite village to Sail and Scar Crag in Long Comb (NY 2060 2070). It lies at an altitude of about 600 m, a kilometre to the west of Causey Pike and trends a few degrees east of north (Map 2). Strens (1962) considered that the vein was emplaced along a pre - Bala tear fault in Mosser - Kirkstile slates of the Skiddaw Slates Group. In the region of Causey Pike and for some distance to the west, the slates have been altered to a lighter - coloured harder rock with minute dark spots (Rose,1955) and this particular lithology has been referred to as Blakefell Mudstone by Dixon (in Eastwood et al., 1931). Rose (1955) has suggested on the basis of the shape of this aureole and its limited extent, that a stock - like intrusion underlies Causey Pike.

An early note of the cobalt mineralization was by Goodchild

(1881) who reported Ward's (1876) account of cobalt (sic) occurring in small specks in a quartz vein between Sail and Scar Crag. An attempt to mine the vein late in the nineteenth century failed. Postlethwaite (1913) recorded that the Keswick Mining Company spent £7000 on a smelt mill and crushing and dressing floors on the strength of favourable chemists reports. However, the chemists were unable to extract the cobalt from the ore and the operation ceased. The vein was worked from four levels.

3.2 Mineralogy

Postlethwaite (1913) noted the minerals 'erythrine and smaltine' as being present in the vein. Davidson and Thompson (1948) reported finding erythrite but not smaltite and also listed 'mispickel, scorodite and psilomelane'. Kingsbury and Hartley (1957) found a quartz - chlorite vein containing apatite, arsenopyrite with a little löllingite, psilomelane and scheelite to the west of Causey Pike. This refers almost certainly to the Scar Crag Vein although Strens (1962) reported that Hartley 'proved unwilling to reveal the locality'. Strens (op.cit.) described a similar mineralogy (scheelite excepted) and stated that 'staining tests (using Williams and Nakhla's,1951, chromographic method) show the cobalt to be concentrated in the löllingite rather than the arsenopyrite'. It is not known on what basis Kingsbury and Hartley (1957) and Strens (1962) have identified löllingite. Neither gave any X - ray data and Strens has looked for löllingite elsewhere (1962 p.118) by etching polished sections with saturated ferric chloride solution.

In the present study, no löllingite was identified in the assemblage (despite considerable searching using X - ray diffraction and electron probe microanalysis, and also working on material in the British Museum collected by Kingsbury) and nor was scheelite found. The cobalt - bearing phases identified were alloclase, skutterudite, cobaltite and glaucodot with somewhat minor amounts of cobalt in arsenopyrite. In order to ascertain if Strens, with limited analytical techniques at his disposal, had possibly misidentified löllingite, polished sections were immersed in a saturated ferric chloride solution for about an hour at room temperature. On re-examination some of the material was strongly etched and when analysed by electron microprobe, these areas had compositions in the glaucodot range (containing between about 10 - 13 wt. % Co).

Alloclase was first named and described by Tschermak (1866) as a bismuthian glaucodot from Oravicza, Roumania. However, Tschermak later concluded (see Krenner, 1929) that alloclase was a bismuthian variety of cobaltite. Krenner (1929) re-examined specimens from the type locality and concluded that alloclase was a high - cobaltian glaucodot. There were initial doubts, then, as to the validity of alloclase as a distinct mineral species, and more recently Gammon (1966) has suggested that the name 'alloclasite' was unnecessary and should be replaced by 'high - cobaltian glaucodot'. Structural data derived from single crystals by various workers (Kingston, 1971; Petruk et al., 1971; Scott and Nowacki, 1976) indicate that alloclase is a distinct species and that there is no logical reason why 'high - cobaltian glaucodot' should be preferred.

In polished section alloclase is not easily identifiable and can be confused with glaucodot and arsenopyrite. Alloclase appears pure white against arsenopyrite (slightly yellow by comparison) in reflected light and has a slightly lower reflectance and a lower polishing hardness. Twinning is not commonly seen in alloclase (Plate 19). The greatest difference optically is in the polarization colours. Whereas arsenopyrite shows tints of blue and orange with partially crossed nicols, alloclase has pinkish mauve and greenish olive tints. Glaucodot has colours intermediate between those of arsenopyrite and alloclase but which are much less intense. Reflectance curves and tables for alloclase, and the methods used, are given in Appendix II (see also Fig.AII.1, Fig. AII.2, and Table AII.1 in Volume II).

The simplest way to distinguish between arsenopyrite, alloclase and glaucodot is by X - ray diffraction. Interplanar spacings for Scar Crag alloclase and glaucodot are in good agreement with previously published data by Berry and Thompson (1962) and Petruk et al.,(1971). Single crystal work on alloclase by Kingston (1971) and Petruk et al., (1971) indicated an orthorhombic structure, but it is now known to be monoclinic, of space group $P2_1$ (Scott and Nowacki, 1976).

Maurel and Picot (1973) observed alloclase in material from Lautaret which had partially transformed to cobaltite, and suggested on the basis of synthetic experiments that this transformation could occur when the S/As ratio was slightly increased. Scott and Nowacki (1976) found that such a transformation of alloclase to either the ordered orthorhombic or the disordered cubic form of cobaltite could be explained by alloclase having a structure closely related to that of marcasite. Such a transformation would produce a crystal of alloclase with lamellae of cobaltite, accompanied by a network of fine cracks. Although cobaltite is found in the Scar Crag assemblage there is no evidence of it having transformed from alloclase.

X - ray diffraction techniques were not suitable for some grains in the Scar Crag polished sections, either on account of small grain size, or where compositional zoning gave ambiguous results. Electron probe microanalysis was used in these instances and also in order to obtain more detailed compositional data. The analyses are given in Table 3.1.

Arsenopyrite has a cobalt content ranging from 0.3 - 1.6 wt.% (Table 3.1, 1 - 11). Its arsenic content, important in geothermometry (discussed in 3.4), was determined using an arsenopyrite standard (Kretschmar's Asp 200 standard) and was about 32.4 - 32.5 at.% As (Table 3.1, 8 - 9). This is in reasonable agreement with the arsenic content obtained by using Kretschmar and Scott's (1976) equation (see 3.4) with the d_{131} values of 1.630 - 1.631 Å (corresponding to 31.6 - 32.4 at.% As).

As the cobalt - iron sulpharsenides are defined on a structural rather than compositional basis, since there is no evidence of a clear break in composition in the CoAsS - FeAsS solid solution series, problems over nomenclature arise when small or zoned grains are analyzed. Various workers have suggested compositional boundaries between the phases . Ferguson (1947) suggested that a composition of ~9 wt.% Co marked the boundary between cobaltian arsenopyrite (syn. danaite) and glaucodot, and this value was confirmed by Gammon (1966) who obtained a range of 2.8 - 11.8 wt.% Co for cobaltian arsenopyrites from Modum, Norway (specimens with more than 9 wt.% Co had lamellae of glaucodot). Vinogradova et al. (1975) have defined glaucodot as having a Co/Fe ratio of 2:3 to 2:1 (corresponding to 12 - 23 wt.% Co) and alloclase a Co/Fe ratio of 3:1 to 6:1 (corresponding to 26 - 30 wt.% Co). These rather arbitrary boundaries are useful as approximations, but analyses from the literature show, for instance, that alloclase can have a cobalt content as low as 24 wt.% Co (e.g. Rudashevskiy et al., 1975), although only one analysis in the present study (Table 3.1, 23) falls below 26 wt.% Co. The other analyses of alloclase range from 26.6 - 32.0 wt.% Co (Table 3.1, 22 - 45), equivalent to $(Co_{0.74}Fe_{0.26})_{1.00}As_{1.04}S_{0.96}$ and $(Co_{0.95}Fe_{0.15})_{1.09}As_{1.04}S_{0.96}$. Glaucodot analyses (Table 3.1, 12 - 13, 15 - 19) were within the limits proposed by Ferguson (1947) but a few fell below the limits of Vinogradova et al. (1975). Only one analysis for cobaltian arsenopyrite was obtained (Table 3.1, 14).

One strongly zoned grain (Plate 19) had analyses ranging from about 5 - 27 wt.% Co, with the majority of zones having compositions corresponding to glaucodot. It was impossible to determine whether the high cobalt zones were actually alloclase, or whether the low cobalt zones were cobaltian arsenopyrite. An electron microprobe line profile across this grain is illustrated in Fig.3.1.

Although nickel has been reported in varying amounts in alloclase and the other sulpharsenides, apparently substituting for iron (e.g. Vinogradova et al.,1975; Ixer et al.,1979), none was detected in any of the cobalt minerals from Scar Crag. The analyses of the Scar Crag sulpharsenides have been plotted on a CoAsS - FeAsS - NiAsS ternary diagram (Fig 3.3).

The only other primary cobalt - bearing mineral in the Scar Crag assemblage is skutterudite, which was identified by electron probe microanalysis on account of its small grain size and has a composition $(Co_{0.88}Fe_{0.12})_{1.00}(As_{0.95}S_{0.05})_{2.73}$.

The mineral assemblage at Scar Crag is quartz, muscovite, rutile, apatite, tourmaline, chlorite, arsenopyrite, glaucodot, alloclase, cobaltite, skutterudite, marcasite, bismuth, bismuthinite, molybdenite, pyrite. Later alteration products are scorodite and erythrite, and haematite and psilomelane also occur.

3.3 Paragenesis

Abundant quartz and apatite, and small quantities of rutile and tourmaline appear to have been the first minerals introduced into the vein, with minor amounts of muscovite (the latter now mostly replaced by chlorite). Quartz is by far the most dominant vein mineral and was probably deposited throughout the period of mineralization.

Early quartz is frequently euhedral (<5mm) and commonly contains regularly arranged inclusions. Later, more massive vein quartz exhibits strongly careous boundaries which suggest recrystallization. Rutile occurs within quartz either as radiating bunches of fine needles (<100 µm in length) or as subhedral grains (<30 µm). Small amounts of tourmaline (Plate 1) are associated with early quartz as subhedral to euhedral grains (<1mm) with blue - brown pleochroism (T-K.6.6). Apatite is common and is found as large euhedra (up to 50mm in hand specimen - H-78K.6.4) growing inwards from vein margins. Chlorite is also abundant and while much is undoubtedly contemporaneous with the sulpharsenide mineralization, both early and late chlorites also occur.

The main ore - bearing assemblage was probably deposited at the same time as, or shortly after, the early gangue phases. Arsenopyrite is the most abundant opaque mineral present and also the earliest sulpharsenide. It occurs as large euhedral and subhedral grains (< 5mm) and aggregates. Arsenopyrite has been overgrown (but not replaced) by glaucodot (P-78K.6.13) and, more commonly, alloclase (Plate 19). In some specimens glaucodot is present as fine zones of differing composition (Plate 19 ; Fig.3.1). Some of these zones have compositions which in fact correspond to alloclase or cobaltian arsenopyrite and may be as thin as 5 µm but are commonly 20 µm or greater. Occasionally, coarse zonations occur (P-K.6.5) and these commonly show some degree of chemical inhomogeneity. In addition, cobalt poor zones of arsenopyrite or cobaltian arsenopyrite have been more readily altered to scorodite than those of glaucodot composition (Plate 19).

Alloclase at Scar Crag overgrows arsenopyrite (P-78K.6.3) and in some specimens forms small (<100 µm) subhedra and regular intergrowths with quartz (Plate 19). Overgrowths on arsenopyrite are commonly up to 1 - 2 mm thick. Alloclase may also enclose anhedral grains

(< 20 μm) of skutterudite (P-78K.6.13), as confirmed by microprobe analysis (Table 3.1, 21).

Cobaltite, also confirmed by electron probe microanalysis (Table 3.1, 20), occurs as small euhedra (< 50 μm) at the outer margin of alloclase, or at the boundary between alloclase and arsenopyrite, or along fractures in these two minerals (Plate 19). In one specimen (P-K.6.11), marcasite overgrows alloclase to a small extent.

Native bismuth is found as inclusions in arsenopyrite and early quartz; bismuthinite is later and is found along fractures in arsenopyrite and alloclase, and at grain boundaries . A few small fibres of molybdenite (< 20 μm) occur and their position in the paragenetic sequence is unclear. Radiating bunches of chlorite have replaced the opaque minerals to a small extent, unlike scorodite which has extensively replaced arsenopyrite. Haematite in aggregates of minute (< 10 μm) botryoidal grains has also replaced arsenopyrite and in addition replaces pyrite, the latter occurring along fractures in replaced arsenopyrite. Psilomelane is found as a joint coating and erythrite has resulted from weathering of the cobalt - iron sulpharsenides.

The paragenetic relations are summarized in Fig. 3.2.

3.4 Discussion

Very little information is available on low temperature phase relations in the ternary system FeAsS - CoAsS - NiAsS (or its constituent binary systems). Klemm (1965) investigated equilibrium solid solution limits in the dry FeAsS - CoAsS - NiAsS system as a function of temperature and his results are shown in Fig.3.4. Comparing these results with the sulpharsenide compositions obtained from the Scar Crag mineralization, most of these minerals should form only above 300°C. Klemm (1965) found a discrepancy between the areas of solid solution obtained from his synthesis experiments and analyses from the literature at 200 - 500°C and suggested that glaucodot may be metastable. Maurel and Picot (1974) also suggested metastability for alloclase below 800°C.

The arsenopyrite in the mineral assemblage at Scar Crag can be employed as a geothermometer through the determination of S/As ratios, provided that an independent estimate can be made of sulphur activity during formation. This technique, based on the work of Kretschmar and Scott (1976), also requires that the arsenopyrite be from an equilibrium aS_2 - buffered assemblage and that it has a combined minor element content less than 1%. Since the Scar Crag arsenopyrite generally only contains less than 0.5% Co, the latter criterion is fulfilled. The question of equilibrium is much more difficult to assess, but it would seem worthwhile to apply the technique and then critically evaluate the results. Accurate determination of the wt.% As in the Scar Crag arsenopyrite samples is essential and two methods have been employed here. Careful measurement of the position of the d_{131} line in X - ray powder diffraction data enables the determinative curve of Kretschmar and Scott (1976) to be used (the equation:- Atomic % As = 866.67 d_{131} - 1381.2 defines this curve). The measured d_{131} values gave a range of 1.630 - 1.631 Å, corresponding to 32.4 - 31.6 at% As. These results are in good agreement with those obtained by the second method, electron probe microanalysis using a homogeneous arsenopyrite standard of known composition (if pure arsenic and pyrite standards are used the results are up to 2% different due to differences in As coordination and bonding between element and sulpharsenide). In the absence of other Fe - As - S minerals at Scar Crag which might have given the aS_2 , it can be approximately estimated from the formation of native bismuth and bismuthinite at this time (Fig.3.2). In Fig.3.5, the bismuth - bismuthinite sulphidation curve (Barton and Skinner, 1967) is plotted on a diagram showing the variation of log aS_2 with temperature; also plotted are the limits of temperature and sulphur activity defined by the range of As content in Scar Crag arsenopyrite. Sulphidation curves for certain Fe - As - S phases are shown along with the curve for the sulphidation of pyrrhotine to pyrite.

The early sulpharsenide assemblage appears to have been in equilibrium with native bismuth and to have formed under the temperature (350 - 390°C) and aS_2 ($\sim 10^{-10}$ atm) conditions defined by area 1 in Fig.3.5. Later assemblages see the appearance of bismuthinite and cobaltite (which Maurel and Picot, 1973, related to an increasing S/As ratio). This could either correspond to an increase in aS_2 or more likely, simply a drop in temperature. The eventual appearance of pyrite ties in with a fall in temperature and conditions closer to those shown by area 2 in Fig.3.5 ($T \sim 300°C$, $aS_2 \sim 10^{-12}$atm). Although arsenopyrites of the compositional range determined could exist with bismuth at much lower values of aS_2 and at lower temperatures, this seems unlikely in view of the subsequent appearance of cobaltite, bismuthinite and pyrite. In addition, a significant increase in aS_2 is ruled out because alloclase would then be expected to have undergone partial transformation to cobaltite (Maurel and Picot, 1973) and this is not observed. The conditions of ore - formation indicated here are well within the 'main line' ore fluid environment outlined by Holland (1965) and other workers.

The only previous estimate of conditions of formation for the Scar Crag Vein has been by Strens (1962) who suggested on the basis of his observed assemblage of löllingite and arsenopyrite, that the Scar Crag Vein was likely to have formed above 491°C, an invariant point in the Fe - As - S system.

The origin of the Scar Crag mineralization could be linked to the possible existence of a stock - like intrusion beneath Causey Pike

(Rose, 1955), which has metamorphosed the surrounding Skiddaw Slates (Eastwood et al., 1931). The only remotely comparable vein in the Lake District occurs in the Carrock Fell tungsten deposit where Shepherd et al. (1976) obtained temperatures of about 295°C (assuming 800 bars pressure) from fluid inclusions in mineralized quartz.

CHAPTER 4

COPPER MINERALIZATION IN THE KESWICK AREA

4.1 Chalcopyrite - pyrite - arsenopyrite veins in the Vale of Newlands

4.1.1 General

A number of copper - bearing veins occur in the Vale of Newlands and at the northern end of Borrowdale, a few kilometres to the south - west of Keswick (see Map 2 and Fig.4.1). The major copper veins in the Vale of Newlands are the Dale Head North (or Long Work) Vein and the Goldscope Vein. Several smaller veins are found at Castle Nook. Due to extensive faulting there is some difficulty in tracing these veins over the Narrow Moor ridge, but south of Derwentwater, near Grange - in - Borrowdale, the Manesty and Copper Plate Veins have been mined and these are probably continuations of some of the Vale of Newlands veins (Postlethwaite, 1913).

Chalcopyrite, pyrite and arsenopyrite are the major ore minerals occurring in the dominantly quartz - chlorite veins which cut through black siltstones of the Kirk Stile Slates (Jackson, 1978) of the Skiddaw Group, near to the junction with the overlying Borrowdale Volcanic Group. The copper veins have a predominantly east - west trend and have been displaced by later north - south faults, subsequently mineralized with galena and sphalerite. It is important to distinguish between these two types of vein particularly when, as at Goldscope, both types have been worked from the same mine. Copper mineralization is also found in the Dale Head South Vein, but the mineral assemblage differs significantly from the other copper veins in the area and it is interpreted as distinct in origin from the copper veins discussed in this part of the chapter. It is dealt with in section 4.3.1.

There are several accounts of the mining history of the Newlands and Borrowdale veins (Ward, 1876; Postlethwaite, 1913; Dewey and Eastwood, 1925; Shaw, 1970). Postlethwaite (1913) quoted from various early records and mentioned Robinson's (1709) account of eleven veins being worked in the Vale of Newlands. At the present time none of the mines are being worked, and a recent attempt to reopen the Dale Head North Mine was refused planning permission (Shaw, 1970).

In this part of the chapter, the Dale Head North Vein has been studied in detail and other similar veins,such as the Goldscope and Copper Plate veins, have been compared with it.

4.1.2 Location of the veins

The Dale Head North (Long Work) Vein crops out,dipping to the north at about 70° (Plate 2), near the head of Newlands Beck below Dale Head (see Map 2; Fig.4.1), and can be traced from the stream [NY 2285 1620] westwards for nearly a kilometre across Far Tongue Gill and over the flanks of Hindscarth, a vertical extent of over four hundred metres. Where the vein cuts Newlands Beck, it is a half metre thick and composed mainly of quartz. In the bottom of the valley it has been stoped out to the surface. Much of the material described was collected from the mouth of a small cross - cut adit to the vein, driven from the west side of Newlands Beck [NY 2280 1625].

A number of smaller northeast - southwest copper - bearing veins have been worked near Castle Nook, to the north of the Dale Head North Vein, and one of these may in fact be its continuation east of a north - south mineralized fault. Strens (1962) found a small vein on Goat Crag [NY 2440 1640] in rocks of the Borrowdale Volcanic Group which he considered might be continuous with the Dale Head North Vein.

The Goldscope Copper Vein cuts across Scope End [NY 2270 1640] in an east - west direction, dipping to the south at about 60°

(Plate 2). Faulting of the vein is extensive, especially to the east of Newlands Beck and Postlethwaite (1913) suggested that the Goldscope Copper Vein is also found at the Salt Well (or Manesty) Mine by the side of Derwentwater. However, there is no evidence to suggest that it is the Goldscope Copper Vein rather than any other of the numerous east - west copper - bearing veins in the vicinity. The Copper Plate Vein, worked to only a minor extent, can be traced from Ellers [NY 2470 1780] west of Derwentwater, for some distance over the Narrow Moor ridge where it is faulted several times, and finally becomes lost above Castle Nook.

4.1.3 Mineral data

Only brief descriptions of the mineralogy of the Dale Head North Vein have been recorded previously (Strens, 1962; Rastall, 1942). The assemblage as determined in the present work is quartz, rutile, muscovite, chlorite, pyrite, cobaltiferous pyrite, arsenopyrite, cobaltite, pyrrhotine, native bismuth, bismuthinite, sphalerite, chalcopyrite, marcasite and galena.

The vein differs from others in the area in that pyrrhotine is abundant. Elsewhere, such as in the Goldscope Copper, Castle Nook and Copper Plate veins, pyrrhotine is only found as minute grains often enclosed in pyrite or arsenopyrite. Comparison of X - ray data for Dale Head North pyrrhotine with that of Morimoto et al. (1975) showed that it is monoclinic, being therefore of the type 2A, 2B, 4C following the nomenclature of Wuensch (1963). Compositions (average - $Fe_{0.876}S$) determined by electron probe microanalysis (Table 4.1, 17 - 22) confirm the identification of monoclinic pyrrhotine at Dale Head (Kissin, 1974; Scott and Kissin, 1973; - see Fig.4.2). On the other hand, pyrrhotine inclusions in pyrite from Castle Nook have a composition (Table 4.1, 40) equivalent to the formula $Fe_{0.898}S$ and may be the hexagonal form (Kissin, 1974; Scott and Kissin, 1973; - see Fig.4.2).

Pyrite, by far the dominant ore mineral in the Dale Head North Vein, commonly contains cobaltiferous zones having up to 10 wt% cobalt (Table 4.1, 27 - 33) and no nickel. Microprobe analyses of cobaltite, however, indicate a minor nickel content (Table 4.1, 23 - 26).

Arsenopyrite was found to have a slightly higher arsenic content in the core (32.8 at% As) than in the rim (31.6 at% As) by electron probe microanalysis (Table 4.1, 1 - 9), as would be expected with continued growth under conditions of falling temperature in an aS_2- buffered assemblage (Kretschmar and Scott, 1976). An average composition for this Dale Head North arsenopyrite was determined by obtaining the d_{131} spacing (1.6301 Å) and applying the equation:- Atomic % As = 866.67 d_{131} - 1381.12 (Kretschmar and Scott, 1976), giving an arsenic content of 31.6 at% As. By comparison, arsenopyrite from Castle Nook has a slightly higher average arsenic content of 32.2 at% As, while microprobe analysis of Goldscope arsenopyrite again shows an arsenic - rich core (34.1 at% As) compared to the margin (32.3 at% As).

Sphalerite from Dale Head North exhibits little or no compositional zoning whether coexisting with chalcopyrite or pyrrhotine and contains no chalcopyrite exsolution blebs. It has a fairly constant iron content of about 13.6 mole% FeS (Table 4.1, 10 - 16). Goldscope sphalerite contains considerably less iron (7.4 mole% FeS ; Table 4.1, 38 - 39).

4.1.4 Paragenetic interpretation

It is evident from the study of hand specimens (H-78K.1.6; H-78K.1.13) that near to the margin of the Dale Head North Vein, the country rock has been fractured and brecciated. Fractures in the slates have been infilled with quartz, pyrite and other sulphides. Fragments of country rock in the vein are frequently subangular and corroded, the result of alteration by the mineralizing fluids.

The Kirk Stile Slates adjacent to the Dale Head North Vein are seen in thin section (T-77K.1.A) to be fine siltstones, extensively chloritized and with numerous small zircons. In polished section (e.g. P-78K.1.6), irregular grains of rutile are locally abundant and minute sheaves of graphite are common.

The Dale Head North Vein itself consists mainly of massive vein quartz, although smaller quartz euhedra are present, particularly in parts of the vein containing ore minerals. While much of the quartz is early, it is thought that deposition took place sporadically throughout the main period of ore mineralization. Chlorite occurs as radiating sheaves and is mostly early. Muscovite has been partially replaced by chlorite. Irregular grains and subhedra of rutile are common in the vein, are considerably larger (<100 μm) than those in the country rock (<20 μm) and may be enclosed in arsenopyrite or pyrite. It is thought that this rutile merely represents a redistribution of rutile from the altered country rock. Some of the quartz and chlorite in the vein may have been derived similarly.

Pyrite is the earliest ore mineral in the vein and has been replaced (Plates 3 and 4) by most of the later sulphides, but not by the sulpharsenides cobaltite and arsenopyrite. Unaltered early pyrite is generally dodecahedral in form and occurs along fractures in the vein margin and within the country rock itself. Frequently, the pyrite euhedra contain cobaltiferous zones (Plates 3 and 20) which appear slightly brownish pink against normal pyrite in reflected light. Typically, a zone (<50 μm) of cobaltiferous pyrite serves as a transition zone between a core of pyrite with cubic habit and pyrite with dodecahedral habit. Such a change of habits has previously been described for bravoite and pyrite by El Baz and Amstutz (1963). Pyrite also occurs as small euhedra associated with marcasite in the replacement of pyrrhotine and chalcopyrite (Plate 20), and as a late stage alteration of pyrrhotine.

The relationship between cobaltite and arsenopyrite is unclear as both minerals form overgrowths on early pyrite (Plate 3). Cobaltite appears bright pinkish white against pyrite and is often euhedral. In addition, it is found as small (<50 µm) euhedra in pyrrhotine, particularly where the latter has replaced pyrite. Arsenopyrite is much more common and occurs either as overgrowths on pyrite , as euhedra (Plate 20) enclosed in country rock and in some instances replaced by quartz and later sulphides, or as larger subhedra (<5 mm) which have been fractured and the later cracks infilled by bismuthinite, pyrrhotine, chalcopyrite, sphalerite and galena (P-78K.1.4).

Anhedral grains of native bismuth and bismuthinite are associated with pyrrhotine. Less commonly,bismuthinite occurs as small grains in porous pyrite. Native bismuth is not as common and may have been replaced by bismuthinite (possibly on account of sulphidation) as it is generally enclosed by the latter (see Plate 4).Bismuthinite forms aggregates up to 200 µm but individual grains exceeding 50 µm are uncommon. The close association between bismuth, bismuthinite, pyrrhotine, chalcopyrite and sphalerite and the lack of any obvious replacement textures has led to some difficulty in deciding the sequence of formation (Fig.4.3). It is thought likely that no great time elapsed between their deposition.

Pyrrhotine commonly surrounds bismuthinite and replaces pyrite to a considerable extent especially along the cobaltiferous zones. Pyrrhotine itself may have been replaced to a minor extent by sphalerite and chalcopyrite, but is more extensively altered to marcasite and pyrite (P-77K.1.G)

Like pyrrhotine, chalcopyrite is always anhedral, frequently interstitial and replaces pyrite. In some instances it shows exsolution of sphalerite in the form of minute 'stars' (Plate 20) and the same specimen (P-BM.Ki.K.1), from the Kingsbury Collection (British Museum - Natural History), also has a few minute grains of gold. Chalcopyrite may enclose or be enclosed by sphalerite; the latter is replaced to a small degree by tennantite (P-78K.1.5).

Marcasite has replaced pyrrhotine and chalcopyrite (Plate 20) and forms aggregates of small grains arranged in a lamellar fashion with cross - cutting euhedra of pyrite (P-78K.1.2). Galena may occur in the interstices between these lamellae. Less commonly, marcasite and pyrite in very fine aggregates are found as a late stage replacement of pyrrhotine.

Galena is interpreted as the last mineral deposited during the period of ore mineralization and it replaces some of the earlier sulphides.

The main paragenetic differences between the Dale Head North Vein and the other veins in the Newlands area are the absence of cobalt minerals and uncommon occurrence of pyrrhotine in the latter. A small zone of cobaltian arsenopyrite was found in material from Castle Nook however, and pyrrhotine occurs as minute inclusions in pyrite and arsenopyrite from the Goldscope Copper, Castle Nook and Copper Plate Veins. Although this pyrrhotine appears to be earlier in the paragenetic sequence than pyrrhotine from Dale Head North, in other respects the parageneses are similar.

Paragenetic relations for the Dale Head North Vein are given in Fig 4.3.

4.1.5 Conditions of formation

Early ore minerals introduced into the Dale Head North Vein include cobaltiferous pyrite and cobaltite. Analyses of cobaltiferous pyrite were compared to Klemm's (1965) synthetic data in the system FeS_2 - CoS_2 - NiS_2 , and fall within the temperature range 360 - 520 °C (Fig.4.4). The applicability of synthetic data to natural assemblages is questionable, however, and there is a discrepancy of enormous dimensions between literature research results and laboratory results in the FeS_2 - CoS_2 - NiS_2 system. A similar discrepancy in the FeAsS - CoAsS - NiAsS system (Klemm, 1965) has already been mentioned (see Ch.3), and cobaltite analyses from Dale Head North Vein were found to fall in the range 350 - 400°C (Fig.4.5), when compared to the synthetic data in this system. Little significance is attached to the temperatures indicated for cobaltiferous pyrite and cobaltite, therefore, as these minerals commonly appear to form as metastable phases.

Arsenopyrite is potentially one of the most useful indicators of temperature and sulphur activity in the vein during mineralization if it is possible to apply Kretschmar and Scott's (1976) arsenopyrite geothermometer. Certain conditions need to be fulfilled for successful application of this approach. Firstly, arsenopyrite should be chosen from aS_2 - buffered assemblages. In vein deposits, arsenopyrite can be assumed to be in equilibrium with other simultaneously deposited minerals, but is unlikely to change its composition in response to changing conditions in the vein owing to its refractory nature (Kretschmar and Scott, 1976). That arsenopyrite from Dale Head North has probably not changed its composition is shown by the presence of an As - rich core (32.8 at% As) surrounded by an As - deficient rim (31.6 at% As). A second condition which must be fulfilled is that arsenopyrite should contain less than 1% of minor elements; no detectable cobalt or other minor element was found in the Dale Head North arsenopyrite. Finally, the arsenic content should be determined either by X - ray diffraction (using an internal standard and applying Kretschmar and Scott's, 1976, equation) or by electron probe microanalysis (using an arsenopyrite standard of proven homogeneity). In the present work, electron probe microanalysis was carried out using Kretschmar's Asp 200 standard, and the results (Table 4.1) are in good agreement with the bulk composition (31.6 at% As) determined by X - ray diffraction.

Sulphidation curves representing arsenopyrite compositions of 31.6 at% As and 32.8 at% As respectively were plotted on a sulphur activity against temperature diagram (Fig.4.6), extrapolating Kretschmar and Scott's (1976) sulphidation curves to somewhat lower temperatures than 300°C. On the same diagram, pyrite/pyrrhotine and bismuth/bismuthinite sulphidation curves were also plotted. A combination of the paragenetic data given earlier, sulphidation curves, and sulphide phase equilibria can now be used to estimate the temperatures of formation and sulphur activities during mineralization.

Monoclinic pyrrhotine cannot have formed above 248°C (Kissin, 1974), but it is possible for higher temperature hexagonal pyrrhotines to have inverted to monoclinic pyrrhotine on cooling below 248°C (see Fig.4.2). This is not thought to have occurred as the monoclinic pyrrhotine is homogeneous.

Native bismuth and bismuthinite are in close association with monoclinic pyrrhotine. Equilibrium in natural assemblages is always difficult to establish with any degree of certainty (Barton et al., 1963), but bismuthinite which has replaced native bismuth may be in equilibrium with monoclinic pyrrhotine. If this is so then formation conditions for these minerals are limited to a small area between $aS_2 = 10^{-13.7}$ atm and $aS_2 = 10^{-14.4}$atm, with temperatures respectively of 248°C and 235°C (see Fig.4.6). At 235°C the invariant assemblage, pyrite - pyrrhotine - bismuth - bismuthinite occurs (Barton and Skinner, 1967). Pyrite was not observed in the Dale Head North paragenetic sequence at this stage and therefore it is proposed that bismuth, bismuthinite and monoclinic pyrrhotine formed above 235°C.

Chalcopyrite and sphalerite are also closely associated with monoclinic pyrrhotine and may be in equilibrium. From Scott and Kissin's (1973) speculative phase diagram (Fig.4.7) of low temperature relations in the FeS - ZnS - S system, sphalerite with an iron content of 13.6 mole % FeS could only be in equilibrium with monoclinic pyrrhotine at temperatures less than 245°C.

Summarizing the above observations, it is proposed that the following approximate sequence of events (represented in terms of temperature and aS_2 variation by the shaded area in Fig.4.6) took place within the Dale Head North Vein. Initial fluids migrating into the vein deposited quartz, chlorite, rutile and muscovite. Early pyrite with cobaltiferous zones was probably deposited at temperatures between 300 - 350°C and with $aS_2 \sim 10^{-10}$atm (Fig.4.6, No.1). There is no definite 'fix' for this early period of mineralization however. Cobaltite could have formed subsequently under similar temperature conditions although at perhaps a lower sulphur activity.

Sulphur activity during arsenopyrite formation must be independently estimated from an aS_2 - dependent assemblage coexisting with arsenopyrite (Kretschmar and Scott, 1976). A reasonable estimate is given by the assemblage monoclinic pyrrhotine - bismuth - bismuthinite ($aS_2 \sim 10^{-14}$atm). At $aS_2 \sim 10^{-14}$atm, early arsenopyrite (32.8 at% As) may have been deposited at about 295°C (Fig.4.6, No.2), a decrease in temperature at constant sulphur activity leading to late arsenopyrite (31.6 at% As) being formed at about 275°C (Fig.4.6, No.3). With the temperature still decreasing, bismuth could have been deposited and subsequently bismuthinite, monoclinic pyrrhotine and sphalerite at temperatures between 240°C and 250°C (Fig.4.6, No.4). Chalcopyrite was probably formed under similar conditions.

Later marcasite, pyrite and galena are interpreted as having been deposited below 235°C at $aS_2 \sim 10^{-14}$atm (or possibly greater).

It is possible to establish a similar sequence of events for the Goldscope Copper, Castle Nook and Copper Plate Veins as the assemblages and parageneses are similar to those at Dale Head North. However, the absence of monoclinic pyrrhotine, and the consequently lower iron content of sphalerite from Goldscope as expected in a more sulphur - rich (or higher temperature?) environment, enables a far less definite estimate to be made for the conditions of formation of the ore mineralization.

Further discussion concerning the Dale Head North and similar veins is to be found in 4.4.

4.2 Mineralization at Wanthwaite, St John's Vale

4.2.1 Location and mineralogy

Two copper - bearing veins occur near Wanthwaite overlooking St John's Vale to the east of Keswick (see Map 2), both are strongly controlled by major east - west faults. The northern vein (not dealt with in detail here) follows the faulted boundary of the St John's microgranite with the Skiddaw Slates for about a kilometre and can be traced over Clough Head [NY 3350 2270] . Little material was found at outcrop or on the mine dumps from this vein although Kingsbury and Hartley (1958) observed ' arsenopyrite, pyrite, sphalerite, galena, stibnite and other sulphosalts in a quartz - carbonate gangue'.

The southern vein appears to be similar although no sulphosalts were found and chalcopyrite is common. The vein is best exposed beneath Wanthwaite Crags to the northeast of the Bram Crag roadstone quarry at [NY 3250 2245]. Here it has been worked to a limited extent, judging by the small amount of spoil material, and the mine adit has collapsed. The vein dips at high angles to the south and has been emplaced along the faulted junction between the Skiddaw Slates and the overlying Borrowdale Volcanic Group. At outcrop, farther east of this adit, the vein is up to a half metre across and consists predominantly of arsenopyrite and pyrite, with very little quartz.

The mineralogy of the southern Wanthwaite vein was found to be simpler than that of other comparable veins and the mineral assemblage was determined as :- quartz, chlorite, rutile, pyrrhotine, arsenopyrite, pyrite, sphalerite, chalcopyrite and galena.

Using Kretschmar and Scott's (1976) equation, the d_{131} interplanar spacing of arsenopyrite (1.6308 Å) gave an arsenic content of 32.2 at% As. There is good agreement between this value and microprobe data (Table 4.1, 41 - 54). Analyses of core zones in arsenopyrites (Table 4.1, 41 - 45) have an average arsenic content of 32.9 at% As, while marginal areas have an average arsenic content of 31.9 at% As (Table 4.1, 45 - 54).

Core areas of arsenopyrite occasionally contain small grains of pyrrhotine (Plate 5). Although these were too small for X - ray diffraction techniques, microprobe analysis indicated a composition of $Fe_{0.931}S$ (Table 4.1, 57), equivalent to hexagonal pyrrhotine (see Fig. 4.2).

Sphalerite is nearly always associated with chalcopyrite exsolution, commonly on a very fine scale with individual blebs of chalcopyrite less than 1 µm. Slightly larger blebs also occur, at grain boundaries and along structural planes (Plate 21). Electron probe microanalysis showed that sphalerite with chalcopyrite exsolution contains 5.8 mole% FeS (Table 4.1, 55) and also has a lower sulphur content than normal. Marginal sphalerite with no chalcopyrite exsolution has a slightly higher iron content (8.0 mole% FeS, Table 4.1, 56) and a normal sulphur content.

4.2.2 Paragenetic interpretation

Hand specimens (e.g. H-78K.15.3; H-78K.15.1) show that the vein is, in some instances, composed almost entirely of sulphides and sulpharsenides to a width of 0.1 - 0.2m. More commonly and marginal to these areas, the ore minerals are found as veinlets in intensely brecciated country rocks. Fragments of tuff and andesite from the Borrowdale Volcanic Group are far subordinate to the shattered and now rounded fragments of siltstone from the Skiddaw Slates. A further period of fracturing in the vein occurred after the deposition of most of the ore minerals and pyrite has subsequently developed along these fractures (H-78K.15.4).

Fragments of Skiddaw Slate in the vein are seen to be extensively chloritized in thin section (T-77K.15.5). Quartz occurs as a minor mineral and was mostly formed early; little deposition appears to have taken place during ore mineralization, but late quartz infills cross - cutting fractures. Some of the early quartz contains fine grains of rutile (<100 µm in length). As in the Dale Head North and other Newlands veins, rutile occurs as fine grains in the country rock but appears to have been remobilized where the slates have been altered by the mineralizing fluids, and deposited as larger grains (<100 µm) which are found at vein margins or as inclusions in arsenopyrite, pyrite or sphalerite. Chlorite occurs as blunt ended laths, mostly at vein margins.

Arsenopyrite is the earliest ore mineral; in polished sections it is seen as small euhedra in altered country rock (<50 µm) or as larger euhedra (<2mm) in the vein itself. Small cores (<50 µm) are overgrown (Plate 6) by later arsenopyrite of slightly different composition (Table 4.1, 41 - 54). Arsenopyrite is sometimes fragmental, with later sulphides infilling fractures or replacing it (Plates 5,6,21); it also occurs as anhedral grains enclosed in pyrite euhedra (P-78K.15.5).

Pyrrhotine is found as small anhedral grains (<50 µm) in, or adjacent to, core zones of arsenopyrite (Plate 5) or, less commonly, as small grains in the centre of euhedral pyrite (P-77K.15.1).

Euhedral cubes of pyrite replace arsenopyrite, and may enclose grains of rutile and, less commonly, pyrrhotine. There is some difficulty in distinguishing different generations of pyrite. Early pyrite tends to occur as euhedral cubes (<100 µm) and has been replaced by sphalerite, chalcopyrite and galena. Later pyrite forms much smaller cubes (20 - 30 µm) and aggregates, replaced to a lesser extent by the other sulphides than early pyrite. Lastly, larger cubes and aggregates of pyrite occur along cross - cutting fractures in the ores and vein breccia (P-78K.15.4).

Sphalerite, with both finely disseminated and regularly orientated chalcopyrite exsolution blebs (<1 - 10 μm), commonly has an outer rim (<50 μm) with no exsolution textures and with a slightly different iron content (Table 4.1, 55 - 56).

Chalcopyrite, in addition to occurring as an exsolved phase in sphalerite (Plate 21), also occurs as larger grains forming discrete areas, which are difficult to interpret paragenetically but which are probably later than sphalerite. Fractures in sphalerite are commonly infilled by chalcopyrite or galena (P-78K.15.1).

Galena is interstitial to sphalerite and replaces pyrite extensively, forming a sieve - like texture (Plate 7). It is interpreted as the last sulphide deposited before a further period of fracturing and late infill of the fractures by pyrite and quartz.

The paragenetic relations are summarized in Fig.4.8.

4.2.3 Conditions of formation

Sulphidation curves for average compositions of core and marginal arsenopyrite have been plotted as before on an aS_2 against temperature diagram (Fig.4.9) using the method of Kretschmar and Scott (1976). Early core arsenopyrite has a maximum temperature of formation of 470°C, and marginal arsenopyrite a maximum temperature of 390°C.

A good independent estimate of the sulphur activity of the early mineralization was obtained using the coexisting minerals hexagonal pyrrhotine and core arsenopyrite. Using Toulmin and Barton's (1964) equation:- $\log_{10} aS_2 = (70.30 - 85.83N)(1000/T - 1) + 39.30\sqrt{(1 - 0.9981N)} - 11.91$, it is possible to determine the variation of sulphur activity with temperature for hexagonal pyrrhotine having a composition $N_{FeS} = 0.965$ (where N_{FeS} is the mole fraction of FeS). This 'contour' was plotted on the sulphur activity against temperature diagram (Fig.4.9) and it intersects the early arsenopyrite sulphidation curve at 310°C and $aS_2 \sim 10^{-13.5}$atm. It is inferred that early mineralization took place under these conditions (Fig.4.9, No.1). Cooling would account for later marginal arsenopyrite with lower arsenic content (31.9 at% As) forming under conditions represented by Fig.4.9, No.2), and further cooling or a rise in aS_2 could lead to pyrite deposition at 235°C (or slightly higher temperatures if a rise in aS_2 is envisaged).

The concentration of iron in sphalerite is a function of aFeS, which at a given temperature is inversely related to the sulphur activity of the coexisting iron sulphide assemblage (Scott and Kissin, 1973). Sphalerite (8.0 mole% FeS; Table 4.1, 56) coexists with pyrite at Wanthwaite and the variation of sphalerite having such a composition, with sulphur activity and temperature (from Barton and Toulmin, 1966) was plotted on Fig.4.9. The area around point No.3 (Fig.4.9) is considered to represent the conditions of sphalerite/pyrite mineralization (225 - 235°C ; $aS_2 \sim 10^{-13} - 10^{-14}$atm).

The composition of sphalerite with exsolved chalcopyrite (Table 4.1, 56) was not plotted as the effect of chalcopyrite exsolution on the iron content, and hence on the sulphur activity, is poorly understood (Brown et al., 1978).

Sulphur activities during the deposition of galena and late pyrite are thought to have been similar to those during pyrite, sphalerite and chalcopyrite mineralization, although temperatures may have been lower.

4.3 Other copper - bearing veins in the Keswick area

4.3.1 Dale Head South Vein

A half kilometre to the south of the Dale Head North Vein, the northeast to southwest trending Dale Head South Vein has been worked high on the steep northerly slopes of Dale Head [NY 2245 1555] (see Map 2). The Dale Head South Vein is unlike the other Newlands copper veins (see 4.1) in that its host rocks are tuffs and andesites of the Borrowdale Volcanic Group. The mineral assemblage is also different and 'it contains some splendid green carbonate but not much yellow copper' (Ward, 1876). There is abundant evidence of supergene alteration.

The assemblage as determined from preliminary studies of hand specimens and polished sections is quartz, calcite, pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, djurleite, blaubleibender covelline, covelline, bornite, goethite, tenorite, malachite, azurite and chrysocolla.

Hand specimens (H-K.01.2; H-K.01.3) generally show small amounts of sulphide mineralization in a vein breccia cemented by quartz. Movement along the fault in which the vein has been emplaced must have occurred both before and after ore mineralization, as some specimens (e.g.H-K.01.4) have fractured sulphides intimately mixed with finely brecciated host rock.

Polished sections exhibit well - developed replacement textures. Where sulphides infill voids in quartz (e.g.P-K.01.2), sphalerite (with a low iron content of 2.2 mole% FeS) is typically replaced by bornite and chalcopyrite (Plate 7). Covelline occurs along late fractures.

Other sections (P-K.01.3; P-77K.01.8) show bornite extensively altered, ultimately to goethite and malachite. Initially, bornite has been altered along structural planes by a lighter coloured phase ('anomalous bornite' ? of Sillitoe and Clark, 1969), which has itself commonly undergone alteration to chalcopyrite, giving a well - developed 'basket - weave' texture. Subsequently, bornite has been completely replaced in some areas by goethite and malachite leaving the chalcopyrite as fine skeletal lamellae. Djurleite has been partially replaced by blaubleibender covelline (P-K.01.4).

These preliminary observations suggest supergene alteration of what may have originally been a chalcopyrite - pyrite - arsenopyrite vein, similar to others in the Newlands area already described. Strens (1962) explained this oxidation assemblage in the Borrowdale Volcanic Group as being due to the abundance of joints, and the consequent free circulation of water and oxygen. It seems just as likely however, that the extensive brecciation of the vein, apparently after mineralization, was responsible for such a free circulation of oxidizing fluids.

4.3.2 Minor occurrences

Few copper occurrences have been discovered in rocks of the Borrowdale Volcanic Group in the Keswick area. Ward (1876) reports an east - west vein east of Thirlspot at the side of Thirlmere [NY 3220 1785] , and an ore specimen from the Kingsbury Collection (British Museum - Natural History) has chalcopyrite partially altered to goethite.

Strens (1965) found minor amounts of chalcopyrite associated with the Borrowdale graphite deposits.

The north - south lead and zinc veins in the Keswick area rarely show much copper mineralization, unlike similar veins in the Caldbeck Fells and Helvellyn areas, where chalcopyrite is locally abundant (see Ch.5).

4.4 Discussion

The chalcopyrite - pyrite - arsenopyrite veins in Newlands and at Wanthwaite, although having slightly different assemblages, are nonetheless thought to have been of similar age. In the past there has been some disagreement as to the ages of both copper and later lead - zinc veins in the Vale of Newlands. Eastwood (1921) proposed two or three periods of mineralization while others either considered all copper and lead - zinc veins to be Caledonian (Rastall, 1942) or regarded them as Tertiary (Trotter,1944). The chalcopyrite - pyrite - arsenopyrite veins are clearly earlier than the galena - sphalerite veins which sometimes displace them, and it has been suggested (Strens, 1962) that the copper veins were emplaced along Caledonian pressure release fractures. A K - Ar isotopic study of the Lake District mineralization by Ineson and Mitchell (1974) gave an isotopic age of 395 Ma for illite from a chalcopyrite - pyrite vein at Castle Nook.

Of the other minor copper occurrences, Strens (1965) suggested a pre - Bala age for the chalcopyrite associated with the Borrowdale graphite deposit. The Thirlspot east - west vein probably has a similar age (i.e. Lower Devonian) to the Newlands copper veins. The age of the Dale Head South Vein is uncertain.

For this Lower Devonian mineralization, Strens (1962) put forward evidence for a roughly vertical zonation. In the area around Keswick, the deepest and presumably highest temperature mineralization is represented by arsenopyrite from Scar Crag [NY 2060 2070]. Higher zones contain arsenopyrite with pyrite and (as at Dale Head North) pyrrhotine. The highest zone contains no arsenopyrite and is dominantly chalcopyrite with sphalerite, pyrite and galena. Only in the Dale Head North Vein is there any evidence for such a zonation; while pyrrhotine and arsenopyrite are common in material derived from the lower levels, specimens from the upper levels consist mainly of chalcopyrite. However, the investigation of the arsenopyrite and cobalt - iron sulpharsenide minerals from Scar Crag in the present study (Chapter 3), suggests a temperature of about 400°C for the early mineralization, higher than temperatures proposed for the earliest minerals in the Dale Head North Vein (300 - 350°C) and the Wanthwaite Vein (~310°C). Some sort of depth/temperature zoning in the region may be present therefore.

Strens (1962) estimated the temperature of the Skiddaw Slates country rock in the Vale of Newlands at the time of copper mineralization at 260 ± 50°C and suggested a range of 270 - 400°C for the formation of the Dale Head North Vein. These estimates were based on a sedimentary and volcanic sequence 9.2 km thick in Lower Devonian times.

Fluid inclusion studies by T.J.Shepherd (personal communication) yielded homogenization temperatures of about 170°C for pseudo-secondary two phase inclusions in quartz coexisting with chalcopyrite from the Dale Head North Vein. In correcting homogenization temperatures, it is usual for the pressure to be estimated from geological evidence for the depth of cover at the time of mineralization, with the assumption that formation pressure is equal to either the lithostatic or hydrostatic load (Roedder, 1967). If 9.2 km is used as an estimate for the thickness of cover then, depending on whether the ore solutions were under purely hydrostatic or purely lithostatic load, the pressures are 900 bars and 2250 bars respectively. Corrected temperatures for these pressures (assuming a salinity of 5% NaCl) are 255°C and 345°C (Lemmlein and Klevtsov, 1961).

Although the higher of these temperatures (345°C) would be in agreement with temperatures proposed for the early mineralization, quartz coexisting with chalcopyrite is, on the basis of the results previously given in this chapter, more likely to have formed at temperatures in the region of 255°C. Further evidence for the lower pressure and temperature estimate is provided by comparison with veins of similar age and stratigraphic setting, although of different mineralogy at Carrock Fell. Here, an estimated pressure of 800 bars was obtained by the use of complex liquid CO_2 inclusions (Shepherd et al., 1976).

To conclude, it is thought that the chalcopyrite - pyrite - arsenopyrite veins in the Vale of Newlands and at Wanthwaite are of Lower Devonian age. They have been emplaced along east - west fractures, developed either by Caledonian pressure release, or the result of intrusion (or perhaps subsequent uplift) of the underlying composite Lake District granite batholith (Bott,1974). In the Dale Head North Vein, early mineralization occurred at 300 - 350°C and $aS_2 \sim 10^{-10}$atm with later minerals forming at ~240°C and $aS_2 \sim 10^{-14}$atm due to cooling of the mineral - bearing fluids. In the Wanthwaite Vein, the early minerals formed at ~310°C with $aS_2 \sim 10^{-13.5}$atm while later mineralization took place at ~225°C and $aS_2 \sim 10^{-13}$atm.

Ultimate origins for the mineralization are discussed in Chapter 9.

CHAPTER 5

LEAD - ZINC MINERALIZATION IN THE LAKE DISTRICT

5.1 General

In the Lake District, three main lead - zinc orefields have been recognised (Eastwood, 1921; Shaw, 1970); the Caldbeck Fells Mining Field, the Keswick Mining Field and the smaller Helvellyn Mining Field. In addition there are a few isolated occurrences elsewhere in the Lake District. Although the lead - zinc mineralization is widespread, many of the veins which have been worked are small. As with the copper mining, the heyday of lead and zinc mining in the Lake District was in the latter part of the last century; although the Greenside Mine and a few others have been worked this century. In fact, of the total estimated production of lead concentrates in the Lake District, the Greenside Mine has contributed about two thirds (200,000 tons; Eastwood, 1959). The total production of about 300,000 tons compares with an estimated total production of 4 million tons of lead concentrates from the North Pennines orefield.

Almost all of the lead - zinc deposits are associated with barytes, which is present in economic quantities in some veins (e.g. Force Crag Vein). Barytes has also been mined at Potts Ghyll and Sandbeds mines in the Caldbeck Fells orefield. The Caldbeck Fells Mining area differs from the others in that copper minerals are locally abundant, especially in the Roughtongill district.

All of the lead - zinc veins appear to be simple void infillings, mostly along normal faults.

In this chapter, the mineralogy and paragenetic interpretation of some of the larger veins is described and used in conjunction with fluid inclusion studies on sphalerite and fluorite to draw conclusions as to likely temperatures and compositions of the ore - forming fluids.

5.2 Caldbeck Fells orefield

The Caldbeck Fells form a belt of undulating country on the northern margin of the Lake District about twelve kilometres northeast of Keswick. A number of lead, zinc, copper and barytes veins have been mined although all the mines are now abandoned. Roughtongill Mine was the last lead, zinc and copper mine to close down in 1878 but barytes has been extensively mined in this century, Potts Ghyll barytes mine being the last to close in 1965 (Shaw, 1970). Southwest of Carrock Fell, tungsten has been mined intermittently at Carrock Mine, which is in production at the present time having reopened in 1977. These tungsten veins fall outside the scope of this chapter. Accounts of the mining history of the area are given in Postlethwaite (1913), Shaw (1970) and Eastwood (1921, 1959).

The principal lead and zinc - bearing veins (see Map 3) in the Caldbeck Fells are the Roughtongill North and South Lodes, Redgill Vein, Driggith Vein, and Drygill Vein. Haygill, Carrock End, and Potts Ghyll Copper veins have been worked for copper and appear to contain no lead and zinc mineralization. Potts Ghyll Barytes and Sandbeds Mines have worked barytes veins.

Apart from the greater amount of copper mineralization associated with lead - zinc veins in this area, another characteristic is the abundance of secondary alteration products. Eastwood (1959) attributed the diversity of minerals to the variety of the country rocks. Most of the lead, zinc, copper, and barytes veins occur along normal faults cutting andesites and tuffs of the Eycott Group

(Wadge,1978a); however, the Roughtongill South Vein occupies a fault in the Carrock Fell Igneous Complex. The Skiddaw Slates Group appears to have been an unfavourable host rock for the lead - zinc mineralization in this area except in Grainsgill where the Carrock East - West Vein has displaced the earlier north - south tungsten veins where it cuts through cordierite hornfels at the margin of the Skiddaw Granite. The Drygill Vein and the Carrock End Vein seem to have been structurally controlled by the junction of the Carrock Fell Igneous Complex with the Eycott Group. To the north, barytes veins occur in the Carboniferous Limestone at Ruthwaite [NY 2400 3675] and barytes also occurs along joints in the limestone.

The country rocks at the margins of the veins have often undergone substantial brecciation (e.g. H-CF.5.2) although fracturing of the vein minerals themselves has been comparatively minor (e.g.H-77 CF.15.9).

The tungsten veins are earlier than than the lead - zinc veins (having been displaced by the latter) and have a north - south direction while the lead, zinc and barytes veins have a tendency to an east - west or northeast - southwest direction. The major copper veins generally have a north - south direction and so may possibly be related to the earlier period of mineralization, although field evidence for this is lacking.

Previous work on the area has concentrated mainly on the abundant and exotic secondary alteration products (e.g. Goodchild, 1881, 1882, 1883; Davidson and Thompson, 1948). Thimmaiah (1956) gave an unpublished account of some aspects of the mineralization of the area.

In the present work, the mineralogy and paragenesis of the

Driggith Vein have been studied in detail and compared with other veins. In addition, results of a limited study of fluid inclusions in fluorite from the east - west lead - zinc crosscourse in Carrock Mine are reported.

An account of the mineralogy of the Carrock tungten mine is given by Hitchen (1934) and the genesis of the tungsten mineralization by Shepherd et al., (1976).

5.2.1 Location and mineralogy of the Driggith Vein

The Driggith Vein has a northeast to southwest direction and dips at about 80° to the northwest. Apart from outcrop workings, the vein was mined from Driggith Mine [NY 3280 3520] and from Sandbeds Mine [NY 3320 3620], both of which are now inaccessible and the workings dangerous. At Driggith, to the southeast of High Pike, the vein forms 'a mineralized fault between a lava and an altered ash' (Eastwood, 1921) of the Eycott Group (see Map 3). To the southwest it becomes more difficult to trace and has not been worked or proven in the vicinity of the Harestones Felsite of the Carrock Fell Igneous Complex, where there is extensive alteration of the country rocks. Beyond this area of alteration, the Roughtongill South Vein is almost certainly the continuation of the Driggith Vein. At Roughtongill, the host rocks are altered gabbros and granophyres of the Carrock Fell Igneous Complex. Eastwood et al., (1968) suggested that the considerable lateral displacements of the steeply inclined junctions of the igneous complex (see Map 3) may be the result of a horizontal component in the dislocations.

The country rocks marginal to the Driggith Vein have undergone intense alteration and Thimmaiah (1956) recognised two phases of alteration of the andesites and tuffs. One, marked by the production of calcite, chlorite and sericite occurs in most of the rocks of the area; near vein margins, however, the rocks have been converted almost entirely to sericite and quartz.

At outcrop near Driggith Mine, the vein consists of about two metres of barren quartz with barytes at either margin. Commonly, the quartz is vuggy and in some places shows cockscomb textures when pseudomorphing early barytes. The vugs are often filled with manganese minerals such as pyrolusite or psilomelane, iron oxides and green crystals of pyromorphite (H-CF.16.1). Thimmaiah (1956) found from underground evidence that quartz and barytes occur near the walls of the vein with quartz and later sulphides in the centre of the vein.

The primary mineral assemblage at Driggith as determined in the present study is quartz, barytes, calcite, chalcedony, pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, bournonite, tetrahedrite and native antimony. Those minerals which are reported as later secondary oxidation products include djurleite, covelline, goethite, native copper, 'limonite', malachite, azurite, anglesite, pyromorphite, and psilomelane. In addition, bornite was found by Thimmaiah (1956).

Of special interest are the antimony - bearing minerals, bournonite, tetrahedrite, and native antimony which are reported from this area for the first time. Bournonite ($CuSbPbS_3$) was quantitatively determined by electron probe microanalysis (Table 5.8, 1 - 2). Native antimony occurs in very fine grains and was analysed qualitatively by that technique. Tetrahedrite contains 10 - 12 wt% silver (Table 5.8, 3 - 4) and has interplanar spacings in agreement with Berry and Thompson's (1962) data for argentian tetrahedrite. The only other antimony minerals previously described from the northern Lake District have been stibnite, from a small mine at Robin Hood, Bassenthwaite (Postlethwaite, 1913) and confirmed by examination of a specimen from the Russell Collection (British Museum - Natural History) by the present author, and stibnite and other sulphosalts including zinkenite, jamesonite and boulangerite from Grainsgill (Kingsbury and Hartley, 1956a).

Sphalerite from the Driggith and Roughtongill Mines has a low iron content of about 3.0 mole% FeS (Table 5.8, 5 - 8).

Although tetrahedrite was only found in material from the Driggith Vein, the other lead - zinc veins in the area such as the Redgill, Roughtongill South, and Silvergill veins were found to vary very little in their primary mineralogy . All of them contained intergrowths of bournonite and native antimony in galena. At Silvergill, there is a botryoidal development of chalcedony and galena (H-CF.10.6) , which seem to have been deposited simultaneously.

There is a considerable literature on the vast number of secondary minerals reported from the Caldbeck Fells, The most productive localities for these being Roughtongill Mine and Drygill Mine. These secondary minerals include hemimorphite, chrysocolla, anglesite, cerussite, mimetite, linarite, pyromorphite, caledonite, leadhillite, tenorite (Goodchild, 1881, 1882, 1883); plumbogummite, brochantite, atacamite, smithsonite, aurichalcite, malachite, limonite, goethite (Davidson and Thompson, 1948); jarosite (Kingsbury and Hartley,1958); mottramite, descloizite and vanadinite (Kingsbury and Hartley, 1956).

The north - south copper veins at Potts Ghyll, Haygill, and Carrock End generally contain chalcopyrite with minor amounts of arsenopyrite and pyrite.

5.2.2 Paragenesis of the Driggith Vein

The paragenetic relations are summarized in Fig.5.1.

Pyrite occurs as small euhedra in the country rock of fine tuff (which has extensive carbonate and sericitic alteration - H-77CF. 15.D). It also occurs as an early phase in the Driggith Vein. Both pyrite and smaller amounts of arsenopyrite are found as corroded inclusions in chalcopyrite and galena. Although they are earlier than the latter, their age relationships were determined only with difficulty. Early barytes mineralization is shown clearly, both by field observations of barytes on either side of the central quartz vein and by the later quartz pseudomorphs after barytes in the centre of the vein. Calcite also appears to be an early phase as it is marginal to later sulphides (T-77CF.15.D).

Following the deposition of these early minerals, sphalerite and chalcopyrite were formed. These generally have mutual boundary relationships and must have been introduced into the vein at roughly the same time. Sphalerite is particularly abundant and commonly (H-77 CF.15.C) infills interstices in corroded quartz pseudomorphing barytes. Galena may also show mutual boundary relationships with sphalerite and chalcopyrite but is regarded as being later, as it generally encloses these minerals and tends to occur towards the centre of the vein (H-CF.15.2).

Argentian tetrahedrite, $(Cu_{0.84}Ag_{0.16})_{10.3}(Fe_{0.43}Zn_{0.57})_{2.0}Sb_{4.3}S_{13}$, (Table 5.8, 3) appears olive - grey against galena and is almost always in anhedral grains <200 µm (P-CF.15.2). Commonly, it overgrows euhedral quartz and may contain grains of bournonite (Plate 22). In contact with both galena and tetrahedrite, bournonite appears greenish grey and often exhibits twinning (P-CF. 15.8 - Plate 22). At Driggith and other lead - zinc veins in the Caldbeck Fells, bournonite occurs in three forms. The first occurrence is as relatively large grains commonly enclosed in argentian tetrahedrite (Plate 22). Secondly it occurs as intergrowths in galena; these may either be platelets, usually no more than a few microns in width (P-CF.17.21) and strongly orientated along structural planes of the galena (Plate 23), or else as rounded blebs <5 - 10 µm arranged in irregular curved 'strings', possibly along galena grain boundaries (P-CF.15.2). Irregular grains of bournonite also occur either associated with native antimony (Plate 23), or as somewhat smaller grains at chalcopyrite/galena grain boundaries (<5 µm). Lastly, bournonite is found in some specimens along cleavages in galena together with chalcopyrite and minor tetrahedrite. This may be the result of post - cleavage remobilization (P-77CF.15.B).

Native antimony is intimately associated with bournonite where the latter occurs as intergrowths and small blebs in galena. It has a high reflectance and is brilliant white against galena, generally occurring as minute (mostly <1 µm) rounded grains rarely greater than 5 µm (Plate 23).

A further period of barytes mineralization took place after the deposition of galena and the antimony - bearing minerals (P-77CF.15.D).

Following the remobilization of some of the sulphides, the primary mineralization suffered considerable alteration by secondary fluids. Galena has been replaced along cleavages and grain boundaries by djurleite and covelline, commonly showing a botryoidal development (Plates 8 and 22). Djurleite was found by X - ray diffraction to be intimately associated with very fine (<1 µm) grains of anglesite. In the replacement of galena by djurleite and anglesite, the galena has been replaced preferentially to the bournonite and native antimony intergrowths (Plate 23). Covelline also replaces chalcopyrite.

Additional secondary minerals include cerussite, 'limonite', native copper (P-CF.15.20), malachite, psilomelane and pyromorphite.

Lead - zinc veins elsewhere in the Caldbeck Fells have similar parageneses to the Driggith Vein.

5.2.3 Fluid inclusions in fluorite from Carrock East - West Vein.

An east - west crosscourse in Carrock Mine cuts and displaces the earlier north - south tungsten veins. In the No 0 Level the east - west vein consists mainly of dolomite and quartz, and has a few thin (<5mm) stringers of sphalerite, chalcopyrite and galena (H-CF.1.4). Pale blue - green fluorite in euhedral cubes was collected in situ from this vein (H-CF.1.1). This mineral grows in vugs in a vein breccia, the majority of brecciated fragments being of greisen or of hornfelsed Skiddaw Slate country rock, associated with the emplacement of the nearby Skiddaw Granite. Further east, the vein is found in Poddy Gill, and here, at outcrop, it is composed of quartz with 'limonite', pyromorphite and the uncommon lead molybdate, wulfenite.

Several fluorite cubes were taken for fluid inclusion analysis. In polished thick sections, the cubes show a small amount of colour zoning. Fluid inclusions are almost entirely related to structural zones in the fluorite rather than to growth zones and are thus regarded as pseudosecondary inclusions. The inclusions are predominantly two - phase (liquid + vapour) at room temperature with, in some specimens, one or two minute unidentifiable daughter phases, none of which dissolved at higher temperatures.

Data from this study are summarized in Table 5.1 and the instrumental methods used are described in the Appendix (II).

The low - temperature phase relations in the pure H_2O - NaCl system are shown in Fig.5.2. Because hydrohalite (and not ice) was always the last solid phase to dissolve, the minimum salinity of the inclusions (assuming pure H_2O - NaCl solutions) has to be greater than that at the eutectic of 23.3 equivalent wt% NaCl. The mean final solution point of hydrohalite of about -20°C (Table 5.1) corresponds to a salinity of approximately 24 equivalent wt% NaCl, assuming pure solutions. If other soluble salts are present (e.g. KCl or $CaCl_2$), they may have a minor effect on this value.

Homogenization data (Table 5.1) indicate filling temperatures (uncorrected for pressure) of about 120°C for the Carrock East - West Vein fluorite, in good agreement with Smith's (1973) homogenization temperature of 122.3°C for primary inclusions in vein quartz from the Sandbeds barytes vein. Shepherd (personal communication) reported homogenization temperatures of 120 - 150°C for inclusions in quartz from the Caldbeck Fells.

5.3 Keswick orefield

The largest of the Lake District orefields, the Keswick area contains copper (see Ch.4) and cobalt (see Ch.3) deposits in addition to lead, zinc and barytes mineralization. Age relations between the different vein types were summarized in Chapters 3 and 4, the generally north - south lead, zinc and barytes veins all being regarded as later than the chalcopyrite - pyrite - arsenopyrite veins. The orefield is centred to the west of Keswick, with isolated occurrences of lead - zinc mineralization reported from Loweswater and Buttermere farther west, and to the north - east of Keswick in Bannerdale and on the slopes of Blencathra (see Map 2).

Thornthwaite and Threlkeld Mines were the most important in the area. At Thornthwaite, several veins were worked and these may represent the northerly continuation of the Yewthwaite - Barrow vein system (Rastall, 1942; Eastwood,1959). Force Crag Mine differs from most in the area in that the vein has an east - west direction and has been worked extensively for barytes.

Throughout the orefield the host rocks are slates and sandstones of the Skiddaw Group. In the mines north - east of Keswick, such as Brundholme, Saddleback and Bannerdale, the host rocks are now chiastolite hornfels within the aureole of the Skiddaw Granite. Rastall (1942) reported cordierite replaced by mica in country rocks at Thornthwaite Mine.

Previous accounts of the mineralization and mining history of the area are in Postlethwaite (1913), Eastwood (1921; 1959), Shaw (1970), Rastall (1942), and Strens (1962).

Many of the mines are now inaccessible; however Force Crag recently reopened in the hope of mining lead, zinc and barytes. Thus, in this study, the Force Crag Vein has been dealt with in detail and fluid inclusion data are given for Force Crag sphalerite and Old Brandlehow fluorite.

5.3.1 Location and mineralogy of the Force Crag Vein

The ENE - WSW trending Force Crag Vein can be traced for about 4 km from the head of Coledale [NY 2020 2175] over Coledale Hause and westwards towards Crummock Water; although the vein appears to be barren towards the west (Eastwood, 1959) and has only been mined at its eastern end. In Coledale it was mined from a number of levels over a vertical extent of about 350 m (Plate 9). Force Crag Mine is the only one in the Keswick area to have been worked recently, and although it closed down in 1966 as a barytes mine, development and exploration took place during 1977 and 1978 with a view to reopening as a lead, zinc and barytes mine.

The vein dips steeply to the north at between 75° and the vertical and varies in width from 0.5 - 6 m. At high levels, the vein consists almost entirely of barytes with a little quartz and some manganese minerals. At lower levels, sphalerite, galena and a small amount of chalcopyrite occur in addition to dolomite and barytes. Here, the sulphides cement a vein breccia in which there is evidence of several periods of fracturing (see section 5.3.2), while barytes forms a solid rib up to a half metre thick with (in No 0 Level) a margin (20 - 40 mm) of galena on either side (H-K.70.5). In No 1 Level, the vein bifurcates into two ribs some three metres apart with a vein breccia of country rock cemented by sphalerite, dolomite and galena in the intervening ground.

The country rocks are shales and sandstones of the Kirk Stile Slates of the Skiddaw Group (Jackson, 1978). Some of the shales have undergone metamorphism and contain small spots of cordierite (Rastall, 1942). Shaw (1970) noted that in upper levels of the mine, where the country rock is black shale, the vein is barren or contains only small amounts of barytes. On the other hand, sandstones appear to have been favourable host rocks and the part of the vein where only barytes is present reaches its maximum development in these rocks. It would seem therefore, that barytes is best developed where the host rocks are competent, and the presence of barytes in lower levels of Force Crag Mine where the host rocks are shales and siltstones may be due either to possible hardening of the rocks as a consequence of metamorphism (Rastall, 1942), or be due to silicification of the brecciated host rocks in early stages of sulphide mineralization.

The Force Crag Vein has a fairly simple mineralogy, in common with the majority of lead - zinc veins in the area. However, unlike many of the other veins, quartz is not so abundant. The assemblage as determined from a study of hand specimens, thin and polished sections is quartz, chlorite, pyrite, marcasite, arsenopyrite, chalcopyrite, galena, bournonite, native antimony, galena, sphalerite, chalcedony, dolomite, chalybite, barytes, and psilomelane. In addition, fluorite (Rastall,1942) cerussite, (Postlethwaite,1913) and stoltzite (Greg and Lettsom, 1858) are also recorded from Force Crag although no precise locations are given.

In some specimens, sphalerite is strongly zoned (seen in polished thick sections prepared for fluid inclusion analysis) although the iron content does not exceed 5 mole% FeS (Table 5.8, 10 - 12). Sphalerite from other veins in the Keswick area also has low iron contents (Table 5.8, 13 - 18). A high iron content in a sphalerite from the Salt Well Mine may be due to an earlier period of mineralization (see Ch.4), because the intersection of one of the early copper veins (Manesty) and the Salt Well lead - zinc vein occurs in the mine.

Elsewhere in the Keswick area the assemblages are very similar to that at Force Crag, although the proportions of minerals vary widely from one vein to another, and most contain considerably less carbonate. Apart from the recorded occurrence of fluorite from Force Crag, this mineral is only found at Old Brandlehow Mine, where it is abundant at outcrop [NY 2455 2060] and in upper levels of the mine.

Intergrowths of bournonite and native antimony, (similar to those described from Driggith, 5.2.2) were identified (optically) in galena from Force Crag and also from Yewthwaite, Goldscope Lead, and Barrow Veins, although not from the Castle Nook Lead Vein. At Barrow Mine, in addition to minute intergrowths of bournonite and native antimony, two other phases occur as minute inclusions in galena

(P-K.12.1). Boulangerite ($Pb_5Sb_4S_{11}$) in minute (<5 µm) rounded, slightly fibrous grains has strong reflection pleochroism and strong anisotropy. It appears greenish grey against galena and, although similar in colour to bournonite, it has a slightly higher reflectance. Qualitative electron probe microanalysis was in agreement with the optical identification. The other inclusion found in galena occurs as small euhedral grains (<5 µm) with hexagonal forms. Appearing grey - white against galena with a slightly higher reflectance, it also has a greater polishing hardness. Quantitative microprobe analysis (Table 5.8, 19) identified the phase as ullmannite (NiSbS). Although cubic, ullmannite from this locality shows slight anomalous anisotropy (cf. Uytenbogaarde and Burke, 1971). In addition to these discrete inclusions, small ullmannite euhedra overgrow framboids of pyrite which appear to have acted as nuclei.

5.3.2 Paragenesis of the Force Crag Vein

The paragenesis of the major minerals can be best observed in hand specimen (Plate 9) and underground in the mine itself. There have been several periods of brecciation and mineralization (e.g. H-K.70.5, H-K.70.2.2, H-K.70.1.1).

Quartz is interpreted as the first mineral formed in the Force Crag Vein after initial fracturing. Along with minor chlorite it has altered the country rock of fine mudstones and siltstones (T-K.70.2.2). Massive pyrite was probably formed at this time and it occurs in aggregates up to 50 mm across. Polished sections show that pyrite occurs either as euhedral grains (< 200 µm) or as sheaves or laths (< 1mm), overgrown at the margin by marcasite and small grains of arsenopyrite (< 50 µm ; see Plate 24).

Brecciation took place after this early period of mineralization, and cementation of this breccia by quartz, chalcedony and carbonates occurred before further brecciation, generally forming larger fragments (H-K.70.11; H-K.70.2.2) than the first period of brecciation.

The main period of mineralization is characterized by the successive deposition of minerals in open voids. Some of the carbonate mineralization, which consists mostly of dolomite (possibly with some ankerite) and, more rarely chalybite (H-K.70.7), has not undergone brecciation and commonly overgrows fragments of country rock and brecciated quartz. Elsewhere, carbonate mineralization is also interpreted as being later because dolomite often overgrows sphalerite (H-K.70.1.1). Chalcopyrite, galena and sphalerite were deposited successively on the early carbonates or directly on to fragments of vein breccia (Plate 9). Chalcopyrite is present as small anhedral to subhedral grains, commonly associated with, and sometimes replaced by, galena. Bournonite is found as minute grains (1 - 2 μm) at the margin between chalcopyrite and galena. In addition it forms fine orientated intergrowths in galena in much the same way as those described from the Driggith Vein (although not nearly so widespread); and also occurs as minute irregular blebs (1 - 2 μm). Native antimony is present as similarly minute inclusions. Sphalerite, the most common ore mineral in the vein overgrows galena, in many instances as euhedra up to several centimetres, and is itself occasionally overgrown by large (<10 mm) cubes of pyrite. Chalcedony and quartz may infill voids.

In addition to infilling voids in the vein breccia (Plate 9), barytes associated with late galena occupies a fracture in the vein breccia in the No 0 and No 1 Levels. In the No 0 Level, away from this vein breccia, the country rocks are siltstones (H-K.70.5) and the vein itself has dolomite and galena (<20 mm) on either side of a central barytes vein (<0.5m). Psilomelane is a late mineral mainly restricted to upper levels in the Force Crag Mine.

The paragenetic relations are summarized in Fig.5.3.

5.3.3 Fluid inclusions in sphalerite from Force Crag

All the sphalerite analysed was collected in situ from the No 0 and No 1 Levels of the Force Crag Mine. Freezing and homogenization data are summarized in Table 5.2.

Only one definite primary inclusion was found (although several of those described as pseudosecondaries may in fact be primary); a relatively large (~0.4 mm) euhedral two - phase (liquid + vapour) inclusion with the vapour bubble forming less than 10% of the total volume at room temperature. The high homogenization temperature of this large inclusion (~169°C) compared to those obtained from inclusions identified as pseudosecondaries (mean 115°C) may indicate that at some time in the past there was a leakage of liquid from the inclusion. Despite this, it is used in Plate 26 to illustrate the stages in the freezing and heating analysis of fluid inclusions.

Suitable pseudosecondary and secondary inclusions for analysis are not abundant in Force Crag sphalerite. It was only possible to use those in iron - poor sphalerite where the phase changes could be adequately observed. Pseudosecondary inclusions are generally larger (<100 μm) than secondary inclusions (<50 μm) and the former are not definitely orientated along growth zones or late fractures. Secondary inclusions are arranged along fractures and cleavages in the sphalerite (Plate 25).

Pseudosecondary inclusions have salinities of about 24.0 equivalent wt% NaCl (using Fig.5.2) and a mean homogenization temperature of 115 °C. Secondary inclusions have salinities of about 24.3 equivalent wt% NaCl (Fig.5.2) and a mean homogenization temperature of 99.6 °C.

5.3.4 Fluid inclusions in fluorite from Old Brandlehow

Pale amber fluorite was collected from outcrop workings of the Old Brandlehow lead - zinc vein on the eastern side of Cat Bells, overlooking Derwentwater [NY 2455 2060] .

Two types of fluid inclusion are recognised. The first includes both irregular and multifaceted inclusions (<500 μm) with the vapour bubble occupying less than 10% of the total volume of the inclusion at room temperature. These are thought to be either primary or pseudosecondary. The second type of inclusion occurs along cleavages and fractures and is much smaller (<30 μm) than the other inclusions and considerably more common.

The pseudosecondary inclusions commonly contain daughter minerals (Plate 25); one inclusion had as many as five, none of which dissolved on heating (and therefore they were not halite, sylvite or any of the other salts soluble at relatively low temperatures). Most of the inclusions only contain three or four daughter minerals; one of these has a platy habit and a brownish red colour and may possibly be specularite or some other iron oxide or hydrated iron oxide, another has a rhombic habit and strong anisotropy and is possibly a carbonate. A cubic phase and an acicular phase could not be identified.

Some secondary inclusions have one or two small unidentifiable daughter minerals.

Primary or pseudosecondary inclusions have salinities of about 23.5 equivalent wt% NaCl and a mean homogenization temperature of 111 °C (Table 5.3). Secondary inclusions have high salinities (25.2

equivalent wt% NaCl - Fig.5.2) and homogenization temperatures of about 94°C. As a consequence of the high salinities, hydrohalite dissolved at temperatures greater than 0.1°C in some instances, where, according to Fig.5.2, it should not exist. Inclusions exhibiting such hydrohalite metastability were ignored in the construction of Table 5.3.

Shepherd (personal communication) reported homogenization temperatures of 100-120°C for inclusions in late quartz in the Keswick Mining Field.

5.4 Helvellyn orefield and other isolated lead - zinc veins

South of the Caldbeck Fells and southeast of the Keswick mining area (Map 1) is a relatively small mining field in which lies what was the most productive lead mine in the Lake District. From 1835 to 1961 the Greenside lead mine, west of Glenridding, produced some '200,000 tons of lead concentrates and about 1½ million oz. of silver' (Eastwood, 1959). The mine finally closed in 1962 when no worthwhile ore was left. Gough (1963,1965) gives comprehensive accounts of the mine from studies undertaken while the mine was still working. Further accounts of the mining history of Greenside and other lead - zinc veins in the Helvellyn orefield are in Eastwood (1921), Postlethwaite (1913), and Shaw (1970).

Only one of the other lead - zinc veins in the area, Hartsop Hall, was worked in this century. Eagle Crag, Wythburn (Helvellyn), Ruthwaite Lodge, Brown Cove, Myers Head (Low Hartsop) and Grasmere veins have been mined with varying degrees of success, mostly in the last century. The area also contains a few copper veins, probably earlier in age than the lead - zinc veins, as is the case elsewhere in the Lake District (see Ch.4 and Ch.6). Shaw (1970) noted that an east-west chalcopyrite - bearing vein in the Hartsop Hall Mine is displaced by the main lead - zinc vein. Other copper occurrences in the area are at Birkside Gill [NY 3300 1270] , a small trial to the west of Angle Tarn [NY 4095 1435] and two minor veins near Haweswater, the Burn Banks Vein and the Guerness Gill Vein (Eastwood in Dewey and Eastwood, 1925).

Lead - zinc occurrences in the Lake District which fall outside the three main lead - zinc orefields include small trials and workings in Silurian rocks near Staveley (Eastwood, 1921), minor lead - zinc mineralization associated with some of the West Cumbria haematite deposits, and lead - zinc veins at Tilberthwaite, near Coniston (described in Ch 6).

All of the lead - zinc veins in the Helvellyn orefield cut tuffs and lavas of the Borrowdale Volcanic Group, which in this area is thought to have a total thickness of 1350 - 2500 m (Gough, 1963). In deep levels of the Greenside Mine, where the Skiddaw Slates were found in the footwall, the mineralization became uneconomic and died out (Shaw, 1970). Most of the veins are controlled by east - west normal faults, although Greenside has a NNE - SSW direction and is associated for part of its length with a quartz porphyry dyke.

Previous work on the mineralization in the area, with the exception of Gough (1963,1965) has concentrated on the mining history of the veins rather than on the controls and nature of the lead and zinc deposits. There is little that can be added to Gough's (1963) account of the Greenside Mine, so this is compared to the mineralogy and paragenesis of other veins in the area. In addition, a limited study was made of fluid inclusions in fluorite from Hartsop Hall Mine.

5.4.1 Mineralogy and paragenesis of the Greenside Vein

Gough (1963) gave the mineralogy of Greenside Vein as quartz, galena , barytes, sphalerite, chalcopyrite, pyrite, marcasite, calcite, dolomite, ankerite, chlorite, witherite, tetrahedrite and bournonite. Material examined in the present study had much the same mineralogy, the only additional mineral found was native antimony as minute inclusions (<2 µm) in galena. In specimens from the main vein and stringers off it (H-H.4.1; H-H.4.3) and also from the mouth of the Glencoyne Adit (P-H.5.1), both native antimony and bournonite occur in very fine intergrowths with galena. Bournonite may show orientation along structural planes in galena (P-H.5.1) or occur as irregular inclusions (<5 µm). Sphalerite from Greenside contains about 3 mole% FeS (Table 5.8, 20 - 21).

Five stages of mineralization were recognised by Gough (1963), the first consists of the main period of ore mineralization with the deposition of carbonates, pyrite, sphalerite, quartz, galena, barytes, and chalcopyrite. The second stage is a remobilization of these early minerals in subsidiary fractures. Veins of calcite, barytes, and ankerite constitute the third, fourth and fifth stages respectively. In thin section (T-H.4.2), the country rock, a tuff, adjacent to a small vein of galena has been sericitized and silicified with some replacement by carbonates which form the margin of the vein (Plate 24). The vein itself shows platy quartz pseudomorphing barytes. Interstices between such plates are generally infilled by coarse - grained quartz or galena but the replaced plates themselves are now mostly chalcedony (Plate 24). Gough (1963) described this phenomenon and noted its occurrence in several other veins in the Lake District.

5.4.2 Mineralogy and paragenesis of other Helvellyn orefield veins

The Eagle Crag Vein has a very similar mineralogy to that at

Greenside, with inclusions of native antimony and bournonite throughout. Specimens from outcrop workings [NY 3545 1435] have small quantities of sulphides in a vein largely composed of quartz. Polished sections (P-H.2.1; P-77H.2.1) show fragmented country rock (tuff), partially altered by the later sulphides, containing small euhedra of pyrite and irregular grains of rutile. A margin of quartz surrounds the subangular fragments and the major sulphides were deposited in the order sphalerite, chalcopyrite, galena. Galena, in addition to bournonite (Plate 23) and native antimony, also contains orientated platelets (<5 µm) of an isotropic grey phase with lower reflectance than bournonite. This was tentatively identified as tetrahedrite (P-H.2.1).

In some specimens from Eagle Crag (P-77H.2.1) , tetrahedrite occurs in larger grains (<5mm). It has a silver content of about 1 wt% Ag and shows a variation in arsenic content between the centre and the margin of the grain (Table 5.8, 23 - 24). Formulae for central and marginal tetrahedrite respectively are $(Cu_{0.99},Ag_{0.01})_{10.3}(Fe_{0.42},Zn_{0.58})_{1.9}(Sb_{0.65},As_{0.35})_4S_{13}$ and $(Cu_{0.98},Ag_{0.02})_{10.3}(Fe_{0.25},Zn_{0.75})_{1.9}(Sb_{0.95},As_{0.05})_4S_{13}$ calculated on the basis of 13 sulphur atoms per molecule (Wuensch, 1964).

The mineralogy of the Hartsop Hall, Myers Head, Brown Cove and other mines is very similar to that described from the Greenside and Eagle Crag Veins. Almost all specimens examined contain minute inclusions of bournonite and native antimony in galena.

In addition to the minerals already mentioned, fluorite was reported from Hartsop Hall by Shaw (1970) who also mentioned wulfenite from a subsidiary vein at Hartsop Hall. Davidson and Thompson (1948) listed stibnite from St Sunday Crag.

5.4.3 Fluid inclusions in fluorite from Hartsop Hall

The Kingsbury Collection (British Museum - Natural History) contains several specimens of fluorite from Hartsop Hall Mine. One of these was used in this study. The specimen had several small (<3mm) pale yellow cubes overgrowing galena and chalcedony. Fluorite is not common at Hartsop Hall, although Shaw (1970) stated that this is the only locality for fluorite in the Lake District in a vein cutting rocks of the Borrowdale Volcanic Group.

No distinction was possible between primary and pseudosecondary inclusions as all of the inclusions are irregular and show no obvious relationship to growth zones. The two - phase (liquid + vapour) inclusions are generally smaller than 100 μm. Secondary inclusions are smaller and alligned along cleavages.

Primary or pseudosecondary inclusions have salinities of about 23.3 equivalent wt% NaCl and a mean homogenization temperature of 111 °C (Table 5.4). Secondary inclusions have similar salinities and a mean homogenization temperature of 102 °C.

Shepherd (personal communication) reports homogenization temperatures of 115 °C (average) in quartz from the Helvellyn Mining Field.

5.5 Discussion

5.5.1 Controls of mineralization

5.5.1.1 Structural controls

The general directions of the Lake District lead - zinc veins are east - west in the Caldbeck Fells and Helvellyn orefields, and north - south in the Keswick area. In all three orefields there are exceptions; for instance, the east - west Force Crag Vein in the Keswick area and the north - south Greenside Vein in the Helvellyn area. Near Glenridding, Gough (1963) recognised three groups of faults, each with a characteristic type of mineralization:-

(i) E - W to ENE - WSW normal faults (quartz - pyrite- dolomite - ankerite - calcite) ;

(ii) N - S, E - W and NE - SW normal faults (galena - sphalerite - quartz - barytes);

(iii) NNE - SSW and NW - SE faults (dolomite - barytes - quartz - calcite - haematite).

These were assigned Caledonian, Hercynian and post - Triassic ages respectively.

The Keswick and Helvellyn orefields lie in the core areas of large anticlinal structures; the Buttermere - Derwentwater anticline and the Ullswater anticline. No such structure is present in the Caldbeck Fells orefield. There, Thimmaiah (1956) suggested that the supposed overthrust mass of Skiddaw Slates may have acted as a barrier for the mineralizing solutions.

With the possible exception of the two Roughtongill veins, the lead - zinc veins were emplaced along normal faults.

5.5.1.2 Host rock controls

In all three orefields, host rock controls were extremely important for localizing mineralization both within a particular vein and also over the orefield as a whole. In the Skiddaw Slates, most of the lead - zinc mineralization occurs within black siltstones, mudstones and sandstones which have undergone varying degrees of metamorphism. At Carrock Mine, a cordierite - andalusite hornfels is the host rock for the lead - zinc mineralization, while those veins to the northeast of Keswick are in the outer part of the metamorphic aureole of the Skiddaw Granite, in chiastolite slates. West of Keswick, Rastall (1942) noted that several veins (including Force Crag and Thornthwaite) are in metamorphosed siltstones containing cordierite (sometimes pseudomorphed by mica). Outside these areas of metamorphism and hardening, the Skiddaw Slates are not, apparently, very favourable host rocks for the mineralization. On a more local scale Shaw (1970) noted that barytes in upper levels of the Force Crag Mine is best developed when the Skiddaw Group host rocks are sandstones rather than more friable shales.

In the Caldbeck Fells and Helvellyn lead - zinc orefields, the most favourable host rocks for mineralization are coarse silicified tuffs of the Eycott and Borrowdale Volcanic Groups. In addition, the junction between the Carrock Fell Igneous Complex and the volcanics, and the igneous rocks of the complex itself appear to be favourable hosts. The Greenside Vein may be controlled by a quartz - feldspar porphyry dyke, although the host rocks are mostly tuffs. Shaw (1970) noted that in deep levels of the Greenside Mine where slates of the Skiddaw Group are the host rock, the vein dies out and is uneconomic.

It appears that hard, competent host rocks are favourable for mineralization while shales and friable rocks are not mineralized to any extent unless hardened by metamorphism.

5.5.1.3 Depth controls

There is little evidence of either lateral zonation across the Lake District lead - zinc orefields, or of a depth zonation within individual veins. In general, the later a mineral is in the paragenetic sequence for a particular vein, the more abundant it is at higher levels in this vein. Examples of this are barytes at Force Crag and fluorite at Old Brandlehow.

5.5.1.4 Basement controls

While the underlying composite granite batholith (Bott, 1974) may have been important in the distribution of the early copper mineralization in the Lake District (see Chapter 9), it appears to have few direct links with the lead - zinc mineralization.

Emplacement of the batholithic granites was presumably responsible, however, for the metamorphism in the Keswick area and the consequent hardening of much of the shales and siltstones prior to fracturing and mineralization.

5.5.2 Age of the lead - zinc mineralization

The lead - zinc veins in the Keswick and Helvellyn areas and the east - west lead - zinc vein at Carrock Mine cut and displace earlier mineralization and must therefore be younger. Trotter (1944) suggested that all the veins are Tertiary in age, while Rastall (1942) assumed a Caledonian age for both the lead - zinc and the earlier copper mineralization. Dunham (1952) proposed a post - Carboniferous to pre - Mesozoic age. Barytes in veins and joints in the Carboniferous Limestone in the northern Lake District, and galena in the same host rock from the Hensingham borehole (Moorbath, 1962) indicates that some part of the lead - zinc mineralization is post - Carboniferous.

The results of lead isotope studies (Moorbath, 1962) and K - Ar isotopic age determinations (Ineson and Mitchell, 1974) on material from some of the lead - zinc veins are summarized in Table 5.5.

Ineson and Mitchell (1974) comment that Moorbath's (1962) data 'suffer from the usual uncertainties in the method used, namely that the system analyzed may not satisfy the single stage evolution criterion, or that the galenas might be contaminated by older lead from the country rocks'. Kanasewich (1968) has also cast doubts on some of Moorbath's interpretations.

In their K - Ar isotope study of wall - rock illites and chlorites, Ineson and Mitchell (1974) recognised several periods of lead - zinc mineralization. However, much of their interpretation has subsequently been regarded as erroneous. At Carrock Mine, for instance, they obtained isotopic ages of 197, 231 and 282 Ma and suggested that the oldest of these (282 Ma) relates to the tungsten veins while the later ages relate to the east - west lead - zinc vein. Shepherd et al., (1976) using muscovite from within the tungsten veins obtained K - Ar ages of c. 387 Ma.

Many of the mines, particularly in the Keswick area, have more than one type of vein (e.g. Goldscope, Brundholme, Castle Nook, Carrock) and as Ineson and Mitchell did much of their collecting from mine dumps, this may also have led to errors in their interpretation.

There is evidence also, of more than one period of mineralization within an individual vein. At Force Crag, the earliest mineralization of quartz, chlorite, pyrite and arsenopyrite underwent considerable brecciation before the main period of galena and sphalerite mineralization. Barytes mineralization is later still, after further movements along the vein. K - Ar ages of 365 and 367 Ma at Force Crag may represent the earliest mineralization, rather than the lead - zinc mineralization. Similarly, at Greenside the intrusion of a quartz - feldspar porphyry dyke prior to mineralization along the same fracture may be responsible for the earliest K - Ar age of 372 Ma.

Because the Skiddaw Slates were generally unfavourable host rocks for the lead - zinc mineralization except where previously hardened by metamorphism (resulting from emplacement of the granite batholith in the Keswick area), or where the wall - rocks along a fault had been silicified by earlier mineralization, many of the early K - Ar dates from the Keswick area may relate to these events rather than to the lead - zinc mineralization.

Bearing in mind the above observations and noting that some of the K - Ar results may be erroneous due to argon loss or incomplete isotopic resetting, a broad view has been taken of the isotopic evidence for ages of the lead - zinc mineralization.

Veins in the Keswick and Helvellyn areas have K - Ar dates which in general fall within the range 330 - 360 Ma. The Caldbeck Fells area, however, has K - Ar dates which are somewhat different and which fall into two distinct ranges of about 230 - 280 Ma and 180 - 190 Ma. The Caldbeck Fells differs from the Keswick and Helvellyn areas in having considerably more barytes present. The Sandbeds and Potts Ghyll Veins are composed almost entirely of barytes. K - Ar ages of 260 - 280 Ma for the Caldbeck Fells may represent this late barytes mineralization rather than the lead - zinc mineralization which is interpreted as being earlier and the same age as similar veins in the Keswick and Helvellyn areas. A K - Ar age of 272 Ma from Brundholme is also probably related to the late barytes mineralization. K - Ar ages of 230 - 260 Ma may represent minor remobilization or are possibly due to argon loss. The extensive secondary alteration in the Caldbeck Fells, particularly in the Roughtongill area is thought to be responsible for the 178 and 189 Ma K - Ar ages obtained from Roughtongill.

5.5.3 Temperatures and compositions of the ore fluids

Strens (1962), using the now discredited sphalerite geothermometer of Kullerud (1953) suggested minimum temperatures of formation of less than 140 °C for lead - zinc veins in the Keswick orefield, with the exception of Force Crag (>233 °C) and Thornthwaite (240 °C). He further proposed that early barytes in some of the veins had been pseudomorphed by quartz below 138 °C and considered late barytes to have formed at 50 - 80 °C. In the Helvellyn orefield, Gough (1963) proposed temperatures of 100 - 400°C for the Greenside Vein.

Results of fluid inclusion studies are given elsewhere in this chapter and generally indicate low temperatures of deposition. In correcting the homogenization temperatures, Strens'(1962) estimate for depth of cover of 1.5 km has been used. Assuming that hydrostatic pressures prevailed, a pressure of 150 bars is indicated (at 100 bars per kilometre). For homogenization temperatures of 100 - 150°C, the pressure correction is approximately + 10°C (Lemmlein and Klevtsov, 1961). Corrected results are summarized in Table 5.6.

Although most of the results in the present study are from fluorite, a late mineral in the paragenetic sequence, their agreement with Smith's (1973) and Shepherd's(personal communication) data and the similarly low temperatures for sphalerite may mean that there was little variation in temperature during the period of lead - zinc mineralization.

Solubility point determinations of hydrohalite indicate high salinities (>23 equivalent wt% NaCl) for all specimens analyzed. The low final melting points for ice (in all cases less than -22°C) suggest that $CaCl_2$ is also present in significant amounts, and low initial melting points (in all cases <-35°C) provide further evidence for this. Yanatieva (1946) found that in the H_2O - NaCl - $CaCl_2$ system, the ice, hydrohalite, liquid and vapour invariant point can shift to as low as -52°C. The presence of several daughter phases in inclusions, particularly those from Old Brandlehow, is further evidence of the complex nature of some of the mineralizing fluids. In general, secondary inclusions have lower temperatures and higher salinities than the primary and pseudosecondary inclusions. They possibly represent a later period of mineralization; at Force Crag, for instance, carbonates, galena and barytes were all deposited after sphalerite.

The slightly higher temperatures from the Caldbeck Fells orefield either represent genuinely higher temperatures of mineralization, or are an expression of relatively low overburden pressures compared to the Keswick and Helvellyn orefields.

5.5.4 Mineralogical and geochemical comparisons

There are mineralogical similarities between lead - zinc veins in the three orefields, in that similar species are present throughout. However, the proportions of the different minerals may vary considerably. Lead - zinc veins in the Keswick area contain a higher proportion of sphalerite to others elsewhere. Likewise, the Caldbeck Fells orefield has certain characteristics which distinguish it from the Keswick and Helvellyn areas. These are firstly, the relative abundance of copper minerals in the veins and secondly, the considerably greater amount of native antimony and bournonite intergrowths in galena compared to veins elsewhere. Possibly the most striking mineralogical contrast between the Caldbeck Fells and the other areas is its wealth of secondary alteration and oxidation products. Various theories have been put forward for this. Rastall (1942) suggested that the interaction of the Carrock Veins (containing arsenopyrite and apatite among other minerals) with the lead - zinc veins could have formed pyromorphite ($Pb_5Cl(PO_4)_3$) and mimetite ($Pb_5Cl(AsO_4)_3$). Mimetite (campylite) is only found at Drygill where an east - west lead vein is close to the northernmost extension of the Carrock Veins (see Map 3), and could have formed by alteration of arsenopyrite (from the Carrock Veins) by lead - bearing solutions. Similar alteration is envisaged in the formation of wulfenite ($PbMoO_4$) in the Carrock East - West lead - zinc vein at outcrop in Poddy Gill

[NY 3280 3275] , the only local source of molybdenum being in the molybdenite of the nearby Carrock tungsten veins. The widespread occurrence of pyromorphite may be explained by the alteration of apatite - bearing country rocks, particularly gabbros of the Carrock Fell Igneous Complex, in the vicinity of Roughtongill, by mineralizing fluids. In the Keswick orefield, Strens (1964) suggested that anglesite, cerussite and pyromorphite could be precipitated as primary minerals if their solubility products were reached and providing H_2S was absent.

Sphalerite from all three lead - zinc orefields has a low iron content, generally less than 5 mole% FeS. Zoning is common but adjacent zones commonly do not differ by more than 3 mole% FeS (Table 5.8). Sphalerite associated with the earlier chalcopyrite - pyrite - arsenopyrite mineralization has considerably higher iron contents (see Ch.4 and Ch.6)

El Shazly et al.(1957) and Gough (1963) analyzed some of the Lake District galenas for antimony and silver (among other elements); the results of these studies are summarized in Table 5.7. At Greenside, Gough (1963) found a direct variation in silver and antimony content across the vein, with the highest concentrations in the centre (500ppm Ag; 5000ppm Sb). The Sb/Ag ratio varied from 10 to 3, the greatest ratios being found at the highest concentrations. Gough found no variation of silver or antimony content in galena with depth, although galena in samples from stringers in the wall rock had lower silver and antimony values than those from the centre of the vein.

Neither Gough (1963) nor El Shazly et al.(1957) recorded any minor minerals in galena, although Gough did suggest that some of his high trace element analyses might be the result of inclusions. It is clear from the present study that in most of the Lake District lead - zinc veins , small inclusions in galena are ubiquitous. Intergrowths of bournonite and native antimony seem to be the most common inclusions, but others noted (some confirmed by electron probe microanalysis) include ullmannite and boulangerite (Barrow) and tetrahedrite (Eagle Crag). Many of these intergrowths are orientated along structural planes and are probably the result of exsolution from galena. This is particularly evident in specimens of galena from Driggith Vein and others from the Caldbeck Fells. Although several antimony - bearing minerals were found, only one silver - bearing phase (argentian tetrahedrite from Driggith) was discovered.

In studying the fine - scale intergrowths in galena it was necessary that the specimen had a perfect polish (see Appendix II). Indeed, if anything, it was preferable to 'overpolish' the galena and so remove any trace of scratches which could mask any minute phases, particularly those with a similar reflectance to galena.

Fleischer (1955) recorded that the maximum concentration of both silver and antimony in galena is 3%. For many years it was generally accepted (e.g. Goodchild,1881) that silver in argentiferous galenas was present as argentite (Ag_2S) solid - solution; however, the maximum solubility of Ag_2S in galena has been determined from synthetic studies (Van Hook, 1960) as 0.4 mole% Ag_2S at 700°C, and it is insignificant at temperatures below 500°C. Garwin (1973) found that the solubility of Sb_2S_3 in galena ranged from 3 ± 1 mole% Sb_2S_3 at 600°C to less than 2 ± 1 mole% Sb_2S_3 at 400°C.

Wernick (1960) synthesized compositions in the $AgSbS_2$ - PbS system and established that solid - solution was complete up to 50 mole% $AgSbS_2$ at 500°C. Amcoff (1976) in an extension of work by Wernick (1960) and Hoda and Chang (1975), found complete solid - solution between PbS and $AgSbS_2$ above 390 °C and determined that the solubility of $AgSbS_2$ in PbS is about 4 mole% at 300 °C and 2 mole% at 250 °C. Amcoff's (1976) diagram of the PbS - rich part of the PbS - $AgSbS_2$ system is given in Fig.5.4.

In the Lake District lead - zinc orefields inclusions in galena, often orientated, are common and consist predominantly of bournonite and native antimony. These undoubtedly account for the high antimony analyses of Gough (1963) and El Shazly et al. (1957), (Table 5.7). Only one silver - bearing phase, argentian tetrahedrite, has been found and it is not widely distributed. Because of this, it is unlikely to account for any of the silver trace element analyses. Silver and some antimony are assumed therefore to be in solid - solution with galena in the form $AgSbS_2$. The trace element analyses (Table 5.7) indicate a consistent excess of antimony over silver however, with most having Sb/Ag ratios of 3:1 or greater, up to 20:1. This is explained by the presence of inclusions of native antimony and sulphosalts such as bournonite.

It is possible that some of the intergrowths of bournonite and native antimony in galena, particularly those from Driggith (Plate 23) orientated along structural planes, are due to exsolution. Hydrothermal solutions containing lead and sulphur, and possibly also some antimony and silver could have gained additional antimony, silver and also copper and sulphur from the alteration of early minerals in the Driggith Vein such as argentian tetrahedrite and chalcopyrite (see Fig. 5.1). On cooling and crystallization of the $AgSbS_2$ - PbS solid solution, antimony would combine with silver in equivalent amounts. The remaining antimony could combine with any other remaining elements and be exsolved in the form of orientated lamellae. Such exsolution lamellae may develop either during rapid cooling and crystallization or during slow cooling, provided that the degree of supersaturation is low (Brett,1964). According to Brett (1964), the orientated exsolution of bournonite and native antimony from galena would be unstable since exsolution lamellae are only stable as long as the lamellar phase is in crystallographic continuity with the host phase. This may explain the limited occurrence of this particular intergrowth and the more widespread presence of larger unorientated blebs of bournonite and native antimony (Plate 23), which nevertheless are still regarded as being the result of exsolution.

5.5.5. Conclusions and comparison with similar deposits

The sequence of mineralization is similar in lead - zinc veins of all three orefields, namely:-

(i) quartz, chlorite, pyrite with minor arsenopyrite and carbonates;

(ii) quartz, chalcedony, sphalerite, chalcopyrite, galena, native antimony, antimony sulphosalts, barytes, fluorite and carbonates;

(iii) quartz, barytes, late carbonates and minor galena.

Individual veins show one or more of these stages which are commonly separated by brecciation.

It is possible that the early minerals formed at temperatures in excess of 150°C, but the main period of mineralization is characterized by temperatures in the region 120 - 150°C, according to evidence from fluid inclusions in fluorite. Late barytes could have been deposited subsequently at lower temperatures, perhaps below 100°C. Fluid inclusion evidence shows that the mineralizing fluids were highly saline brines with 23 - 24 equivalent wt% NaCl, and a significant $CaCl_2$ content.

Mineralogical and geochemical similarities between the veins in the three lead - zinc orefields are not readily explained by the isotopic ages (Ineson and Mitchell, 1974; Moorbath, 1962). Many interpretations are possible. Early fracturing with the deposition of quartz, chlorite and minor pyrite and arsenopyrite (as at Force Crag), probably correlates with some of the earliest K - Ar ages ranging from 360 - 380 Ma (Devonian). With the exception of Force Crag, the trend of these early - formed veins is predominantly N - S, or NNW - SSE. Following a further period of fracturing, and the formation of additional fissures (mainly NE - SW or E - W) as well as brecciation in some of the earlier ones, the main stage of lead - zinc (with or without barytes) mineralization was deposited in Upper Devonian - Dinantian times, fitting the K - Ar isotopic ages of 330 - 360 Ma. Much of the barytes in these veins was early and subsequently pseudomorphed by quartz. Later barytes mineralization with associated minor galena, particularly well developed in the Caldbeck Fells area, formed in Stephanian - Permian times (K - Ar ages 260 - 280 Ma) and the extensive alteration of the lead - zinc ores and also host rocks in the Roughtongill area appears to have occurred in Jurassic times (K - Ar ages 178 and 189 Ma).

The Lake District lead - zinc orefields have much in common with the larger orefield in the North Pennines which, although similar, has significant differences. The North Pennine orefield comprises two areas, the Alston and Askrigg Blocks, where Carboniferous rocks overlie stable areas of Palaeozoic strata and Caledonian granite bodies (Bott, 1967; Dunham et al., 1965).

In the Alston area, galena, sphalerite, barytes and fluorite mineralization occurs in fissure veins and replacement bodies cutting Lower Carboniferous sediments (Dunham, 1948) and the quartz dolerite Whin Sill (K - Ar isotopic age, 295 Ma; Fitch and Miller, 1967). These Carboniferous rocks unconformably overlie the top of the Weardale Granite (Dunham et al., 1965), dated by K - Ar methods at 360 ± 6 Ma (Moorbath and Dodson, 1961). Although the host rocks are older (Ordovician) in the Lake District, the lead - zinc ores occur either above or marginal to the underlying composite Lake District Caledonian granite batholith (Bott, 1974).

In the North Pennines, Dunham (1948) recognized a concentric mineral zoning, with a central fluorite zone (above the Weardale Granite) and a marginal barytes zone. In the Lake District there is no such obvious mineral zoning although the fluorite occurrences at Force Crag, Old Brandlehow, Carrock East - West and Hartsop Hall lie above the granite batholith.

Fluid inclusion studies on fluorite from the Alston area (Sawkins, 1966) indicate high temperatures (150 - 200°C) in the fluorite zone with lower temperatures (50 - 130°C) for mineralization in the outer barytes zone. Lake District fluorites indicate temperatures of 100 - 130°C, which appear to be more comparable to those obtained from Askrigg Block fluorites by Rogers (1978). Salinities of fluid inclusions in Lake District fluorites (23 - 24 equivalent wt% NaCl) are similar to those determined from Alston and Askrigg Block fluorites (Rogers, 1978; Sawkins, 1966).

The age of the lead - zinc mineralization in the North Pennines is generally assumed to be Permian (e.g. Rogers, 1978), although lead isotope dating by Moorbath (1962) suggests a Permo-Carboniferous age (280 ± 30 Ma). This is later than that for the main lead - zinc mineralization in the Lake District, but is similar to that proposed earlier for the late barytes (with minor galena) mineralization.

The basic mineralogy is similar in both the Lake District and North Pennine orefields, the major difference being the amount of fluorite, an uncommon mineral in the Lake District but abundant in the North Pennines. Galenas from the North Pennines have a similar micromineralogy to those from the Lake District, with numerous antimony sulphosalt inclusions (Vaughan and Ixer, in press). Iron contents in sphalerite from the Alston area are much higher than those from either the Lake District or from the Alston Block (Vaughan and Ixer, in press).

Possible origins for the Lake District lead - zinc mineralization are discussed in Chapter 9.

CHAPTER 6

COPPER MINERALIZATION IN THE CONISTON - GREENBURN - TILBERTHWAITE AREA

6.1 General

Copper mining in the southern part of the Lake District has been concentrated in an area of approximately sixteen square kilometres to the north of the village of Coniston (Map 4). Within this area are the minor copper trials near Seathwaite Tarn, discussed in Chapter 7, and the more productive Coniston, Tilberthwaite and Greenburn mining areas described in this chapter. Eastwood (in Dewey and Eastwood, 1925) suggested that the Coniston mines are the oldest in the north of England and may have been worked by the Romans.

All the copper mineralization is in the form of epigenetic fissure infillings. The veins are steeply dipping and cut tuffs and rhyolites of the Borrowdale Volcanic Group which strike in a northeasterly direction (see Map 4) and dip to the southeast at high angles. The copper veins in the Lake District generally have an east - west direction and, although the Seathwaite, Greenburn and Tilberthwaite veins conform to this general rule, those at Coniston have a northwest to southeast trend.

The veins have not been worked recently and the condition of those levels still open is such that collecting from them is hazardous. Surface exposures of veins are also poor and consequently the majority of specimens collected from the Coniston area are from mine dumps. Chalcopyrite, pyrite and arsenopyrite are the dominant ore minerals in the veins, with gangue minerals generally quartz, chlorite, and calcite or dolomite. In addition to these chalcopyrite - pyrite - arsenopyrite veins, there are several small galena and sphalerite - bearing veins. Cobalt and nickel mineralization at Coniston is described in Chapter 8.

The mining history of the area is not as well documented as for the northern Lake District, but Postlethwaite (1913), Eastwood (in Dewey and Eastwood, 1925), and Shaw (1970) give detailed accounts. The most productive veins were the Paddy End and Bonser Veins, all the others being somewhat minor by comparison. In fact, Shaw (1970) states that while the Coniston area contributed about three quarters of the total Lake District production of copper, the Bonser Vein produced about half of this total.

Little previous work has been done on the mineralization, but Wheatley (1971) and more recently Dagger (1977) and Firman (1978b) have given generalized descriptions, concentrating mainly on the genesis of the ores rather than their mineralogy. Mitchell (1940, 1963) and Hartley (1932) have mapped parts of the area.

In addition to the main area, centred on Coniston Mines (Plate 10), deposits of similar type have been worked to a minor extent at Cockley Beck [NY 0140 2470] and at Ulpha [SD 1870 9250] in rocks of the Borrowdale Volcanic Group. Further south in Furness, Rose and Dunham (1977) report chalcopyrite and chalcocite in the haematite ores in the Carboniferous Limestone at Anty Cross, near Dalton.

6.2 Bonser Vein

6.2.1 Location and general details

The Bonser Vein was the largest and richest of the Coniston copper veins and is thought to be continuous with the Thriddle Vein which was worked beneath Levers Water. It cuts Tilberthwaite Tuffs and the Paddy End Rhyolite and, while the vein is not entirely barren in the tuffs as suggested by Mitchell (1940), the most favourable host rock is the rhyolite, and the vein appears to die out when meeting strongly cleaved tuffs at its eastern end.

Near Levers Water, the Bonser Vein trends WNW - ESE but this changes slightly to nearly east - west, east of Red Dell Beck. At outcrop the vein dips steeply to the south but Shaw (1970) states that at depth, the vein dips at shallower angles to the north. In places the vein was several metres wide and carried, according to Kendall (1884), 'chalcopyrite equal to a continuous solid rib 8¼ inches wide'.

The vein has been stoped out over a length of about 0.5 kilometres and to a depth of 375 metres from the surface. Mining, which reached its peak in the last century, came to a halt due to the increasing amount of magnetite in the ore resulting in difficulties in separation. The mine is now flooded up to the Deep Level, but part is still accessible by way of the Deep Level crosscut adit. A small part of the vein remaining in the roof of the Deep Level is approximately a metre in width and is mostly barren with quartz and irregular veinlets of chlorite, and few stringers of chalcopyrite.

The majority of specimens collected from the Bonser Vein were obtained from a spoil tip north of the Youth Hostel [SD 2885 9870], which appears to have been used as a dump for magnetite - rich ore which was difficult to process. Other specimens were obtained from tips around the Old Shaft [SD 2880 9900].

6.2.2 Mineralogy of the Bonser Vein

Although the mineralogy of the Bonser Vein is basically the same as that of other copper veins in the Coniston area, and indeed the rest of the Lake District, the assemblage has certain distinctive characteristics. Wheatley (1971) and Dagger (1977) have previously described the mineralogy of the Coniston veins.

The mineral assemblage as determined in this work from a study of hand specimens and thin and polished sections is quartz, chlorite, calcite, dolomite, stilpnomelane, magnetite, pyrrhotine, pyrite, marcasite, native bismuth, bismuthinite, laitakarite, joseite, arsenopyrite, chalcopyrite, sphalerite, galena and cosalite.

Magnetite occurs in only one other vein in the Coniston area, the Long Crag Vein, which is described later in this chapter. Some Bonser Vein specimens are composed almost entirely of magnetite (H-78Co.2.A; H-Co.2.14; H-77Co.2.B), and Shaw (1959) stated that the amount of magnetite in the ore increased with depth. An analysis of a magnetite specimen by Wheatley (1972) shows it to contain approximately 0.2 wt% manganese and trace quantities of titanium, vanadium, and tin.

Native bismuth and bismuthinite are abundant in the Bonser Vein, compared to their more limited occurrence in other copper veins in the Coniston and Keswick areas. In some specimens (e.g. H-78Co.2.C) they are clearly visible in hand specimen and are most common in material derived from magnetite - rich parts of the vein. Examination of polished sections (P-78Co.2.C; P-Co.2.11.iv) showed that in addition to native bismuth and bismuthinite another phase was present. In reflected light, this phase has a slightly higher reflectance than bismuthinite, although considerably lower than native bismuth. It appears pale grey against native bismuth (cream - white) and bismuthinite (grey), and has a strong bireflectance in oil; the mineral also has a distinct anisotropy (although not as strong as for bismuthinite) with rotation tints varying from cream - buff to dark brown. It was not possible to identify the phase by X - ray diffraction owing to the small grain size, but electron probe microanalysis demonstrated the presence of bismuth, selenium, sulphur and minor tellurium (Table 6.1, 12 - 14, 16, 17). A small (<20 µm) tellurium - rich area was found when examining the specimen on the microprobe, containing 13.9 wt% Te (Table 6.1, 15). This phase is optically indistinguishable from the selenium - rich phase.

In discussing the bismuth sulphotellurides and bismuth sulphoselenides it is usual to refer to the metal / non - metal ratio A:X, where A is Bi, Pb, Sb, and X is Te, Se, S (Godovikov et al., 1971). In the case of the bismuth sulphoselenide from Coniston, the A:X ratio is very nearly 4:3 (Table 6.1) with A entirely bismuth and X, selenium, sulphur, and tellurium. The analysis (Table 6.1, 15) which had a high tellurium content has an A:X ratio of about 3.5:3 which would seem to indicate a slightly bismuth - deficient joseite. It is similar, in fact, to an analysis by Peacock (1941) of a phase which he classified as joseite and which contained 79.2 wt% Bi; 15.9 wt% Te; 3.2 wt% S; and 1.5 wt% Se.

The bismuth sulphoselenide shows a variable composition between the compositional limits 8.6 - 13.2 wt% selenium, corresponding to formulae of $Bi_{3.97}(S_{1.88}Se_{1.07}Te_{0.05})_3$ and $Bi_{4.08}(S_{1.17}Se_{1.74}Te_{0.09})_3$ respectively (Table 6.1, 12, 13). The A:X ratio is fairly constant at about 4:3. This is consistent with the mineral described by Berry and Thompson (1962) as 'selenjoseite', which Berry (1963) suggested should be dropped in favour of laitakarite, previously named and described by Vorma (1960) from Orijarvi, Finland.

The analysis given by Vorma (1960); 78.3 wt% Bi; 15.5 wt% Se; 3.3 wt% S, is close to that of analysis 13 (Table 6.1) and consistent with a chemical formula of Bi_4Se_2S or $Bi_4(Se,S)_3$. The other analyses differ somewhat from this. However, the analyses from the Bonser Vein are closer to those of laitakarite than the only other similar mineral reported, namely ikunolite (Kato, 1959), which has a S:Se ratio of 92:8 and contains only a few weight percent. selenium.

Vorma (1960) suggested that the selenium end - member of the mineral $Bi_4(Se,S)_3$ be named laitakarite and the sulphur - rich member as ikunolite. No analyses falling within these two extremes have been previously reported, nor has any tellurium content been mentioned before. The compositional variation among the bismuth sulphotellurides and bismuth sulphoselenides as a whole is large and is explained by the fact that appreciable quantities of lead and selenium can isomorphously substitute for bismuth and sulphur / tellurium with only minor structural change (Clarke, 1974).

Comparison of X - ray data for pyrrhotine from the Bonser Vein with that of Morimoto et al. (1975) showed that it is monoclinic, and following Wuensch's (1963) nomenclature, of type 2A, 2B, 4C. The composition (~$Fe_{0.88}S$; Table 6.1, 1 - 2) determined by electron probe microanalysis confirms that the pyrrhotine is monoclinic (Scott and Kissin, 1973; Kissin, 1974). The absence of any hexagonal pyrrhotine in exsolution was verified by etching tests.

Arsenopyrite in small euhedral grains in pyrrhotine (P-78Co. 2.A) had about 44 wt% As when analyzed by electron microprobe using Kretschmar's Asp 200 standard (Table 6.1, 6 - 7). Similar analyses were obtained from a different specimen (P-Co.2.5) with larger grains of arsenopyrite which have a slightly arsenic - rich core (Table 6.1, 8 - 9). Another specimen (P-77Co.2.E) had a much higher arsenic content, although again with an arsenic - rich core (Table 6.1, 10 - 11).

Sphalerite from the Bonser Vein, coexisting with pyrrhotine in P-78Co.2.A. has between 13.6 and 14.4 mole% FeS (Table 6.1, 13 - 15).

The presence of stilpnomelane, a complex hydrated alumino-silicate of magnesium and iron, first recorded from the Bonser Vein by Russell (1925), was confirmed in the present work. Although detailed analysis was not attempted, it was identified by its optical characteristics and also by X - ray diffraction. In thin section (T-77Co.2.B; T-Co.2.11) it is strongly pleochroic in shades of brown, and characteristically it occurs as fine acicular crystals overgrowing chlorite or as interstitial growths in magnetite.

Cosalite ($Pb_{1.9}Bi_{2.0}S_5$ - Table 6.1, 18) was identified in one polished section (P-Co.2.21) where it occurs as an inclusion in galena. It is strongly pleochroic and in one orientation has nearly the same reflectance as galena.

6.2.3 Paragenesis of the Bonser Vein

Previous paragenetic interpretations on the basis of an incomplete mineralogy have been given by Wheatley (1972) and Dagger (1977). These authors have also not distinguished between the various veins at Coniston and refer to no particular mine or vein.

The interpretation of the paragenetic sequence for the Bonser Vein (summarized in Fig.6.1) proved difficult, due mainly to the lack of large representative ore specimens and the fact that the part of the vein examined in situ in the Deep Level of the mine contained little ore mineralization.

Fracturing and brecciation of the country rocks adjacent to the vein appears to be less than that associated with many veins in the Lake District and especially the nearby Paddy End Vein. Angular fragments of tuffaceous country rock are included in the vein, although thin sections (T-Co.2.11) show them to be little altered with only minor silicification present in addition to the chloritization produced by the regional metamorphism. One specimen (H-77Co.2.E) has euhedral arsenopyrite penetrating a cleaved tuff which has been extensively altered by chlorite and quartz.

In hand specimen, many of the textures suggest that the vein minerals were deposited successively in open voids (H-Co.2.15). Only minor fracturing has occurred during, and possibly after, mineralization.

Of the gangue minerals, quartz is the major phase and was deposited periodically throughout the paragenetic sequence. Much of it is massive milky vein quartz, but some is euhedral (Plate 27). Chlorite is abundant and mostly early, forming botryoidal masses (T-Co.2.11) and some smaller acicular grains. Stilpnomelane in fine acicular crystals (<200 μm) and matted aggregates (<1 mm), overgrows chlorite (T-Co.2.11; Plate 11) and also occurs in interstitial areas in magnetite (T-77Co. 2.B). Calcite and dolomite are also considered to be mainly early, with dolomite the later of the two minerals. A later carbonate stage infills vugs in the quartz vein.

Magnetite was the first ore mineral deposited and it shows two habits. One is as lamellar, and in some instances, radiating grains (<2 mm) with subhedral habit (Plates 10 and 27) commonly associated with quartz, calcite and chlorite (P-78Co.2.A); the other as a more massive development (e.g.H-77Co.2.A; P-Co.2.1) which is anhedral to subhedral. This uncharacteristic lack of crystal form shown by magnetite may be explained by interpreting the textures as magnetite pseudomorphing an earlier phase such as haematite. Magnetite occurs as isolated inclusions in most of the other ore minerals.

Arsenopyrite occurs in large, fractured euhedral or subhedral grains. Early arsenopyrite in euhedral, commonly zoned rhombs

(<1 mm), has in some instances penetrated cleaved and altered tuffs (P-77Co.2.E). Elsewhere it is associated with chalcopyrite (e.g.P-Co. 2.5) and sphalerite (e.g.P-77Co.2.M). These later sulphides commonly infill fractures in the larger grains (e.g. P-77Co.2.G). Small (<20 μm) rhombs of arsenopyrite (P-78Co.2.A) included in pyrrhotine may have formed simultaneously.

Pyrrhotine is not common in the ore - bearing material collected from the Bonser Vein, with only one specimen having any great quantity of the mineral (P-78Co.2.A). In this specimen it is later than magnetite and contains inclusions of sphalerite (Plate 11), minor chalcopyrite and arsenopyrite. Pyrrhotine itself occurs as large anhedral grains (<100 μm), in aggregates forming areas up to 10 mm across. It has subsequently been replaced by marcasite and pyrite.

Sphalerite inclusions in pyrrhotine (<50 μm) are generally associated with chalcopyrite. In some specimens the chalcopyrite forms a thin (<20 μm) margin between sphalerite and pyrrhotine. Sphalerite and chalcopyrite are also present along fractures in earlier minerals. One specimen (P-77Co.2.C) has subhedral pyrite partially replaced by banded sphalerite and chalcopyrite. Sphalerite does not contain chalcopyrite in exsolution but in some specimens has been replaced by minute blebs of chalcopyrite along grain boundaries. Chalcopyrite, always anhedral, commonly occurs inlarge masses and is found in association with both early and late minerals.

The position of pyrite in the paragenetic sequence is problematical. It occurs with both pyrrhotine and magnetite (P-78Co.2.A) but is certainly later than both these minerals. Along with marcasite it replaces pyrrhotine to a small extent, but also forms aggregates which appear to replace calcite; some of these exhibit a skeletal development along calcite cleavages (Plate 27). Botryoidal chlorite

(P-Co.2.11.ii) is overgrown by pyrite euhedra (<1 mm); larger pyrite euhedra (<2-3 mm), commonly with growth zoning, are found as inclusions in quartz (P-78Co.2.C.ii). Pyrite therefore, was deposited throughout much of the main period of ore formation.

Bismuthinite forms inclusions in pyrite and occurs along fractures in quartz. In the latter instance, the grain size may be quite coarse (<1 mm) and aggregates form extensive areas (P-78Co.2.C.i) commonly associated with chlorite (Plate 12), chalcopyrite and native bismuth. An acicular silicate, probably chlorite, grows along bismuthinite cleavage planes in some specimens (Plate 27).

Bismuthinite has been replaced by the bismuth sulphoselenide, laitakarite (Plate 27), which occurs as aggregates (<100 μm) of small anhedral grains (<10 μm), with a few minute and optically indistinguishable inclusions of joseite. A mineral with similar optical properties to laitakarite occurs as very fine grains (<1 μm by 5 μm) orientated along bismuthinite's cleavage direction. This is interpreted as an exsolution texture.

Native bismuth is less common than bismuthinite as inclusions in pyrite and is generally interstitial (e.g.P-78Co.2.C.ii), forming areas up to several millimetres across. It is associated with both bismuthinite and laitakarite (Plate 27).

Galena was the last sulphide formed and it occurs in association with late chalcopyrite and sphalerite (P-77Co.2.M; P-77Co.2.F), and may replace pyrite (Plate 28). One specimen (P-Co.2.21) has galena with minute inclusions of bismuth and also larger (<100 μm) inclusions of cosalite.

In summary, it may be said that the mineralization was largely continuous, with minimal fracturing within the vein during mineralization and, with the exception of magnetite pseudomorphing haematite, and pyrite and marcasite replacing pyrrhotine, relatively minor amounts of replacement.

6.2.4 Discussion

K - Ar isotopic age determinations on wall rock chlorites and illites by Ineson and Mitchell (1974) gave an age of ~383 Ma for a spoil heap sample from the Bonser Vein. For the Coniston area as a whole, they obtained a mean age of 388 Ma and a range of 367 - 402 Ma (from five samples), and suggested that the youngest of these values may be spurious because of minor argon loss. This is interpreted to suggest that emplacement or remobilization of the ores into their present position occurred at some time in the Devonian. A Devonian age for the mineralization is in agreement with field evidence, which shows that the veins were unaffected either by folding or regional metamorphism (since no remobilization of the ores has occurred) resulting from the Caledonian earth movements.

The age of about 383 Ma for the Bonser Vein is close to the Lower Devonian ages obtained for most of the Lake District granites by Brown et al. (1964). The nearest exposed granite is the Eskdale Granite which lies some 8 km to the northwest of the Coniston veins (see Map 1). This has been dated at 429 ± 9 Ma (Caradoc) by Rundle (1979). Bott (1974), in an interpretation of gravity data, suggested that the exposed granites were connected at depth, however, Rundle (1979) argues that the Eskdale Granite was a separate and much earlier intrusion, and that the main batholithic granite was emplaced in end - Silurian times beneath the Eskdale mass. Unlike the early mineralization elsewhere in the Lake District (see Chapter 3 and Chapter 4), the Coniston veins do not lie above the roof region of Bott's (1974) proposed granite batholith, but above the southern margin.

If mineralization took place during the Devonian, then an estimated depth of cover would be 7 - 9 km, made up of:-

Devonian	0 - 2 km	(estimated);
Silurian	6.0 km	(Rickards, 1978);
Ordovician	1.0 km	(Mitchell, 1940).

If folding of some of the older rocks is taken into account, the true depth might approximate the higher estimate (i.e. 9 km).

The geothermal gradient in the Earth's crust varies from approximately 10°C / km in stable cratonic regions, to about 50°C / km in active orogenic belts (Smith, 1963). A mean or 'normal' gradient is generally taken to be between 20°C / km and 35°C / km. Miyashiro (1973) suggested that the temperature gradient in an area during low grade regional metamorphism (as suffered by the Lake District during the Caledonian orogeny) is at least 25°C / km. Estimates of wall - rock temperatures for the Bonser Vein vary from 175 - 225°C (at 7 km and 9 km respectively) assuming a geothermal gradient of 25°C / km; and 245 - 315°C (at 7 km and 9 km respectively) with a geothermal gradient of 35°C / km. It is possible that even higher temperatures existed during the early stages of mineralization due to the additional temperature gradient established by the recently emplaced nearby granite bodies.

Combining the paragenetic interpretation with published thermochemical data for coexisting minerals, an estimate can be made of conditions in the Bonser Vein during mineralization. The stability of some individual minerals in the assemblage is important. Cosalite, which is a late mineral closely associated with galena in the Bonser

Vein, has a stability limit of 425 °C (Craig, 1967). Native bismuth shows no textural evidence of crystallization from a melt, nor of subsequent melting. From this it is concluded that native bismuth probably formed below its melting point of 271.5 °C. Klement et al. (1963) reported a lowering of melting point of 7.6 °C per kilobar of total pressure, and consequently a lower temperature may be considered. If a hydrostatic load (100 bars / km) alone is assumed, then the pressure (using previous estimates of depth) would be 800 - 900 bars; if a purely lithostatic load is assumed (250 bars / km) then the pressure would be 2000 - 2250 bars giving maximum temperatures of ~265 °C and ~255 °C respectively for the formation of native bismuth in the Bonser Vein.

Monoclinic pyrrhotine cannot have formed above 248 °C (Scott and Kissin, 1973) unless it has inverted from a higher temperature hexagonal pyrrhotine. Such an inversion is thought improbable in this instance since the monoclinic pyrrhotine is homogeneous.

Sphalerite inclusions in monoclinic pyrrhotine are in physical contact with it and therefore equilibrium may be assumed (Barnes and Kullerud, 1961). It is possible for sphalerite having compositions of 13.6 - 14.4 mole% FeS (as in the Bonser Vein; Table 6.1, 3 - 5) to be in equilibrium with monoclinic pyrrhotine at temperatures of less than 248 - 245 °C, according to the speculative low - temperature phase diagram (Fig.6.2) of Scott and Kissin (1973). Above 250 °C , pyrite, rather than pyrrhotine would be expected in the assemblage, and, in the Bonser Vein, pyrite is not observed at this stage.

Further information on temperatures and sulphur activities at the time of ore deposition was obtained using Kretschmar and Scott's (1976) arsenopyrite geothermometer. Bonser Vein arsenopyrites were analyzed using an arsenopyrite standard of proven homogeneity (Kretschmar's Asp 200 standard). Different specimens showed slight compositional variation, none however was found to contain cobalt or any other detectable impurity which might affect the application of the geothermometer. Two generations of arsenopyrite were determined from the analyses. Higher arsenic content arsenopyrite analyses (Table 6.1, 10 - 11) are from euhedral grains which have penetrated the highly altered (silicified) chloritized country rock of cleaved tuffs (P-77Co.2.E) and are interpreted as being early. Lower arsenic content arsenopyrites occur in pyrrhotine (P-78Co.2.A), and in association with chalcopyrite (P-Co.2.5), and are probably slightly later. Both early and late arsenopyrites are compositionally zoned with a higher arsenic content in the core. The small arsenopyrite euhedra (<20 µm) enclosed in pyrrhotine are not zoned; the two analyses (Table 6.1, 6 - 7) from different grains illustrate only a slight compositional variation. Kretschmar and Scott's (1976) arsenopyrite geothermometer should only be applied when the arsenopyrite was formed in equilibrium with an aS_2 - dependent assemblage. The early arsenopyrite may not have been in equilibrium with such an assemblage, but the small arsenopyrite euhedra in pyrrhotine almost certainly fulfil these conditions.

The relevant arsenopyrite sulphidation curves were plotted on a sulphur activity against temperature diagram (Fig.6.3), extrapolating Kretschmar and Scott's (1976) curves to somewhat lower temperatures than 300°C. A number of other sulphidation curves were also plotted on this diagram and, in addition, the magnetite / haematite stability fields were plotted at both 350°C and 400°C, with their respective oxygen activities. In order to obtain estimates of oxygen activity in the vein, a sulphur activity against oxygen activity diagram was constructed (Fig.6.4) in a manner similar to that described by Holland (1959, 1965) to show the stability fields for various mineral species in the assemblage at temperatures of 250 °C and 350 °C. Thermodynamic data have also been taken from Barton and Skinner (1967) using sulphidation curves that they had obtained from several sources.

There is no definite 'fixed point' on the aS_2 - temperature diagram (Fig.6.3) for the early magnetite (haematite) mineralization in the Bonser Vein. Early arsenopyrite with 34.1 at% As in the core cannot have formed below temperatures of about 330 °C at $aS_2 \sim 10^{-13}$atm (see Fig.6.3). The outer zone could have formed above 290 °C at $aS_2 \sim 10^{-14}$ atm. However, some doubt exists as to whether the early arsenopyrite is from an aS_2 - buffered assemblage, and so these temperatures must be regarded with some degree of caution. Paragenetic relations of this early arsenopyrite are unclear but it is probably later than the formation of magnetite and haematite (now totally pseudomorphed by magnetite). At 350 °C haematite is a stable phase only with $aO_2 > 10^{-25.4}$ atm (see Fig.6.3) and magnetite could pseudomorph haematite (as observed in the Bonser Vein) provided that either the aO_2 dropped below $10^{-25.4}$atm at 350 °C or below $10^{-32.4}$atm at 250 °C (see Fig.6.4). Many interpretations are possible, but despite the problems of 'fixing' the early mineralization, it is thought that area A (Fig.6.4) and areas 1 and 2 (Fig.6.3) may provide reasonable estimates of formation conditions. It is possible that the early haemátite mineralization formed in an environment with considerably lower sulphur activities than those shown on the diagrams.

The early gangue minerals, quartz, chlorite, and stilpnomelane were probably deposited at about the same time as magnetite formation. Eggleton and Chappell (1976) worked on stilpnomelanes from metal sulphide deposits associated with magnetite, chlorite, quartz, pyrrhotine, and chalcopyrite (similar in fact to the Bonser Vein assemblage). They hoped that primary variation in the Fe^{3+}/Fe^{2+} ratio might be related to the associated mineralogy and indirectly to oxygen activity, inferred from such mineral pairs as pyrite - pyrrhotine or quartz - magnetite. However, the Fe^{3+}/Fe^{2+} ratio was related to grain size and the length of time the material had been exposed to the atmosphere. Therefore, it would seem that stilpnomelane from dump material is of little use in determining oxygen activity at the time of mineralization.

Barton et al. (1977) in a study on mineralization from Creede Mining District, Colorado, suggested that the presence of pyrite, haematite and chlorite as major constituents of the ores and the absence of magnetite, was evidence that chlorite had usurped the magnetite stability field. However, the specific position of the reaction curves for chlorite is conjectural due to a lack of thermodynamic data. Stilpnomelane and chlorite from the Bonser Vein are therefore of little use in determining or restricting conditions for the mineralization. The gangue carbonates, calcite and dolomite, can provide useful information only if several assumptions are made.

For the main stage of sulphide mineralization, the area of interest in the aS_2 - temperature diagram (Fig.6.3) is limited, by the absence of the assemblage bornite - pyrite, to the chalcopyrite stability field. This area is further restricted by the presence of pyrrhotine, magnetite and quartz in the assemblage rather than fayalite (see Fig.6.3). Monoclinic pyrrhotine in the assemblage with late arsenopyrite, magnetite, sphalerite, chalcopyrite, quartz, calcite /

dolomite and chlorite, cannot have formed above 250°C (Kissin, 1974). Sphalerite with compositions of 13.6 - 14.4 mole% FeS may have formed in equilibrium with monoclinic pyrrhotine at temperatures of less than 245 - 248°C (Scott and Kissin, 1973). It is assumed that the small arsenopyrite euhedra enclosed in pyrrhotine were formed simultaneously along with some of the sphalerite and chalcopyrite in the assemblage. Area 3 (Fig.6.3) is thought to best represent conditions for the deposition of minerals in this stage of the paragenetic sequence, with T ~ 240°C and $aS_2 \sim 10^{-16}$atm. Lower temperatures and therefore lower sulphur activities (due to the shape of the arsenopyrite 31.3 at% As and 32.1 at% As stability curves) are also possible however, but are thought unlikely, there being no evidence for any significant deviation from the curve indicated by areas 1 - 4 (Fig.6.3).

Stability fields at 250°C have been constructed on the $aS_2 - aO_2$ diagram (Fig.6.4.) and it now remains to fit the data obtained from the aS_2 - temperature diagram (Fig.6.3) to this. The presence of calcite and/or dolomite is now of interest. Holland (1965) suggested that at about 250°C the activity of CO_2 in ore - forming fluids probably lies between 10^2 and 10^{-2}atm. The calcite / anhydrite stability curve for $aCO_2 = 1$ atm has been plotted on Fig.6.4. Silica could not have been present in excess at this stage of carbonate deposition since if it were, then the silicate would form and this is not observed. Assuming $aCO_2 \sim 1$ atm, and T ~ 240 - 250°C, the area of interest must lie in the calcite stability field as anhydrite is not observed at any stage in the paragenetic sequence in the Bonser Vein. Magnetite, albeit a somewhat refractory mineral, shows very little evidence of having been replaced by pyrrhotine and this is taken to indicate that the composition of the mineral - bearing fluids during the deposition of pyrrhotine was not far removed from the magnetite stability field. Area B (Fig.6.4) has therefore been positioned to overlap slightly the magnetite stability field and incorporate the arsenopyrite (31.3 at% As and 32.1 at% As), pyrrhotine and calcite stability fields. Oxygen activity at T ~ 240 °C and $aS_2 \sim 10^{-16}$atm is between $aO_2 \sim 10^{-38}$atm and $aO_2 \sim 10^{-44}$atm with $aCO_2 \sim 1$ atm.

Although bismuth and bismuthinite are commonly associated with magnetite, they are thought to be later and were probably formed at about the same time as pyrite. There is no evidence of their being associated with pyrrhotine, consequently the proposed path (Areas 1 - 4 Fig.6.3) illustrating the changes in fluid composition during mineralization, does not include the bismuth - bismuthinite - pyrite - pyrrhotine invariant point at 235°C and $aS_2 \sim 10^{-14}$atm. Pyrrhotine has been replaced by marcasite and pyrite and this must have taken place when the sulphur activity increased or the temperature decreased such that the pyrite / pyrrhotine sulphidation curve was crossed and pyrrhotine was no longer stable. Area 4 (Fig.6.3), at T ~ 200°C and $aS_2 \sim 10^{-15}$atm, incorporating the bismuth / bismuthinite sulphidation curve in the pyrite stability field may represent the conditions of the later mineralization. The bismuth sulphoselenide, laitakarite, and bismuth sulphotelluride, joseite, may have formed under similar conditions.

Late galena and cosalite could have formed subsequently at perhaps slightly lower temperatures with similar sulphur activities.

In summary, the Bonser Vein is interpreted as having been formed by the successive deposition of minerals as a consequence of cooling of the mineralizing fluids. This may have resulted from the fluids being slowly cooled in contact with wall rocks of lower temperature. Early minerals haematite, magnetite and arsenopyrite may have formed at temperatures of ~ 350 - 400°C. The assemblage of quartz, chlorite, stilpnomelane, magnetite, calcite / dolomite, monoclinic pyrrhotine, chalcopyrite, sphalerite and arsenopyrite (late), was subsequently deposited at temperatures of ~ 240°C. Later minerals such as pyrite, marcasite, bismuth, bismuthinite, laitakarite and galena formed at temperatures as low as ~200°C.

Although the early oxides probably formed under conditions where the sulphur activity was insignificant, the presence of early arsenopyrite suggests sulphur activities of $aS_2 \sim 10^{-12}$atm to $aS_2 \sim 10^{-14}$atm. Lower sulphur activities of $aS_2 \sim 10^{-16}$atm and $aS_2 \sim 10^{-15}$ atm are indicated during subsequent stages of mineralization.

At 350 °C the oxygen activity could have been between $aO_2 \sim 10^{-24}$atm and $aO_2 \sim 10^{-29}$atm, decreasing to around $aO_2 \sim 10^{-38}$atm to $aO_2 \sim 10^{-44}$atm at 250 °C. At this temperature, carbon dioxide activity was probably about $aCO_2 \sim 1$ atm.

6.3 Other veins in the Coniston - Greenburn - Tilberthwaite area

Other veins in the area were studied in less detail than the Bonser Vein, and are dealt with on a comparative basis. This is partly due to the overall similarity between many of the veins, and is also due to a lack of readily available representative material for some of them.

6.3.1 Coniston area

North of the Bonser Vein, in the Deep Level cross - cut adit, the Drygill Vein has been worked for a few metres. Specimens collected in situ (H-77Co.19.A) have arsenopyrite, sphalerite and pyrite with minor chalcopyrite in quartz and chlorite. Compositions of sphalerite (13.4 and 13.6 mole% FeS - Table 6.1, 22 - 23) and arsenopyrite (32.3 at% As - Table 6.1, 24) are similar to those obtained from the Bonser Vein.

Apart from the Bonser Vein , the Paddy End Vein was the most productive in the region. It is different from the Bonser Vein, however, in that early oxide phases appear to be absent. The vein is composed predominantly of quartz, carbonate (ferroan dolomite) and chalcopyrite (H-78Co.9.A). Brecciation is widespread and fracturing of the early mineralization of quartz and chalcopyrite took place before cementation by the carbonate (H-Co.9.4). Polished sections of Paddy End Vein material have chalcopyrite with inclusions of native bismuth and bismuthinite, and euhedral pyrite (P-78 Co.9.A). One specimen (P-Co.9.17) is composed mostly of tennantite (Table 6.1, 19 - 21) with arsenopyrite and chalcopyrite. The tennantite has a composition (Table 6.1, 19) $Cu_{9.9}(Fe_{0.52},Zn_{0.48})_{2.1}(As_{0.98},Sb_{0.02})_{4.0}S_{13}$, using the formula (ideally $Cu_{10}(Fe,Zn)_2(As,Sb)_4S_{13}$) suggested by Wuensch (1964) and is therefore slightly arsenic - rich relative to sulphur. Collecting in situ from the Paddy End Vein proved impossible owing to the dangerous state of the workings, and all the material collected was from the mine dumps at [SD 2840 9870].

Wall rock alteration of the Paddy End Vein and a number of subsidiary veins at 'Simon's Nick' [SD 2800 2900] has involved impregnation with pyrite, in addition to the silicification and chloritization seen in the Bonser Vein. This is a common feature throughout the area and the Brim Fell Vein consists almost entirely of pyrite.

East of the Paddy End Vein a small cross - cut (Courteney's Crosscut) [SD 2835 9905] gives access to the South Vein which was sampled in situ. Hand specimens (H-77Co.18.1; H-77Co.18.3) consist of quartz and chlorite with pyrite and a little chalcopyrite.

Surface workings at Black Scar [SD 2745 9960]may be on the north - westerly extension of the Paddy End or Bonser Veins. Here the mineralization is an oxidation assemblage with covelline, bornite, azurite, malachite, and chrysocolla cementing fractured quartz.

6.3.2 Mineralization in the Greenburn Valley and north of Wetherlam

Near the site of the dressing floors of the derelict Greenburn Mine, three east - west veins were formerly worked. The northernmost of these, the Low Gill Vein, was of little importance and is still accessible from a small adit in the bank of Greenburn Beck [NY 2935 0235]. It is of interest mainly for the presence of erythrite growing in the roof; however, no primary cobalt minerals were found.

The Gossan and Sump Veins were worked from shafts, now flooded, in the valley floor, and samples of the mineralization were collected from old ore dumps adjacent to these shafts. Gossan Vein samples (H-Co.1.1) have massive chalcopyrite in quartz with minor chlorite. In polished section (P-Co.1.1), native bismuth and galena occur as inclusions in chalcopyrite (Plate 28). The Sump Vein, the most southerly of the three Greenburn Veins, has sphalerite, arsenopyrite, pyrite and chalcopyrite in a quartz - chlorite matrix. The sphalerite has a slightly lower iron content (6.8 - 8.2 mole% FeS; Table 6.1, 25 - 26) than that in the Coniston veins and arsenopyrite contains less arsenic, core areas having 31.0 at% As and marginal areas, 29.5 at% As (Table 6.1, 27 - 28). This may be explained if either (or both) lower temperatures or higher sulphur activities than those in the Bonser Vein are envisaged.

Overlooking the Greenburn Valley, high on the northern flanks of Wetherlam are three east - west veins: the Long Crag, Pave York and Birk Fell Veins, which may occupy the same east - west fracture, in spite of having different mineralogies. Hellens Vein, east of Wetherlam, has a similar trend and may lie along the easterly continuation of this fracture.

The Long Crag Vein [NY 2865 0160] is of special interest because it is the only vein in the southern Lake District, other than the Bonser Vein, in which magnetite occurs. This occurrence has not been previously recorded and was first mentioned by E.Holland (pers. comm.). Mineralization from the main cross - cut adit to the vein contains minor quantities of chalcopyrite in quartz. Higher on the fellside, the vein has been worked at outcrop (probably by the Elizabethans) and it is here that magnetite - bearing specimens are found. Polished sections of the mineralization (P-77Co.11.A; P-77Co.11.B) show magnetite intimately associated with haematite, and also interstitial bismuthinite, native bismuth and chalcopyrite (P-77Co.11.C; Plates 14, 15, and 28).

The Pave York Vein, located to the northeast of the Long Crag Vein, has been mined from three levels. Much of the dump material is similar to that from veins elsewhere in the Coniston area, i.e. quartz and chlorite with chalcopyrite, but Postlethwaite (1913) reported that copper oxide was also worked, although no tenorite was identified in this study. One specimen from this locality (H-Co.8.4) has a thin (10 - 15 mm) veinlet containing sphalerite, chalcopyrite, bornite and tennantite. Sphalerite has a low iron content of 1.0 mole% FeS (Table 6.1, 30) and tennantite a composition of $Cu_{10.1}(Fe_{0.45},Zn_{0.55})_{2.0}(Sb_{0.03},As_{0.97})_{4.5}S_{13}$ (Table 6.1, 29). Polished sections of this Pave York Vein material show some excellent replacement textures, with chalcopyrite and bornite intergrowths replacing sphalerite, and with tennantite, chalcopyrite and bornite being replaced by covelline and hydrated copper carbonates (Plates 12,13,14).

East of the Pave York Vein is the Birk Fell Vein, which cuts across Birk Fell Hause [NY 2940 0160]. The vein was sampled at outcrop. Specimens consist of fractured quartz, cemented by bornite with minor arsenopyrite and chalcopyrite (H-Co.14.4). In polished section (P-BMR.4145). tennantite forms veinlets in arsenopyrite and is found at margins between arsenopyrite and bornite. The composition of this tennantite is similar to that from both the Paddy End and Pave York Veins, with a chemical formula - $Cu_{10.2}(Fe_{0.49},Zn_{0.51})_{2.0}(Sb_{0.00},As_{1.00})_{4.5}S_{13}$ (Table 6.1, 31). Arsenopyrite is replaced along fractures by fine - grained chalcocite (Plate 28), and has an unusually high arsenic content (33.9 - 34.9 at% As; Table 6.1, 32 - 35). One section (P-Co.14.3) clearly shows bornite and chalcocite along fractures in chalcopyrite, and these minerals are therefore regarded as being of secondary origin.

Still farther east is Hellens Vein, composed predominantly of quartz and chlorite with arsenopyrite, pyrite, chalcopyrite, sphalerite, and galena (H-77Co.4.B; H-Co.4.1). Sphalerite (11.2 - 11.4 mole% FeS, Table 6.1, 40 - 41) and arsenopyrite (30.8 - 33.7 at% As; Table 6.1, 36 - 39) compositions are comparable to those of the Bonser Vein.

6.3.3. Mineralization in the Tilberthwaite area

At the head of Tilberthwaite Ghyll a number of east - west copper - bearing veins have been worked. The most northerly of these, the Man Arm Vein [NY 2940 0120], has chalcopyrite in thin quartz veins cutting tuffs (T-Co.5.3) of the Borrowdale Volcanic Group. This is typical of many of the Tilberthwaite veins , which are in general thin and which were rather unproductive, with the possible exception of the North Vein. Several of the veins were sampled in situ (e.g. Speddings

Vein and the Ghyll Head Vein) but consist only of chalcopyrite, pyrite, quartz and chlorite.

Totally different in character to the copper veins in the area are the lead - zinc veins in the lower part of Tilberthwaite Ghyll. These have a northeast to southwest direction and are parallel to the Hole Rake Fault, a large tear fault which has guided the southern section of Tilberthwaite Ghyll. Whether the veins actually lie along the fault or are along smaller parallel subsidiary fractures is not known. Mineralization occurs at [NY 3030 0060] on the south side of the ghyll and on its north side at [NY 3040 0080]. Apart from quartz and chlorite, the vein consists mainly of sphalerite and galena at both localities. Polished sections of material from the more southerly vein have an early assemblage of pyrite, arsenopyrite and chalcopyrite with later sphalerite, tetrahedrite and galena. Sphalerite has an iron content of 10.8 mole% FeS (Table 6.1, 42) and contains exsolution blebs of chalcopyrite (P-77Co.16.1). Analyses of tetrahedrite (Table 6.1, 44 - 45) show a high silver content with a formula (based on 13 sulphur atoms per molecule; Wuensch, 1964) of $(Cu_{0.72},Ag_{0.28})_{9.3}(Fe_{0.87},Zn_{0.13})_{1.9}(Sb_{1.00},As_{0.00})_{3.9}S_{13}$ (Table 6.1, 45). This is a slightly higher silver content than in any of the analyses reported by Springer (1969). It is also higher than in any of the other Lake District tetrahedrite analyses (see Ch 5), and is comparable with an analysis obtained for tetrahedrite from the Teesdale area of the North Pennines (Vaughan and Ixer, in press), and with some analyses from Jersey tetrahedrites (Ixer and Stanley, in preparation).

The vein on the northern bank of Tilberthwaite Ghyll has a similar mineralogy and may be an offshoot of the same vein, or perhaps be the same vein displaced by a dip fault running NW - SE through the ghyll. Elsewhere along Hole Rake Fault, mineralization has been reported near Hole Rake Moss [SD 2950 9940] and also near Coniston, where Eastwood (in Dewey and Eastwood, 1925) mentioned that a lead vein with galena and sphalerite was found when searching for the Bonser Vein on the far side of a crosscourse in the Deep Level, probably along the Hole Rake Fault. It is suggested, therefore, that either the Hole Rake Fault itself or subsidiary fractures have undergone a later galena - sphalerite mineralization in addition to minor early arsenopyrite - pyrite - chalcopyrite mineralization.

6.4 Summary and further discussion

The mineral veins of the Coniston - Greenburn - Tilberthwaite areas occur in tuffs and rhyolites with minor andesites of the Borrowdale Volcanic Group, and are not found in rocks of Silurian or younger age. Mitchell (1940) noted that the rhyolites were more favourable hosts for the mineralization than the tuffs; this is probably due to the brittle character of the rhyolite.

Dagger (1977) suggested that the deposits occur in a series of conjugate shears, tension fractures and strike faults formed during the main phase of folding affecting the rocks. However, it is also possible that many of the fractures were formed due to pressure release after the main phase of folding.

The mineralization was more or less continuous and few veins show evidence of fracturing after one period of mineralization and before another. The major exceptions to this are the Paddy End Vein, where later carbonate cements a mineralized breccia, and the Tilberthwaite lead - zinc vein where the early mineralization was fractured prior to the deposition of sphalerite and galena.

Early arsenopyrite - chalcopyrite - pyrite (or pyrrhotine) mineralization, commonly including bismuth and bismuthinite (and in the cases of the Bonser Vein and the Long Crag Vein, magnetite and haematite), is generally followed by sphalerite and galena. Quartz and chlorite are ubiquitous gangue minerals and carbonates (calcite and dolomite) are common. Where mineralized veins have undergone later fracturing, they may have an oxidation assemblage, with secondary copper minerals such as bornite, chalcocite, covelline, malachite and azurite. The anomalous lead - zinc occurrence in Tilberthwaite Ghyll almost certainly has more in common with the Lake District lead - zinc mineralization (see Chapter 5) than with the early copper mineralization, although the latter is represented in the assemblage.

The presence of magnetite and haematite at Long Crag Vein, some 500 m above the only other recorded occurrence of magnetite in deep levels of the Bonser Vein, raises some serious doubts about Dagger's (1977) theory of a vertical zonation. There is no field evidence of any kind (and the mines are now largely inaccessible) to suggest any such vertical zonation in the area from magnetite at depth, through arsenopyrite, to chalcopyrite and pyrite at high levels as proposed by Dagger (1977).

According to Ineson and Mitchell (1974) the copper veins at Coniston have a mean K - Ar isotopic age of 388 Ma (range 367 - 402 Ma) and would therefore have been emplaced after the Caledonian tectonic activity in the area and close to the time of granite emplacement in the Lower Devonian (Brown et al., 1964). At such a time, wall - rock temperatures would have been 175 - 315°C (assuming 7 - 9 km depth and geothermal gradients of 25 - 35°C / km). Temperatures obtained from the interpretation of coexisting phases in the Bonser Vein, using available thermochemical data for the assemblages, are close to these estimates. The earliest mineralization in the Bonser Vein may have been deposited at temperatures perhaps as high as 350 - 400°C, while the main period of ore mineralization occurred at temperatures below 250°C.

CHAPTER 7

COPPER MINERALIZATION AT SEATHWAITE TARN, NEAR CONISTON

7.1 General

Although the copper mineralization at Coniston has previously been reasonably well documented (Dewey and Eastwood, 1925; Wheatley, 1971 and 1972; Dagger, 1977; and Firman,1978b), the small trials near the head of Seathwaite Tarn to the northwest of Coniston have received little attention.

Four quartz veins containing small amounts of sulphide mineralization course east - west across remote mountainous terrain at 375 - 525 m O.D. The veins dip steeply to the north and are less than a metre in width (Eastwood in Dewey and Eastwood, 1925) cutting through Seathwaite Tarn andesites and coarse tuffs and agglomerates assigned to the Tilberthwaite Group (Mitchell, 1963) of the Borrowdale Volcanic Group (see Map 4).

The veins were worked from three adits, marked as Lower, Middle and Upper Levels on the O.S. six - inch sheet SD 29 NE. The entrances to the workings are all blocked and the material referred to in this chapter was collected from spoil tips at the mouth of the adits.

The southernmost vein, worked from the Lower Level adit, consists mainly of quartz with haematite and very little chalcopyrite or pyrite. The vein material worked from the Middle Level has, in addition to quartz, a considerable amount of carbonate (ferroan dolomite, H-Co.6.51) associated with a little chalcopyrite and pyrite.

The two northernmost veins have been worked from the Upper Level adit [SD 2662 9975], 'driven 100 fathoms NNW' (Eastwood, in Dewey and Eastwood, 1925). Sulphide mineralization was not found in situ at the surface outcrop of the veins, but the spoil heap derived from the adit has yielded a variety of copper sulphides and the rare copper bismuth sulphide, wittichenite - Cu_3BiS_3 (Stanley and Criddle, 1979; Criddle and Stanley, 1979; see Appendix III.).

7.2 Mineralogy

The only previous description of the mineralogy at Seathwaite is that of Eastwood (in Dewey and Eastwood, 1925) who found 'in addition to copper pyrites, an appreciable quantity of copper glance'.

Hand specimens (H-Co.6.1; H-Co.6.2) show small amounts of sulphides and haematite cementing fractured and brecciated massive vein quartz. The main ore mineral assemblage, determined by X - ray diffraction, electron probe microanalysis and reflected light studies on polished sections, consists of digenite, djurleite and bornite with smaller quantities of wittichenite, chalcopyrite, covelline, blaubleibender covelline, arsenopyrite, cobaltite and pyrite in a haematitized quartz - chlorite matrix. Digenite and djurleite were identified by X - ray diffraction using the recent work of Potter and Evans (1976). Blaubleibender covelline was identified by its optical characteristics, particularly by comparison with normal covelline using oil immersion techniques.

Cobaltite contains no detectable nickel and has a small amount of iron substituting for cobalt (Table 7.3, 1 - 4). Arsenic/sulphur ratios are variable. Arsenopyrite has a small, but detectable cobalt content (Table 7.3, 5) and an arsenic content of 33.0 at% As.

7.2.1 Wittichenite

Wittichenite, associated with microcrystalline haematite, occurs along grain boundaries, fractures and structural planes in the digenite and djurleite (Plates 16 and 29). It is also found in graphic intergrowths with digenite and bornite (Plates 15,29 and 30).

The occurrence of wittichenite at Seathwaite is the first confirmed for the British Isles. Previously, Garby (1848, p 86) reported that 'cupreous bismuth was found at Huel Buller (Cornwall) in perfect hexagonal prisms'. These crystals 'were tin - white and lustrous' but the lustre was soon lost on exposure. Collins (1871, p 106) mentioned this occurrence, and others from Botallack and Levant, and suggested that Garby's cupreous bismuth 'may possibly have been' wittichenite.

It is also possible that klaprotholite (klaprothite) observed in polished section from Redruth, Cornwall (Krieger, 1940) was wittichenite, for in Nuffields' (1947) X - ray study of klaprothite, which included an examination of some of Krieger's material (from Wittichen, not Redruth) he concluded that klaprothite was identical to wittichenite. However, Springer and Demirsoy (1969) found that klaprothite from Wittichen had the same chemistry as emplectite but was different optically; they concluded that klaprothite was identical with cuprobismutite, a dimorph of emplectite (Cu Bi S_2). Recently, Moh (1977) obtained a mixture of emplectite and wittichenite when attempting to synthesize klaprothite ($Cu_6Bi_4S_9$).

The wittichenite from Seathwaite was compared to a specimen (BM 1437) from Wittichen, Baden. In addition to the physical properties listed below, visible spectrum reflectances and quantitative colour values are given in Criddle and Stanley (1979 - Appendix III)

7.2.1.1 Optical characteristics

In specimens from Seathwaite, wittichenite appears white to creamy white with a slight anisotropy, the rotation tints varying in shades of brown. Wittichenite from Wittichen on the other hand is associated with a different assemblage and appears greyish white.

7.2.1.2 Microhardness

The Vickers Hardness Number was measured on twelve grains from both Seathwaite and Wittichen material. Wittichenite from Seathwaite had VHN_{100} 180 (standard error of the mean ± 2.04) with a range of 170 - 187. Topotype material had VHN_{100} 186 (standard error of the mean ± 1.58) and range 178 - 197.

The indentations were slightly fractured at their corners, had concave sides and were almost square in outline. Measurement procedures are given in Appendix II.

Results from both Seathwaite and Wittichen wittichenite are in agreement with previously published data for the species by Parnamaa (1963), Young and Millman (1964) and Nordrum (1972), (see Table 7.1)

7.2.1.3 Structure

The interplanar spacings for both Seathwaite and Wittichen wittichenite obtained from X - ray powder photographs (see Appendix II for details of method) are in excellent agreement with Berry and Thompson's (1962) data for wittichenite from the type locality (Table AII.3)

Cell parameters were calculated from the first 28 lines using an unpublished computer programme for the orthorhombic system, and are in agreement with previously published data (see Table 7.2).

7.2.1.4 Composition

Six areas of wittichenite on the Seathwaite sections and seven on the Wittichen section (BM 1437) were analyzed by electron microprobe (Table 7.3). In both cases, three of the analyses were on areas used for reflectance measurements.

Average compositions $Cu_{3.05}Bi_{1.04}S_{2.91}$ for Seathwaite and $Cu_{3.00}Bi_{1.05}S_{2.95}$ for Wittichen material compare well with published data (Sugaki et al., 1974; Kocman and Nuffield, 1973) and the stoichiometric composition (Cu_3BiS_3).

Wittichenite from both localities is chemically homogeneous. Solid solution with silver, which has previously been reported (Oen and Kieft, 1976, and Sugaki et al., 1974), was not found.

7.3 Paragenesis

The earliest mineralization at Seathwaite was of quartz with chlorite and minor amounts of haematite. The main sulphide assemblage was deposited after brecciation of these quartz - chlorite veins. In the mineralized parts of the vein the quartz fragments are commonly no more than a few centimetres across. Minor quantities of euhedral pyrite (P-Co.6.5; Plate 30), arsenopyrite (<0.1 mm ; P-Co.6.5) and euhedral to subhedral cobaltite (P-Co.6.1; Plate 30) were introduced into the breccia before cementation by copper sulphides.

Digenite and djurleite are interpreted as the first formed copper sulphides. Both replace early quartz and haematite and, to a lesser extent pyrite and arsenopyrite. Digenite and djurleite were contiguous in none of the polished mounts in which both minerals were found. For this reason it was not possible to determine their age relationships with any certainty. Sillitoe and Clark (1969) suggest that digenite may be formed by the oxidation of djurleite, and that further oxidation may lead to the formation of covelline and blaubleibender covelline. Both these minerals have replaced digenite at Seathwaite (P-Co.6.1; P-Co.6.4) but their position in the paragenetic sequence as a whole is unclear. Blaubleibender covelline has replaced digenite in some specimens; digenite has also been partially replaced by bornite and chalcopyrite (Plate 16).

Digenite and djurleite have been replaced to some degree by most of the later minerals: bornite replaces digenite extensively (Plate 30) and, less commonly, forms sigmoidal replacement textures with djurleite (Plate 30). Wittichenite occurs as discrete areas (<0.2mm) in graphic intergrowths with digenite and bornite (Plates 15, 29 and 30) but is more commonly associated with microcrystalline haematite (Plates 16 and 29). Together they separate digenite and djurleite from early quartz, and occupy fractures within these phases; they also replace digenite along its octahedral cleavages (Plate 29) and at grain boundaries. It was not possible to determine whether the wittichenite was contemporaneous with, or was introduced before, the microcrystalline haematite. A thin margin (<0.5 μm) of bornite, or chalcopyrite, or both commonly separates wittichenite from digenite and djurleite. One small irregular grain of gold (P-Co.6.1iii) found in bornite may have been introduced at this stage of mineralization.

Exsolution textures of chalcopyrite in bornite occur (P-Co.6.2) but are less common than the replacement of bornite by chalcopyrite and covelline. In such instances the replacement proceeded along fractures and structural planes in the bornite. Covelline also defines cleavages in digenite and in some specimens replaces it extensively. Similarly, blaubleibender covelline, in replacing digenite utilized the host's structure, and as with covelline, diffuse and more extensive replacements spread out from the earlier linear features (P-Co.6.4.).

Later minerals include botryoidal haematite, siderite, and small amounts of malachite.

These observations are summarized in the paragenetic diagram (Fig. 7.1).

7.4 Discussion

7.4.1 Comparison of Seathwaite wittichenite with other occurrences

Wittichenite from the type locality of Wittichen, Baden, West Germany is associated with native bismuth, emplectite, tetrahedrite, barytes and other copper and copper - bismuth sulphides (Nuffield 1947; Mehnert, 1949). Although assemblages from elsewhere differ from that at the type locality, there is a general and not unexpected association of wittichenite with copper sulphides and other copper - bismuth sulphides (e.g. Medici, 1972; Sugaki et al., 1974; Escande et al., 1973 and Thompson, 1950). Although no other copper - bismuth sulphides or bismuth minerals were found at Seathwaite, a number of copper and copper - iron sulphides are associated with wittichenite.

Wittichenite exhibits an interesting variety of forms and textures. Lawrence (1963) reported crystals of acicular habit with elongated rectangular outline. Escande et al.(1973) also found wittichenite in acicular crystals, associated with copper sulphides and bismuthian tetrahedrite in a quartz - fluorite - barytes vein, north of Faymont, France. More commonly, however, wittichenite occurs as intergrowths with other minerals. Nordrum (1972) regarded rod - like rectangular bodies of wittichenite orientated along structural planes in bornite as being due to guided replacement rather than exsolution. Oen and Kieft (1976) reported chalcopyrite and wittichenite exsolution textures in bornite from Mangualde, Portugal. They also recognized a second stage whereby wittichenite had segregated into larger blebs through recrystallization and accumulation, and interpreted the intergrowths as having formed by unmixing of high - temperature bornite solid - solutions.

Ramdohr (1969) noted myrmekitic intergrowths of wittichenite in chalcocite but this type of intergrowth has more commonly been found in bornite (Krieger, 1940; Nordrum, 1972). At Seathwaite, wittichenite, in addition to occurring along the margins of digenite and djurleite, is also found as graphic intergrowths in digenite and bornite. Whether these are due to unmixing in both digenite and bornite, or whether the intergrowths in bornite could have been inherited from digenite which has subsequently been replaced by later bornite is not known.

7.4.2 Conditions of formation

It is apparent from the paragenetic diagram (Fig.7.1) that the mineralization at Seathwaite was discontinuous and consisted of three episodes: an early quartz, chlorite and haematite stage which was subsequently brecciated; an arsenopyrite, pyrite and cobaltite stage and finally the main copper sulphide and copper - bismuth sulphide stage which has undergone subsequent oxidation.

Deposition of minerals of the first two stages probably occurred under conditions similar to those of early arsenopyrite - pyrite - chalcopyrite veins elsewhere in the Lake District. As has been shown in Chapters 4 and 6, the maximum temperature of formation proposed for this early mineralization was 300 - 350°C, the main period of chalcopyrite deposition occurring at considerably lower temperatures (<250°C). Early haematite at Seathwaite, rather than magnetite, may possibly signify slightly lower temperatures and/or higher oxygen activities than at Coniston. There is no diagnostic evidence, however, for conditions within the vein during the deposition of these early minerals.

Similar problems occur when interpreting the main stage mineralization of copper sulphides, bornite, chalcopyrite and wittichenite. Digenite, although metastable at room temperature, almost always contains a small amount of iron and is considered to be stable only in the Cu - Fe - S system (Morimoto and Koto, 1970). This has not been proved ,however, and remains a matter for debate. Roseboom (1966) found that although both natural and synthetic djurleite breaks down at 93 °C to hexagonal chalcocite and high digenite, this occurs reversibly and unless djurleite in ores occurs as large pure masses or as crystals its presence is not necessarily evidence of deposition below 93 °C. At Seathwaite, djurleite occurs as masses not more than a few millimetres across and, although there is no evidence of it replacing digenite it cannot be said for certain whether deposition was originally above or below 93 °C. Buhlmann (1971) and Sugaki and Shima (1972) have shown that wittichenite is stable in the Bi_2S_3 - Cu_2S system up to about 520°C. Above 320°C wittichenite solid - solution occurs. Although Oen and Kieft (1976) interpret phase relations of wittichenite from a pegmatite deposit at Mangualde, Portugal as indicating formation temperatures of less than 271°C, wittichenite from Seathwaite shows different textures and is thought to have formed at considerably lower temperatures. At 100°C, stable phases in the Bi_2S_3 - Cu_2S system are chalcocite (and digenite), wittichenite, emplectite, $CuBi_3S_5$, and bismuthinite (see Fig.7.2).

Fine 'basket - weave' textures of chalcopyrite in much of the bornite at Seathwaite are thought to result from exsolution. Brett (1964) found that exsolution textures of chalcopyrite in bornite were not diagnostic of any particular temperature or cooling rate.

A similar assemblage to that at Seathwaite, although without wittichenite and haematite, is reported by Sillitoe and Clark (1969) from Chile. They regarded djurleite, digenite, blaubleibender covelline and covelline as being of supergene origin, the result of oxidation of hypogene chalcopyrite, chalcocite and bornite, and they suggested an oxidation sequence of djurleite → digenite → blaubleibender covelline → covelline. Putnis et al. (1977) also suggested that blaubleibender covelline formed due to low - temperature oxidation of more copper - rich phases. At Seathwaite, blaubleibender covelline replaces digenite extensively although covelline replaces it only along fractures and cleavages. This is explained by Potter (1977), who suggested that blaubleibender covellines form because of the difficulty in nucleating normal covelline with a hexagonal close packed (Evans and Konnert, 1976) structure from digenite which has a cubic close packed (Koto and Morimoto, 1970) structure.

The complexity of the phase relations in the Cu - Fe - S and Cu - S systems particularly at low temperatures, the strong tendency of the Cu - S system to exhibit metastability and the lack of available material from the Seathwaite locality lead to difficulties in interpretation and no definite conclusions can be drawn as to conditions of formation.

7.4.3 Origin of Seathwaite mineralization

Eastwood has suggested (in Dewey and Eastwood, 1925) that the veins at Seathwaite are probably continuations of the Coniston copper veins (see Chapter 6). Certainly, the Seathwaite trials were made in the hope that deposits of a similar size to those at Coniston would be found. Field evidence for any link between the Paddy End and Bonser veins and the Seathwaite veins is not entirely convincing for although the Bonser Vein is nearly east - west in direction, most of the Coniston veins have a NW - SE trend whereas the Seathwaite veins have an east - west trend (Map 4). Generally though, copper veins elsewhere in the Lake District have an east - west direction.

Broad similarities in the parageneses of both groups of veins do exist, however, although more copper sulphides have been identified in one stage of mineralization at Seathwaite than have yet been found at Coniston. The major Coniston copper veins, the Paddy End Vein and the Bonser Vein, carry significant amounts of native bismuth and bismuthinite. In the Paddy End Vein they occur mainly as inclusions in chalcopyrite; in the Bonser Vein, native bismuth and bismuthinite are commonly associated with magnetite, probably derived from deep levels (Shaw, 1959) in the mine. The presence of wittichenite at Seathwaite and native bismuth and bismuthinite at Coniston may offer some support for Eastwood's (in Dewey and Eastwood, 1925) suggestion that the veins are continuous. Furthermore, the workings at Black Scar to the northwest of Levers Water are possibly on the northern continuation of the Paddy End Vein, and here the assemblage consists of malachite, blaubleibender covelline and bornite (P-Co.22.1). Firman (1978b) also lists tenorite, azurite and chrysocolla, and this presumed oxidation assemblage from the outcrop workings has distinct similarities to the Seathwaite mineralization.

It would seem unlikely that there is no relationship between the Seathwaite and Coniston veins and there are several ways in which the deposits may be linked. Firstly, the Seathwaite mineralization could be primary and could have been deposited from mineralizing fluids similar, in terms of overall chemical composition, to those forming the Coniston mineralization. If this were so, the observed mineralogical differences might be explained by deposition under different physicochemical conditions. Early mineralization at Seathwaite, i.e. quartz, chlorite, pyrite, haematite, arsenopyrite, and cobaltite might well have a primary origin. However, the extent of fracturing and brecciation of the early quartz, and the subsequent cementation of the early mineralization by copper sulphides and wittichenite is evidence that the later minerals are probably not primary. At Coniston, where the mineralization is undoubtedly primary, the vein breccia is marginal to the main veins and there was little brecciation before or during mineralization.

Secondly, the Seathwaite copper mineralization may represent the oxidation zone of veins similar in type to those at Coniston. In other words, economic mineralization may be present at depth at Seathwaite.

Thirdly, the Seathwaite copper mineralization may have formed as a result of copper and bismuth - bearing fluids migrating through a vein system from the Coniston veins, such movements of solutions being facilitated by the brecciation and fracturing of the quartz veins.

Ramdohr (1969) suggested a supergene origin for wittichenite, and stated that wittichenite was formed in processes of enrichment where solutions containing copper ions have attacked native bismuth and bismuthinite; in such cases, secondary chalcocite is usually associated. Whether or not such fluids migrated west from the Coniston veins or upwards from mineralization at depth is not known.

The interpretation of the association of wittichenite with haematite is also problematical, but both early and possibly later haematite may be explained by Shepherd's (1973) theory concerning the genesis of the Cumbria haematite deposits. The essential concept of this theory is the release of iron from a concealed granite basement, co-extensive with the Eskdale intrusive (see Map 1) by circulating sub-surface brines. Late stage alteration of the granite could have produced a chemical breakdown of the primary constituents and localized precipitation of the iron as free haematite. Remobilization of this early haematite by circulating sub-surface brines could account for the epigenetic haematite deposits at Seathwaite. Similar models involving circulating formation waters have been proposed (Dagger, 1977; Firman, 1978b) to explain the nearby copper deposits at Coniston, and are discussed more fully in Chapter 9.

In conclusion then, it is thought that following the deposition of early primary mineralization, a variety of supergene oxidation products were deposited through remobilization and redeposition of earlier primary copper minerals, similar to those found at Coniston, and which may exist in depth at Seathwaite.

CHAPTER 8

COBALT AND NICKEL MINERALIZATION AT CONISTON

8.1 General

The material studied and described in this chapter was obtained solely from collections in the British Museum (Natural History). Cobalt and nickel - bearing mineral specimens, labelled as having come from Paddy End Vein , Coniston or merely Coniston, were examined from both the Russell and Kingsbury Collections. None of the specimens had any information as to where in the Paddy End Mine they were found, and the specimens from the two collections are so different as to suggest that they are probably not from the same part of the mine but from different localities, and are hence treated seperately.

The Russell Collection specimens were found to contain nickeline, rammelsbergite, safflorite, native bismuth, pyrite, marcasite, cobaltite, gersdorffite and chalcopyrite in a calcite and chlorite matrix with minor quartz.

The specimens from the Kingsbury Collection consist dominantly of cobaltite, with glaucodot, cobaltian arsenopyrite, pyrite, pyrrhotine, gold, a bismuth telluride (possibly wehrlite), and chalcopyrite in a dolomite matrix.

Cobalt and nickel minerals from Coniston have been largely ignored by previous workers, although Goodchild (1883) mentioned the occurrence of erythrite in a cross vein and Russell (1925) gave a brief account of the specimens which have been extensively investigated in this chapter.

Russell (1925) reported that according to the mineral statistics of the U.K. for 1855, three tons of nickel and cobalt ores were raised from Coniston Mine. Account books of the mine showed that in

1873 nearly half a ton of nickel ore was sold. The specimens from the Russell Collection were obtained from Joseph Hellen, an old Coniston miner who suggested that cobalt and nickel minerals occurred in the Bonser Vein as well as the Paddy End Vein. This may account for the observed mineralogical differences between material from the Russell and Kingsbury Collections.

8.2 Cobalt and nickel minerals from the Russell Collection

Small fragments were taken of five specimens from the Russell Collection labelled as follows:- R 856 smaltite; R 857 smaltite; R 577 niccolite; erythrite; chloanthite with native bismuth.

Russell (1925) stated that the smaltite crystals 'were simple cubes with markedly curved faces, brilliant and tin - white in colour with sometimes a slight bluish iridescent tarnish or black coating', and that the largest 'cube' measured nine millimetres along the edge. These crystals were intimately associated with nickeline, the latter forming 'eyes' or irregular patches surrounded by smaltite in a calcite matrix.

In the past, smaltite and chloanthite were names given to cobalt and nickel diarsenides which appeared to have cubic symmetry. Smaltite being cobalt - rich and chloanthite, nickel - rich. However, Holmes (1947) and Roseboom (1962) found that X - ray patterns of various specimens of 'chloanthite' and 'smaltite' were found to correspond to those of skutterudite, lollingite, rammelsbergite, safflorite or mixtures of these. Consequently, Hey(1963) recommended retention of the names smaltite and chloanthite as terms of convenience to be used only for undetermined, apparently cubic, cobalt and nickel arsenides. However, their retention seems unsatisfactory since they are no longer 'mineral names'.

8.2.1 Mineralogy and paragenesis

8.2.1.1 'Chloanthite with native bismuth' specimens

The Russell Collection specimens are very similar in character to each other, with the exception of the specimen labelled 'chloanthite with native bismuth' (P-BMR.1, P-BMR.2, P-BMR.3). Polished sections show a fine skeletal growth of native bismuth in rammelsbergite, which makes up most of the specimen and is presumably what has been described in the past (Russell, 1925) as chloanthite.

Native bismuth (<1 mm) occurs as skeletal or dendritic growths, and is interpreted as being an early phase. Small euhedra (<30 µm) of gersdorffite are commonly found at the margin between native bismuth and rammelsbergite (Plate 31). Microprobe analysis of this gersdorffite (Table 8.1, 2) showed no significant substitution of iron and cobalt for nickel, and only a slight excess of arsenic over sulphur ($NiAs_{1.10}S_{0.90}$), well within the limits found by Yund (1962) of $NiAs_{1.77}S_{0.23}$ to $NiAs_{0.77}S_{1.23}$. Nickeline also forms a thin (<10 µm) margin between native bismuth and rammelsbergite.

Rammelsbergite shows well formed interpenetrating lamellar twins (Plate 31) which are sometimes developed in a plumose texture growing from native bismuth dendrites. Although initially identified by its optical properties, the presence of rammelsbergite rather than pararammelsbergite (the dimorph, stable at room temperature) was confirmed by X - ray diffraction. Against native bismuth (cream - white) rammelsbergite appears bright white, and it has a weak bireflectance. It is strongly anisotropic with rotation tints varying in shades of blue, orange, brown and grey.

As with gersdorffite, rammelsbergite has only minor substitution of iron and cobalt for nickel and a small amount of sulphur

(0.4 wt%) substitutes for arsenic; $(Ni_{0.98},Co_{0.02})_{1.02}(As_{0.99},S_{0.01})_{1.98}$ - Table 8.1, 1. The rammelsbergite contains inclusions of blunt - ended acicular crystals (<3 mm) of what may have been a silicate mineral and which is now pseudomorphed by later calcite and pyrite.

Commonly, safflorite overgrows rammelsbergite and characteristically shows a strong zonal texture under crossed nicols, individual zones varying in width from 5 to 30 µm. Not only are these zones optically distinguishable due to differing hues of the blue and yellow rotation tints, but there is a considerable compositional variation between individual zones (Table 8.1, 3 - 10). Iron and nickel substitute extensively for cobalt, and safflorite zones contain up to 14.5 wt% nickel (Table 8.1, 4) and up to 8 wt% iron (Table 8.1, 9). Also, sulphur substitutes for arsenic, and some zones contain up to 7.4 wt% S (Table 8.1, 6). These values of nickel and sulphur are higher than any reported by Roseboom (1963) and Petruk et al.(1971) and are discussed further in Section 8.2.2.

Pyrite and marcasite have partially replaced safflorite at its margin and have also pseudomorphed an earlier, possibly silicate, phase. Marcasite occurs as small (<100 µm) inclusions within pyrite. Calcite appears to be mostly later than the sulphides and arsenides.

The paragenetic relations are summarized in Fig.8.1.

8.2.1.2 R 857, R 856, R 577 and 'erythrite' specimens

These specimens are described together as they have many characteristics in common. The specimen marked 'erythrite' (P-BMR. 9 - 11) has the hydrated cobalt arsenate as an alteration product, presumably of safflorite which, with rammelsbergite and nickeline, makes up most of the specimen. In all of the polished sections, the major minerals are the diarsenides, safflorite and rammelsbergite and the arsenide, nickeline, with calcite as the major gangue phase. Safflorite, which is the last formed of the diarsenides, has in the past been referred to as smaltite (Russell, 1925).

The paragenetic relations are summarized in Fig.8.2. The early minerals occur as cores to nickeline rosettes (P-856BMR.13), or as in R 857 (P-857BMR.4-6) as small inclusions of pyrite and cobaltite in a fine - grained aggregate of rammelsbergite with minor safflorite. Early gangue minerals are chlorite and calcite with minor quartz.

In P-BMR.11, cobaltite forms the euhedral core (<15 μm) of typically asteriform (due to later safflorite overgrowths) grains (<50 μm). Electron probe microanalysis (Table 8.1, 19 - 22) of one of these grains (P-BMR.11; Plate 31) showed the presence of zoned cobaltite with a high nickel content in the centre, surrounded by rammelsbergite with over 7 wt% cobalt, and finally overgrown by safflorite. An electron microprobe line profile across this grain is given in Fig.8.3. Because of the small grain size, X - ray diffraction to determine whether rammelsbergite or pararammelsbergite is present was not possible. However, pararammelsbergite rarely shows twinning (Uytenbogaarde and Burke, 1971), and, as the rammelsbergite in these small grains is commonly twinned (Plate 31), it was inferred that pararammelsbergite is not present.

Analysis of the grains by electron microprobe indicates an increase in arsenic content from the centre to the margin and a corresponding decrease in the sulphur content.

The best development of the arsenides and sulpharsenides is found later in the paragenetic sequence with the growth of well -formed rosettes (Plates 17 and 18) and dendrites of nickeline overgrown by rammelsbergite, safflorite and pyrite. Nickeline frequently overgrows the fine - grained early nickel/cobalt mineralization already described and may also contain euhedral rhombs of early calcite. Where it occurs in such overgrowths, nickeline may have minute inclusions (<20 μm) of euhedral pyrite and, less commonly, cobaltite, safflorite and rammelsbergite. Dendritic development of nickeline is common, and irregular grains (<1 mm) may also form the cores of rosettes.

Rammelsbergite (<1 mm) overgrows and partially replaces nickeline (Plate 18). As before, it was distinguished from pararammelsbergite by X - ray diffraction, and the presence of lamellar twinning. Near the contact with nickeline, rammelsbergite has a small but significant sulphur content of about 2 wt% (Table 8.1, 12 - 13). Although there is no difference optically between this and rammelsbergite with a lower sulphur content (Table 8.1, 14 - 16), its presence is shown on the electron microprobe X - ray image (Plate 18) and line profile (Fig. 8.4).

Safflorite, although having similar properties to rammelsbergite in plane polarized light, was distinguished by its blue and orange - yellow rotation tints in crossed nicols, compared to the mauves, browns and greys of rammelsbergite. It overgrows and partially replaces rammelsbergite (Plate 31) and has a strong zonal texture, with individual zones less than 30 μm in width. These zones show no great difference in composition, with only minor substitution of nickel and iron for cobalt, and sulphur for arsenic (Table 8.1, 17 - 18).

Safflorite stars have frequently grown at the margins of safflorite - rammelsbergite - nickeline rosettes, in a matrix of calcite. Elsewhere, small subhedral pyrite grains (<5 μm) have grown in calcite at safflorite margins (Plate 18).

8.2.2 Discussion

It is apparent from the paragenetic interpretation (Fig.8.2) that the cobalt/nickel - bearing specimens from the Russell Collection show two stages of probably continuous mineralization. Both sequences show an increase in arsenic content; pyrite → cobaltite → rammelsbergite → safflorite for the early stage and nickeline → rammelsbergite → safflorite for the later stage, which was abruptly terminated by the deposition of pyrite.

Early cobaltite (Table 8.1, 19 - 20) has compositions which fall into the high temperature (500 - 600°C) field of Klemm's (1965) synthetic work. However, early gersdorffite (Table 8.1, 2) would indicate deposition below 300°C according to Klemm (op. cit.). In fact, coexisting gersdorffite and skeletal native bismuth almost certainly formed below 271°C, the melting point of bismuth. As described in previous chapters, Klemm's (1965) work shows large discrepancies between analyses from the literature and his synthesis experiments.

The gersdorffite analysis (Table 8.1, 2) falls within the range of natural gersdorffite compositions observed by Yund (1962) and those from Cobalt, Ontario (Petruk et al., 1971). The sulpharsenide analyses have been plotted on Fig. 8.6.

Yund (1962) found that synthetic rammelsbergite could contain about 1 wt% sulphur at 700°C and suggested that this was probably the maximum sulphur content of natural rammelsbergite. Analyses of natural rammelsbergite from the Coniston assemblage, however, show more than 2 wt% sulphur substituting for arsenic (Table 8.1, 12, 13, and 21).

Yund (1962) also found that the pararammelsbergite /

rammelsbergite inversion occurred at 590°C for pure $NiAs_2$ in equilibrium with nickeline and under the vapour pressure of the assemblage. Substitution of sulphur for arsenic lowers the inversion temperature as does the subtitution of cobalt and iron for nickel, but Yund (op. cit.) was unable to give a minimum temperature for the formation of rammelsbergite in nature. Rammelsbergite analyses from Coniston are comparable with those from elsewhere (Petruk et al., 1971) although one (Table 8.1, 21) contains more cobalt than suggested by Roseboom (1963).

X - ray diffraction studies of Coniston safflorites were inconclusive in determining which structural type of safflorite is present, due to compositional zoning. However, the analyses correspond to the safflorite II and safflorite IV types (Radcliffe and Berry, 1968).

Analyses of natural safflorites, rammelsbergites and lollingites (Radcliffe and Berry, 1968) indicate complete solid - solution between safflorite ($CoAs_2$) and löllingite ($FeAs_2$), limited solid - solution between safflorite ($(Co,Fe)As_2$) and rammelsbergite ($NiAs_2$) and no solid - solution between rammelsbergite and löllingite. Radcliffe and Berry (1968) plotted these analyses and suggested a limit (see Fig.8.5) for most natural compositions, representing the approximate extent of the solvus at low temperatures (200 - 300°C). Most of the analyses of Coniston safflorites and rammelsbergites (see Fig.8.5) fall within Radcliffe and Berry's (1968) limits, however the few analyses lying outside (Fig.8.5, 4, 6, 21) all have relatively high sulphur contents. It is thought possible therefore, that the presence of a few wt% sulphur substituting for arsenic in rammelsbergite and safflorite might extend the area of solid - solution between these minerals.

Nickel (1969) has suggested on theoretical grounds that the crystal structure adopted by the diarsenides of the transition metals (among others) is that permitting spin pairing of the non - bonding electrons in the t_{2g} cation orbitals, and that this governs the limits of solid - solution fields in the $FeAs_2$ - $CoAs_2$ - $NiAs_2$ system. He proposed that there is a complete transition between the löllingite structure ($FeAs_2$) with 4 non - bonding d - electrons and the safflorite structure ($CoAs_2$) with 5 non - bonding d - electrons, and between the safflorite structure and rammelsbergite ($NiAs_2$) which has the 6 non - bonding d - electron marcasite structure. In other words moving from the iron, to the cobalt, to the nickel end members there is a progressive occupancy of the non - bonding electrons in the t_{2g} cation orbitals, and this determines the solid - solution limits in the $FeAs_2$ - $CoAs_2$ - $NiAs_2$ system. This theory adds support to the suggested extension of the solid - solution field between $(Co,Fe)As_2$ and $NiAs_2$ and also explains the lack of solid - solution between löllingite ($FeAs_2$) and rammelsbergite ($NiAs_2$).

No definite conclusions can be reached as to the conditions of formation of the cobalt/nickel mineralization at Coniston from the study of the few specimens in the Russell Collection. It is thought unlikely, however, that temperatures would exceed those previously suggested for the epigenetic copper mineralization from the Coniston area, already described in Chapter 6. The compositions of the diarsenides may indicate deposition between 200 - 300 °C, and the presence of skeletal native bismuth would suggest formation temperatures below its melting point (271 °C), giving a probable range of 200 - 271 °C.

8.3 Cobalt minerals from Paddy End, Coniston in the Kingsbury Collection

A few fragments of mineralized material were taken from a box in the unsorted Kingsbury Collection, labelled 'Cobalt and nickel minerals, Paddy End, Coniston'. It is not known from where Kingsbury obtained the samples but it is thought unlikely that he collected them in situ. The specimens themselves are not labelled and are totally different in appearance (and also mineralogy) to those described from the Russell Collection.

The study of polished sections showed that the major ore minerals are cobaltite and pyrrhotine, with smaller quantities of chalcopyrite, pyrite, cobaltian arsenopyrite and glaucodot, and minor amounts of galena, gold and a bismuth telluride. Dolomite is the major gangue phase and only small amounts of quartz are present.

8.3.1 Mineralogy and paragenesis

The sulpharsenide minerals, cobaltite, cobaltian arsenopyrite and glaucodot are interpreted as being early. Cobaltian arsenopyrite with up to 4 wt% cobalt (Table 8.1, 25 - 26) occurs in large (<1.5 mm) subhedral to euhedral grains (P-BMK.1) and was identified initially by X - ray diffraction and confirmed by electron probe microanalysis. Commonly, large grains show alternating cobalt - rich (7.1 wt% Co - Table 8.1, 28) and cobalt - poor (3.6 wt% Co - Table 8.1, 29) zones which exhibit a fine 'herringbone' structure when viewed under crossed nicols. These zones may vary in width from less than 10 µm to 50 µm. From one of these larger zones a composition (Table 8.1, 27) corresponding to glaucodot was obtained by microprobe analysis. High cobalt and glaucodot zones have been preferentially replaced by later pyrrhotine and, less commonly, by chalcopyrite (Plate 32).

Cobaltite is thought to be later than the cobaltian arsenopyrite and glaucodot and is nearly always euhedral (Plate 32). Individual grains more than a millimetre across are common, and where fractured, the cracks have been infilled by later sulphides. In addition, minute subhedra (<5 µm) of cobaltite occur marginally to cobaltian arsenopyrite (P-BMK.7). Electron probe microanalysis of cobaltite showed no growth zoning, but a slightly variable composition both within and between individual grains (Table 8.1, 23 - 24). Up to 7 wt% iron and 8 wt% nickel were found to substitute for cobalt, while one of the analyses (Table 8.1, 23) showed an excess of arsenic over sulphur.

Pyrite is later than cobaltite and sometimes overgrows it (P-BMK.9), but is more commonly found as irregular grains (<400 µm) with corroded margins, enclosed and partially replaced by pyrrhotine. It also grows in a fine anastomosing network along grain boundaries and cleavages in the dolomite gangue (P-BMK.9).

Pyrrhotine replaces pyrite and occurs in large anhedral grains (<1 mm). In addition, it has replaced cobaltian arsenopyrite, particularly along cobalt - rich zones, and is commonly in close association with chalcopyrite, galena and other late minerals. It is also found along cleavages in cobaltite, where it is associated with galena (P-BMK.3). X - ray diffraction and electron probe microanalysis indicated the presence of monoclinic pyrrhotine (Table 8.1, 30). Exsolution of hexagonal pyrrhotine was not found when monoclinic pyrrhotine was etched with concentrated HI solution. Pyrrhotines from elsewhere in the Lake District are also generally the monoclinic form (see Chapters 4 and 6).

Chalcopyrite is, like pyrrhotine, always anhedral and commonly encloses small grains of sphalerite and galena. Mutual boundary relationships usually exist between chalcopyrite and pyrrhotine and textural relations indicate little time interval between the deposition of pyrrhotine and the latest opaque phase recognized, gold (see Fig. 8.7).

Associated with chalcopyrite, pyrrhotine and galena was a pure white phase which occurs either as anhedral grains (<20 µm) along fractures in cobaltite or cobaltian arsenopyrite, or more commonly as myrmekitic intergrowths in chalcopyrite or pyrrhotine. In both instances gold is also commonly present (Plate 32). The phase has a small bireflectance, barely visible in oil immersion, and is moderately anisotropic, rotation tints varying in shades of buff and brown. The polishing hardness is low, lower than for chalcopyrite and about the same as for galena. The small size of the grains meant that X - ray diffraction was not possible and it was only possible to quantitatively analyze the larger grains by electron probe microanalysis. Qualitative analysis suggested, however, that the phase in myrmekitic intergrowths is of the same composition. The analysis showed the presence of about 70 wt% bismuth and 30 wt% tellurium (Table 8.1, 34 - 36), corresponding to a chemical formula of $Bi_{4.1}Te_{2.9}$. This phase may well be wehrlite, on account of its composition and optical properties and is dealt with further in the discussion section (8.3.2).

Gold is commonly associated with the bismuth telluride (P-BMK.1) and is found in small anhedral grains (<30 µm), but more commonly as minute (<5 µm) grains, or along hairline fractures in cobaltite. A significant amount of silver was present in solid - solution, although not enough for the phase to be termed electrum (Table 8.1, 31 - 33).

Of the gangue minerals, dolomite appears to be predominantly early, while quartz sometimes infills later fractures along with the sulphides, chalcopyrite, sphalerite, and galena.

The paragenetic interpretation is summarized in Fig.8.7.

8.3.2 Discussion

The bismuth telluride, tentatively identified (in the absence of X - ray data) as wehrlite has a composition (Bi ~ 59 at%; Te ~ 41 at%) similar to that found and described by Lazarenko (1959) as wehrlite (Bi - 60.4 at%; Te - 39.6 at%); it also lies within the range (Bi - 61 - 55 at% ; Te - 39 - 45 at%) that Sarkar and Deb (1969) found for the same species. However, the analyses from the Lake District fall outside the compositional limits (Bi 55 - 45 at%; Te 45 - 55 at%) suggested for wehrlite by Abrikosov and Bankina (1958) from synthetic investigations in the Bi - Te binary system. The Lake District analyses also differ from the compositions of wehrlite obtained from natural occurrences by Warren and Peacock (1945) and from the theoretical composition (Bi ~ 50 at% ; Te ~ 50 at%).

Warren and Peacock (1945) have suggested that close structural similarities between hedleyite (~ 30 at% Te) and wehrlite (~ 50 at% Te) provide evidence for a range of solid - solution in the Bi - Te system between 30 and 60 at% Te. Synthetic work by Brown and Lewis (1962) has suggested that an unbroken solid - solution series exists from 32 - 60 at% Te (Bi_6Te_3 - Bi_2Te_3), which includes the naturally occurring minerals tellurbismuth and wehrlite (see Fig.8.8) but not hedleyite, and which they designated the β phase. They suggested that the work of Abrikosov and Bankina (1958), who considered wehrlite to be a naturally occurring γ phase, was erroneous due to the long annealing periods necessary to obtain homogeneous products from their coarse - grained cast alloys, and resulting in ambiguous interpretation. Brown and Lewis (1962) found single phase alloys with appropriate cell dimensions within the compositional ranges thought by Abrikosov and Bankina (1958) to contain two phases. The phase diagram given in Fig.8.8 is from Brown and Lewis's (1962) work.

The mineral assemblage of the cobalt - bearing specimens from the Kingsbury Collection was not found to be of much use in determining formation conditions. Other assemblages containing arsenopyrite (see Chapters 4 and 6) have satisfied the conditions necessary for the application of Kretschmar and Scott's (1976) arsenopyrite geothermometer, however arsenopyrite from the Kingsbury Collection specimens has a greater cobalt content than 1 wt% Co and therefore cannot be used.

The presence of early pyrite subsequently replaced by pyrrhotine can be explained either by a rise in temperature, or a decrease in sulphur activity. Provided that the monoclinic pyrrhotine has not inverted from a higher temperature hexagonal pyrrhotine (and there is no evidence for this), the maximum temperature of formation is 248°C (Scott and Kissin, 1973).

Cobaltite analyses have been plotted on the ternary FeAsS - CoAsS - NiAsS diagram (Fig.8.6, 23 - 24) along with cobaltian arsenopyrite and glaucodot analyses (Fig.8.6, 25 - 29). According to Klemm (1965) some of these analyses would indicate formation temperatures of as high as 500 - 600°C, but as mentioned previously there are serious discrepancies between the synthetic data and natural assemblages in the FeAsA - CoAsS - NiAsS system.

The limited amount of material available and the lack of knowledge of the field relations has made interpretation difficult and few diagnostic conclusions can be drawn. Although there are significant differences between the Kingsbury assemblage and those previously reported from the Paddy End and Bonser Veins (Chapter 6) there are some similarities and it seems unlikely that there was any great difference in temperature between them. Suggested temperatures are in the range 200 - 300°C.

CHAPTER 9

CONCLUSIONS

9.1 Classification of Lake District mineralization

Detailed knowledge of the mineralogy of the copper, lead, zinc and cobalt deposits can be used in conjunction with their structural and stratigraphic relations, and the available isotope data, to establish a classification for the Lake District mineralization. A summary of this classification is given in Table 9.1.

In the present study, the earliest hydrothermal deposit in the Lake District, the graphite deposit in Borrowdale, supposedly of pre - Bala age (Strens, 1962, 1965) or of Devonian age (Ineson and Mitchell, 1975), was not investigated.

The Lower Devonian or Caledonian mineralization is characterized by the presence of chalcopyrite, pyrite and arsenopyrite. These three minerals are almost always present, both in mineralization directly associated with granitic intrusions (as with the Shap and Skiddaw Granites) and in mineralization cutting the Lower Palaeozoic strata. Other minerals which are of widespread occurrence in the Lower Devonian veins (except the common gangue minerals) include native bismuth, bismuthinite and pyrrhotine. Typically, these veins have an east - west direction, but in the Caldbeck Fells area they have a north - south trend and in the Coniston area, a northwest - southeast trend.

Sphalerite from the Lower Devonian assemblages usually has an iron content greater than 5 mole% FeS, whereas sphalerite associated with the later lead - zinc mineralization generally contains less than 5 mole% FeS. Galena from the early assemblages is nearly always free of inclusions, but where these do occur (as in the Bonser Vein) they are bismuth sulphosalts (e.g. cosalite), rather than antimony sulphosalts which are found in galenas of the later lead - zinc deposits.

Oxidation assemblages of this early mineralization are of uncertain age.

The stibnite occurrences of St Sunday Crag (Davidson and Thompson, 1948) and Robin Hood, Bassenthwaite (Postlethwaite, 1913) are also of uncertain age but have been placed between the early copper mineralization and the lead - zinc mineralization in Table 9.1. This is because of the absence of antimony minerals associated with the early mineralization (antimony sulphosalts reported from Grainsgill by Kingsbury and Hartley, 1956a, are probably associated with the Carrock East - West lead - zinc vein rather than the tungsten veins) and the presence of antimony minerals at an early stage in the paragenetic sequence in many of the lead - zinc veins.

Isotopic evidence (Ineson and Mitchell, 1974) suggests that the main period of lead - zinc mineralization took place in Upper Devonian to Lower Carboniferous (Dinantian) times (c.330 - 360 Ma), with a late period of barytes mineralization of Upper Carboniferous (Stephanian) to Permian age (c.260 - 290 Ma).

The haematite mineralization of West Cumbria, associated with minor barytes, dolomite, and fluorite, is generally thought to have either a Permo - Triassic age (Shepherd, 1973) or a Post - Triassic age (Gough, 1963; Strens, 1962; Dunham et al., 1978).

Isotopic ages of 180 - 190 Ma (Ineson and Mitchell, 1974) from Roughtongill could relate to the widespread alteration of the primary ore mineral assemblages and host rocks in the Caldbeck Fells area with the production of numerous secondary minerals.

9.2 Compositions and temperatures of the ore - forming fluids

9.2.1 Lower to Mid - Devonian or chalcopyrite - pyrite - arsenopyrite type mineralization

Fluid inclusion data (Shepherd et al., 1976) indicate that the mineralizing fluids of the Carrock Fell tungsten deposit were moderately saline brines (6.8 - 9.6 equivalent wt% NaCl), periodically charged with CO_2 and enriched in tungsten. Homogenization temperatures (corrected for 800 bars pressure) average 295°C for inclusions in mineralized quartz and 275°C for inclusions in barren quartz.

Interpretation of the arsenopyrite and cobalt - iron sulpharsenide mineralization at Scar Crag (see Chapter 3 and Ixer et al., 1979) suggests that the early sulpharsenide minerals in the assemblage formed at slightly higher temperatures (350 - 400°C) than proposed by Shepherd et al. (1976) for the Carrock mineralization. The sulphur activity of the early Scar Crag mineralization was probably $\sim 10^{-10}$ atm; later minerals probably formed at lower temperatures (~300°C) and $aS_2 \sim 10^{-12}$ atm.

Mineralization in the Bonser Vein and in the Dale Head North and Wanthwaite veins is more typical of the Lower Devonian mineralization than the Carrock and Scar Crag occurrences. Early magnetite (and haematite) and arsenopyrite in the Bonser Vein were probably deposited at temperatures of ~350 - 400°C (see Chapter 6) with sulphur activities, $aS_2 \sim 10^{-12}$ atm to $aS_2 \sim 10^{-14}$ atm and oxygen activities, $aO_2 \sim 10^{-24}$ atm to $aO_2 \sim 10^{-29}$ atm (at 350°C). The main chalcopyrite - pyrrhotine - arsenopyrite assemblage was deposited at temperatures of about 240°C, and later minerals at yet lower temperatures of about 200°C. Sulphur activities of 10^{-15} to 10^{-16} atm, and oxygen activities of 10^{-38} to 10^{-44}

atm are indicated for the main period of mineralization in the Bonser Vein, with $aCO_2 \sim 1$ atm at 250°C.

In the Dale Head North Vein (see Chapter 4), early pyrite with cobaltiferous zones was probably deposited at temperatures between 300 - 350°C with $aS_2 \sim 10^{-10}$atm. Arsenopyrite was deposited at 295 - 275°C with $aS_2 \sim 10^{-14}$ atm. Bismuthinite, monoclinic pyrrhotine, chalcopyrite and sphalerite were formed at lower temperatures of 240 - 250°C ($aS_2 \sim 10^{-14}$ atm), and late marcasite, pyrite and galena at <235°C ($aS_2 \geq 10^{-14}$atm).

In the southern Wanthwaite Vein, the early minerals arsenopyrite and pyrrhotine formed at about 310°C with $aS_2 \sim 10^{-13.5}$atm, while later chalcopyrite, sphalerite and pyrite were deposited at ~225°C and $aS_2 \sim 10^{-13}$ atm.

In general, it seems that sulphur activities decreased from ~10^{-10} atm at 300 - 400°C to ~10^{-12} - 10^{-16}atm at 200 - 300°C during the Lower to Mid - Devonian mineralization. In the Bonser Vein, the mineral assemblage enabled an estimate of oxygen activities to be made; these decreased from $aO_2 \sim 10^{-24}$ - 10^{-25}atm at 350°C to $aO_2 \sim 10^{-38}$ - 10^{-44}atm at 250°C. These observations are in reasonable agreement with Holland's (1965) 'main line' ore fluid areas, within which the commonly observed hydrothermal minerals are stable.

Evidence from fluid inclusions in quartz coexisting with chalcopyrite from Castle Nook (Shepherd, personal communication) gives further information on the compositions of the mineralizing fluids, indicating that they were low to moderately saline brines (~5 equivalent wt% NaCl). Corrected homogenization temperatures obtained were 255°C (assuming a purely hydrostatic load of 900 bars) or 345°C (assuming a purely lithostatic load of 2250 bars) for an estimated depth of cover of 9 km.

The formation temperatures and ore fluid compositions determined for the Lower to Mid - Devonian mineralization indicate that there was little regional variation in conditions over the Lake District as a whole. However, local variations in the composition and temperature of the fluids did occur, and these are reflected in the differing mineralogies of the veins. The greatest mineralogical differences (see Table 9.1) from the common chalcopyrite - pyrite - arsenopyrite type assemblages occur in deposits which are closely associated with the Lower Devonian granitic intrusions at Carrock (associated with the Skiddaw Granite), Shap (joint infillings in the Shap Granite and aureole), and Scar Crag (which lies above a supposed stock - like intrusion - Rose, 1955). Elsewhere there is little mineralogical variation, except in the Coniston area, where early magnetite (pseudomorphing haematite) in the Bonser Vein indicates high initial aO_2/aS_2 ratios relative to other Lake District veins of similar age.

9.2.2 Lower Carboniferous or galena - sphalerite type mineralization

Some of the mineralogical distinctions between this Upper Devonian to Lower Carboniferous lead - zinc mineralization and the Lower Devonian copper mineralization have already been discussed (see 9.1). Fluid inclusion studies indicate considerable differences in both the temperatures of the mineralizing fluids and their compositions.

The study of fluid inclusions in fluorite and sphalerite of the lead - zinc mineralization (see Chapter 5) shows that the mineralizing fluids were highly saline brines (>23 equivalent wt% NaCl), often with a complex chemistry (illustrated by the common occurrence of several daughter phases) and always containing significant $CaCl_2$. Corrected homogenization temperatures lie between 110° and 130°C (see Table 5.6). The slightly higher temperatures obtained for the Caldbeck Fells area may be due to relatively lower overburden pressures compared to the Keswick and Helvellyn areas. The results of this study are in agreement with previous data (Smith,1973; Shepherd, personal communication).

The lead - zinc veins generally have a simple primary mineralogy except where the earlier chalcopyrite - pyrite - arsenopyrite type mineralization is also represented in the assemblage (as at Force Crag and Tilberthwaite, and to a minor extent at Driggith). Unlike the earlier Lower Devonian mineralization, the lead - zinc veins contain few minerals diagnostic of any particular temperatures or conditions of formation, therefore it was not possible to propose reasonable estimates of sulphur or oxygen activities.

Although the North Pennines lead - zinc deposits are of a different age and contain considerably more fluorite to those of the Lake District, there are chemical and mineralogical similarities between them. Fluid inclusion studies on fluorites from the North Pennine ores (Sawkins,1966; Rogers,1978) show that the mineralizing fluids had high salinities (similar to those from Lake District fluorites), and temperatures of 150 - 200°C in the Alston Block and 50 - 130°C in the Askrigg Block. Temperatures obtained from fluid inclusion studies on Lake District fluorites (100 - 130°C) are similar to those of the Askrigg Block.

9.2.3 Upper Carboniferous (Stephanian) - Permian barytes mineralization

Very little can be deduced concerning the temperatures and compositions of the mineralizing fluids which deposited the barytes mineralization. It is possible that the secondary fluid inclusions in fluorite of the lead - zinc mineralization may represent this later mineralization. If this is so, then highly saline brines (23 - 25 equivalent wt% NaCl) having temperatures of 100 - 110°C are indicated.

Veins of this type occur in the north and east of the Lake District and are uncommon elsewhere.

9.3 Origins of the mineralization

9.3.1 Lower to Mid - Devonian mineralization

Wheatley (1971), who worked mainly on the volcanogenic sulphide deposits at Avoca, Eire and Parys Mountain, Anglesey, proposed that the felsic volcanic activity exemplified by the Paddy End Rhyolite in the Coniston area, implies that a magma of similar composition existed at depth. On cooling, this magma would have been a locus for circulating connate fluids which may have received additions from juvenile sources on migrating upwards within fault fissures which developed in response to the Caledonian Orogeny. The main problem with this theory is the great length of time which would have elapsed from the felsic volcanic activity which formed the Paddy End Rhyolite at c. 460 Ma, to the deposition of the mineralization in Lower to Mid - Devonian times (c.380 Ma).

Most recent workers on Lake District mineralization have recognized that some relationship exists between the Lower to Mid - Devonian mineralization and both the underlying composite granite batholith and the exposed Lower Devonian granitic intrusions.

Shepherd et al. (1976), in a fluid inclusion and isotope study of the Carrock Fell tungsten deposit, suggested that during the cooling of the Skiddaw Granite non - magmatic, moderately saline fluids were drawn into the northern part of the granite by convective flow from the volcanic rocks to the north. Metasomatic alteration of the granite then occurred with greisenization in the Grainsgill area, and chloritization farther south. A diffuse geochemical halo was created with tungsten preferentially concentrated in the metasomatic micas. The fluids, enriched in silica, mixed with unreacted non - magmatic fluids and moved along open channelways (N - S faults) depositing quartz, wolframite and scheelite.

Dagger (1977) suggested that the copper mineralization in the Lake District was controlled by the granite batholith, with mineralization occurring above the flanks of the batholith and close to ridges in the roof zone. In this model, the granite provided the heat source for the mineralization, being responsible for the redistribution of trace amounts of copper and other ore - forming elements from the Borrowdale Volcanic Group.

Firman (1978b) also noted the close spatial relationship between the mineralization and the granite batholith and proposed that the chalcopyrite - pyrite - arsenopyrite veins might originally have had a volcanic source and that pre - Bala volcanic exhalations may have 'contributed to formation waters which were later recirculated when the Lower Devonian granites were intruded'.

It is apparent from Fig.9.1 that in the northern and central Lake District, the Lower to Mid - Devonian (or 'Caledonian') mineral veins are generally near, and parallel to, ridges in the roof region of the underlying composite granite batholith. Deposits in the southern Lake District near Coniston lie above the South Wall (Bott,1974) of the batholith and are mostly parallel to its margin. Such fractures could have formed during emplacement of the batholith after the main period of Caledonian deformation. A structural relationship with the Lower Devonian granite bodies is not, therefore, in doubt. However, the origin of the mineralizing fluids is less certain.

Fluids derived from the dewatering of the Skiddaw Group or from Silurian strata seem unlikely agents for the mineralization. Copper mineralization in the Skiddaw Group occurs only near its junction with the Borrowdale Volcanic Group, and is absent from the Silurian strata.

The most likely source for the mineralizing fluids is the Borrowdale Volcanic Group. Elsewhere in the Southern Caledonides, at Avoca and Parys Mountain, volcanogenic copper mineralization associated with felsic volcanic activity was deposited in Lower Palaeozoic strata (Pointon, 1979; Thanasuthipitak, 1974). The mineralogy of these stratabound deposits is comparable to that of many of the Lake District copper veins and it is possible that chemically similar fluids existed as formation waters in the Borrowdale Volcanic Group (or in volcanic rocks of the Eycott Group in the northern Lake District).

Certain minerals (e.g. wolframite, scheelite, molybdenite, apatite, purple fluorite and tourmaline) are only found in veins close to, or cutting, the Lower Devonian granite intrusions. It is reasonable to assume that many of the Lake District veins of this age had a magmatic component, dependent on their proximity to the granitic intrusions, in addition to a non - magmatic component. This would indicate a mixing of fluids derived from formation waters of the Borrowdale Volcanic Group or volcanic rocks of the Eycott Group (possibly contributing Cu, Fe, Zn, Pb, Bi, As, S) with partly magmatic fluids associated with the Lower Devonian granites (possibly contributing W, Mo, P, B, F, O, Fe?, Co?). The granites would also have provided a heat source for the circulation of these fluids.

The observed mineralogical differences between many of the

Lower to Mid - Devonian veins can be explained by any or all of the following:

(a) Variation in the ratio of magmatic to non - magmatic fluids;

(b) Petrological and chemical differences between granitic intrusions forming the composite granite batholith;

(c) Petrological and chemical variations in the volcanic rocks of the Eycott and Borrowdale Volcanic Groups;

(d) Minor contributions (possibly Co, Fe, Mn, As, S) from formation waters derived from other sources such as the Skiddaw Group.

9.3.2 Upper Devonian to Lower Carboniferous mineralization

The Upper Devonian to Lower Carboniferous lead - zinc veins differ from the earlier copper veins in showing no obvious relationship to the granite batholith. The veins occur above the roof region and above the North and South Walls (Bott, 1974) of the batholith and are generally N - S or NE - SW in direction, implying an overall E - W tension (Firman, 1978b). The Force Crag and Tilberthwaite lead - zinc veins show evidence of the earlier chalcopyrite - pyrite - arsenopyrite mineralization in addition to the galena - sphalerite mineralization.

Firman (1978b) proposed that uplift of the Lake District towards the end of the Devonian was responsible for the opening of relatively shallow fissures in and above the central and eastern parts of the batholith. These fissures provided channels for mineralizing formation waters, depleted in Cu, Fe, As, S and other elements (due to the deposition of the earlier copper mineralization) and convectively recycled.

Deposits of similar age and mineralogy but of sedimentary or syn - diagenetic origin (Russell,1978) are found in Carboniferous limestones in Ireland. In Scotland, vein deposits similar to those of the Lake District occur in Lower Palaeozoic rocks at Tyndrum (Pattrick, in press) and Leadhills. For these Scottish and Irish deposits, Russell (1978) suggested that the metals and some of the sulphur could have come from Lower Palaeozoic geosynclinal sediments, and that the thermal energy driving the hydrothermal systems may have been heat left over from the Caledonian Orogeny. Halliday (1977) proposed that this Upper Devonian to Lower Carboniferous episode of metallogeny was related to widespread volcanism during the evolution of shelf and geosynclinal seas in Western Europe. In the Lake District, the Lower Carboniferous (Courceyan, Butcher in Mitchell et al., 1978) Cockermouth Lavas are the only evidence of volcanic activity at this time.

If some part of the lead - zinc mineralization originated from the Lower Palaeozoic sediments (as proposed by Russell,1978, and Firman,1978b) it is difficult to understand why deposition did not occur earlier, at the time of the Lower to Mid - Devonian mineralization. It is evident (from 9.2) that the temperatures and compositions of the ore fluids of the two mineralizations were significantly different; for instance, the fluids depositing the lead - zinc mineralization had considerably higher salinities (23 - 25 equivalent wt% NaCl) and lower temperatures (110 - 130°C) to those involved in the earlier mineralization (5 - 10 equivalent wt% NaCl and 200 - 400°C). If the Lower Palaeozoic rocks were the source for the lead - zinc mineralization (in addition to contributing to the earlier copper mineralization), then an additional component would be required to explain these observed differences. Sulphur isotope studies on the Irish base metal deposits of Lower Carboniferous age (Greig et al., 1971) have shown that Carboniferous seawater was involved in mineralization. Hence, it is possible that seawater also contributed to the Lake District lead - zinc mineralization, being drawn in by convective flow generated either by the still - cooling batholith or, more likely, by the magmatic activity associated with the Lower Carboniferous Cockermouth Lavas.

If the Lower Palaeozoic sediments were not the source of the metals, then they may have been leached from the basement granites in a similar manner to that outlined above.

The differences in temperature between the lead - zinc and the earlier copper mineralization could be explained by the lower geothermal gradients in the region as a result of the cooling of the basement granites, or may be due to the erosion of much of the overlying strata subsequent to uplift.

9.3.3 Upper Carboniferous to Permian barytes mineralization

Similarities between the Lake District lead - zinc mineralization and the fluorite - galena - sphalerite - barytes deposits of the North Pennines have been mentioned previously (9.2.2 and Ch.5). However, there are also significant differences which make it possible that there is no link between the lead - zinc mineralization of the Lake District and the North Pennines mineralization. Firstly, the Lake District deposits are of Upper Devonian - Lower Carboniferous age, while the North Pennines mineralization clearly postdates the quartz dolerite Whin Sill (K - Ar isotopic age c. 295 Ma; Fitch and Miller, 1967) and is generally regarded as having an Upper Carboniferous (Stephanian) to Permian age. Secondly, fluorite is not common in the Lake District but is abundant in the Alston area of the North Pennine Orefield. Thirdly, the Lake District lead - zinc mineralization occurs and fluorite on cooling and sulphides and barytes on meeting H_2S and SO_4^{2-} in fluids in structural traps.

9.4 Suggestions for future work

The Lake District has long been a rewarding area for geological research, and, since this has generally created still further problems, there is no shortage of possible topics for study. This is particularly true for the mineralization.

The mineralogy of some of the most important veins has been described and interpreted in this thesis. However, there are still several deposits which remain to be investigated and others which require further study if, and when, representative material can be collected. In addition, a few individual mineralogical topics (for example, the bismuth sulphoselenides and sulphotellurides found at Coniston and the bismuth sulphotellurides at Carrock Mine) need investigating.

In order to obtain further information regarding the temperatures and compositions of the ore - forming fluids, detailed fluid inclusion analysis is necessary, preferably working on both gangue (e.g. quartz, barytes) and ore minerals (e.g. sphalerite). As Firman (1978a) has suggested, one of the most promising fields for research is to attempt to determine the relationship between the mineralizing fluids and the granitic intrusions, through combined chemical, fluid inclusion and stable isotope studies.

APPENDICES

APPENDIX I

ABBREVIATIONS

(a) Mineral names

ah - anhydrite

all - alloclase

an - anglesite

asp - arsenopyrite

bcv - blaubleibender covelline

bm - bismuthinite

bn - bornite

brt - bournonite

bt - barytes

cb - cobaltite

cbp - cobaltiferous pyrite

chl - chlorite

cpy - chalcopyrite

crs - cerussite

ct - calcite

cv - covelline

dg - digenite

dj - djurleite

dm - dolomite

gf - gersdorffite

gl - glaucodot

gn - galena

hm - haematite

h-po - hexagonal pyrrhotine

lö - löllingite

lt - laitakarite

m-po - monoclinic pyrrhotine

mr - marcasite

mt - magnetite

nc - nickeline

po - pyrrhotine

qtz - quartz

rm - rammelsbergite

sf - safflorite

sl - sphalerite

stp - stilpnomelane

thd - tetrahedrite

tm - tourmaline

tnt - tennantite

whr - wehrlite

wt - wittichenite

(b) Other abbreviations

Prefix P - refers to polished sections (followed by reference number)

Prefix T - refers to thin sections (followed by reference number)

Prefix H - refers to hand specimens (followed by reference number)

Å - Angstrom unit (= 10^{-7} mm)

nm - nanometre (= 10^{-6} mm)

µm - micrometre (micron = 10^{-3} mm)

T - temperature in °C

R - Reflectance (R%)

n - refractive index

k - absorption coefficient

N - mole fraction (e.g. N_{FeS} - mole fraction of FeS)

a - activity in atmospheres (other pressures in bars)

APPENDIX II

SPECIMEN PREPARATION AND ANALYTICAL METHODS

(a) Preparation of polished sections

Thick (3 - 4 mm) sections of material were cut from hand specimens with a diamond saw and, after trimming and the removal of saw marks using 400 mesh silicon carbide grit on a rotating cast iron lap (water lubricated), these were placed in polythene moulds and mounted in cold setting araldite. After removal from the mould the edges of the specimens were bevelled to prevent damage to the laps during the polishing stage. The specimens were initially ground by hand using 600 mesh silicon carbide grit on a water - lubricated sheet of plate glass (used solely for 600 mesh grits) so as to remove any araldite covering them and also to obtain a perfectly flat specimen surface. Further grinding with successively finer (800 and 1200 mesh) grades of aluminium oxide was carried out in a similar manner using separate sheets of plate glass for each grade.

After drilling a small hole in the back of the specimens, grinding was continued using 6µm diamond paste on oil lubricated Hyprocel laps on Engis polishing machines. 1µm and ¼µm diamond pastes on similar laps and machines were used to polish the specimens. Unless quantitative reflectance work or electron probe microanalysis was to be carried out on the sections, polishing was stopped at the 1µm stage. Final polishing was achieved using a paste of γ - alumina and water on a clean finger. Polishing times varied but were kept as short as possible in order to avoid polishing relief.

The procedure for making doubly polished thick sections (0.5 - 1.0 mm) for fluid inclusion analysis was similar to that outlined above. Small specimens of material for analysis (fluorite and sphalerite) were mounted in cold setting araldite and sectioned to a thickness of 1 - 1.5 mm using an oil - lubricated 10" saw with automatic specimen feed. This ensured that as little strain as possible was placed on the specimen and enabled the two surfaces to be cut parallel. Grinding was then carried out on a rotating cast iron lap with water lubricated silicon carbide grits. Both sides of each section were ground using 600 mesh and subsequently 800 mesh grits such that the specimen was <1 mm thick prior to polishing. The sections were polished using a specially constructed holder in a similar way to that outlined earlier for 'normal' polished sections. After one side had been polished it was protected from scratching by covering it with adhesive tape.

(b) Quantitative reflectance measurement procedures

Quantitative reflectance values were obtained for alloclase using a similar method to that described by Criddle in Criddle and Stanley (1979) for wittichenite (see Appendix III).

Areas measured were carefully examined for freedom from inclusions and scratches using a Nomarski objective. Measurements were made at the British Museum (Natural History) with a Zeiss Universal microscope equipped with ×16 air and ×16 oil objectives, immersion oil (Zeiss) with $n_D = 1.5150$ at 23°C (as recommended by COM), and a SiC standard. The equipment is semi - automated. A step driven wavelength scanning line - interference filter and a digital voltmeter are on - line to a Hewlett Packard 9830 programmable calculator. Unpublished computer programmes written by G.S.Bearne (B.M.) were used to make measurements at 10 nm intervals from 400 - 700 nm and to derive from the measured reflectances the absorption coefficients (k) and the refractive indices (n).

A modified Lanham stage was used to level and interchange the specimens and the standard which were focussed in white light. For the alloclase specimen, ten spectral scans were made on the measured grain (from P-78K.6.3 , and having a composition corresponding to Table 3.1, 36) in air and in oil and the results averaged (Table AII. 1). One of the scans in oil was discounted due to the obvious presence of an air bubble. The data were plotted and the curves smoothed graphically (Fig.AII.1). The absorption coefficients (k) and refractive indices (n) calculated from the measured reflectance values were also plotted (Fig.AII.2). Instrumental sensitivity below 450 nm resulted in low precision (as can be seen from the standard deviations) mainly due to low readings on the digital voltmeter, and little reliance can be placed on results below this wavelength.

(c) Micro - indentation hardness

A Leitz instrument was used to measure the Vickers hardness number (VHN) of wittichenite (see Table 7.1) and also alloclase, glaucodot and arsenopyrite. Suitable grains for measurement were those without surface scratches or defects and of sufficient area to allow indentation well away from grain boundaries. The indenter, employing a load of 100g, was lowered mechanically on to the specimen over a period of 15 seconds with a loading speed of about 10μm / second, and left for a further 15 seconds before removal.

The diagonals of the indentation were measured using a rotating micrometer ocular, and the final VHN value was calculated using the averages of the two diagonals of the quadrilaterals. At least ten grains were measured for each mineral and the results were averaged. The standard error of the mean was calculated from the formula:-

$\frac{\sqrt{\Sigma(H - \bar{H})^2}}{n^2}$ where $\bar{H}$ is the mean, H an individual observation and n the total number of readings.

The results for alloclase, arsenopyrite and glaucodot are summarized in Table AII.2. Although the arsenopyrite values differ significantly from those obtained by Young and Millman (1964), possibly due to the small number of readings taken, the values for glaucodot are in good agreement with those given by Gammon (1966).

(d) X - ray diffraction

X - ray diffraction techniques were utilized for routine identification of minerals where optical methods were found to be unsatisfactory or non - diagnostic, or where compositions could be determined through variations in cell parameters (e.g. arsenopyrite, cf Kretschmar and Scott, 1976), or where structural data were required for uncommon species (e.g. wittichenite and alloclase).

Usually, powder photographic methods were used, involving scratching a small amount of material from a polished section using a mounted diamond fixed to a microscope. The grains were attached to a thin fibre of glass with a small amount of cow gum or collodion. This fibre was then transferred to an 11.483 cm diameter Debyje - Scherrer powder camera and centred. Exposure times varied, depending on the amount of material, the size of the collimator used, the operating voltage, and whether CuKα (using Ni filter) or CoKα (using Fe filter) radiations were used. After development of the film, lines were measured and corrections applied to compensate for film shrinkage, before calculation of the interplanar spacings (d - values). Intensities were estimated visually.

X - ray data for wittichenite and alloclase are given in Table AII.3 and Table AII.4 respectively.

(e) Electron probe microanalysis

The instrument used was a Cambridge Instruments Microscan V , operated generally at 15 kV but occasionally at 20 kV and employing a beam current of approximately 0.2μA. The standards and radiations measured are given in Table AII.5.

Before analysis, polished sections were coated with a vacuum - evaporated film of carbon about 200 Å thick, and silver dag was used to ensure good conductivity between the specimen holder and the specimen. At least three ten second readings were taken for each point analyzed and background readings were also noted. Standards were measured both before and after analysis of the specimen.

After correction for background and dead - time (Sweatman and Long, 1969), results were corrected using a computer programme devised by Duncumb and Jones (1969).

Analyses totalling less than 98% and more than 102% were discarded, and if necessary, the phase was re - analyzed.

(f) Fluid inclusion analysis

Fluid inclusions are droplets of fluid (usually microscopic) preserved in naturally occurring minerals, and represent samples of mineralizing fluids from some time in the geological past. They are generally designated as primary, pseudosecondary or secondary inclusions, on the basis of their shape and their relationship to growth zones and cleavages.

Thermometric analysis of fluid inclusions in fluorite and sphalerite from Lake District localities was carried out at the Institute of Geological Sciences, London, using the TH 600 heating and freezing stage designed by Dr T.J.Shepherd. This equipment is attached to a Leitz microscope employing long working distance objectives, and was conceived as a dual purpose stage for analysis over the range -180°C to +600°C, with a maximum resolution of ±0.1°C (Shepherd, personal communication).

The equipment consists basically of a thermal block inside a temperature controlled chamber. This chamber has upper and lower glass windows which permit transmitted light to be used during analysis. The upper window is double, allowing a flow of dry air or nitrogen to be passed between the glass layers, thus reducing the amount of condensation at low temperatures. At the centre of the chamber is the thermal block containing a sapphire window on which the specimen to be analysed is placed. The thermocouple is located close to this central window, immediately beneath the specimen.

Small fragments of doubly polished thick (0.5 - 1.0 mm) sections of fluorite and sphalerite were removed from the araldite setting medium and placed on the thermal block inside the chamber. When the equipment was used in the freezing mode, oxygen - free nitrogen, pre - cooled with liquid nitrogen, was circulated through the thermal block. After freezing of the inclusion fluids, the temperature was raised by energizing a resistance heater within the block; the heating rate being controlled by varying the flow of coolant gas and adjusting the power to the resistance heater. When approaching phase transitions (e.g. the final melting point of ice and the final solution point of hydrohalite) the rate of temperature increase was kept below 0.5°C / minute, so as to ensure the attainment of equilibrium. Above room temperature the flow of coolant gas was shut off leaving the heater to achieve the desired temperature. Phase transition temperatures were read off a digital display unit.

A calibration correction was applied to the results obtained, after the equipment had been calibrated with standard melting point substances.

APPENDIX III

PUBLISHED PAPERS

(a) Mineralization at Seathwaite Tarn, near Coniston, English Lake District: The first occurrence of wittichenite in Great Britain.

C.J.Stanley and A.J.Criddle (1979)

(b) New data on wittichenite

A.J.Criddle and C.J.Stanley (1979)

(c) Cobalt -, nickel -, and iron - bearing sulpharsenide minerals from the North of England.

R.A.Ixer, C.J.Stanley, and D.J.Vaughan (1979)

MINERALOGICAL MAGAZINE, MARCH 1979, VOL. 43, PP. 103–7

Mineralization at Seathwaite Tarn, near Coniston, English Lake District: The first occurrence of wittichenite in Great Britain

C. J. STANLEY

Department of Geological Sciences, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET

AND

A. J. CRIDDLE

Department of Mineralogy, British Museum (Natural History), Cromwell Road, London SW7 5BD

SUMMARY. Ore specimens from the abandoned copper mine at Seathwaite Tarn, Cumbria, were studied in polished section by reflected light microscopy. The mineral paragenesis is described and related to current views on Lake District ore genesis. A common origin with the neighbouring deposit at Coniston is proposed. Wittichenite was identified in the ore, and is the first authenticated occurrence in Great Britain.

COPPER mineralization in the Lake District is best seen at Coniston, the centre of mining activity in this area in the late nineteenth century. The mineralization here has been reasonably well documented (Dewey and Eastwood, 1925; Wheatley, 1971 and 1972; Dagger, 1977; Firman, in press), but the small workings near the head of Seathwaite Tarn to the north west of Coniston have received little attention.

Four quartz veins containing small amounts of sulphide mineralization course east–west across rugged, mountainous terrain at 1250–1750 feet OD. The veins dip steeply to the north and average two feet in width (Eastwood in Dewey and Eastwood, 1925), cutting through Seathwaite Tarn andesites and coarse tuffs and agglomerates assigned to the Tilberthwaite Group (Mitchell, 1963) of the Ordovician Borrowdale Volcanic Series (see fig. 1).

The two northernmost veins have been worked from an adit driven 100 fathoms NNW (Eastwood in Dewey and Eastwood, 1925); this is marked on the OS six-inch sheet SD 29 NE as Upper Level (SD 2662 9975). The adit is now collapsed and sulphide mineralization was not found *in situ* at the surface outcrop of the veins. The small spoil heap derived from the adit has yielded a variety of copper sulphides and the rare copper bismuth sulphide, wittichenite. This is the first confirmed occurrence of wittichenite in the British Isles.

Previously, Garby (1848, p. 86) reported that 'cupreous bismuth was found at Huel Buller (Cornwall) in perfect hexagonal prisms'. These crystals 'were tin white and lustrous' but the lustre was soon lost on exposure. Collins (1871, p. 106) mentioned this occurrence, and others from Botallack and Levant, and suggested that Garby's cupreous bismuth 'may possibly have been' wittichenite.

It is also possible that the klaprotholite (klaprothite) observed in polished section from Redruth, Cornwall (Krieger, 1940) was wittichenite, for in Nuffield's (1947) X-ray study of klaprothite, which included an examination of some of Krieger's material (from Wittichen, not Redruth) he concluded that klaprothite was identical to wittichenite. However, Springer and Demirsoy (1969) found that klaprothite from Wittichen had the same chemistry as emplectite but was different optically: they concluded that klaprothite is identical with cuprobismutite, a dimorph of emplectite.

Mineralogy. The only previous description of the mineralogy of Seathwaite is by Eastwood (in Dewey and Eastwood, 1925) who found 'in addition to copper pyrites, an appreciable quantity of copper glance'. The mineralogy of the Seathwaite vein material reported here was studied in polished section by reflected light microscopy. The main sulphide assemblage consists of digenite, djurleïte, and bornite, with smaller amounts of wittichenite, chalcopyrite, blaubleibender covelline, covelline, arsenopyrite, cobaltite, and pyrite in a hematitized quartz–chlorite matrix. Wittichenite, usually associated with microcrystalline hematite, occurs along grain boundaries, fractures, and structural planes

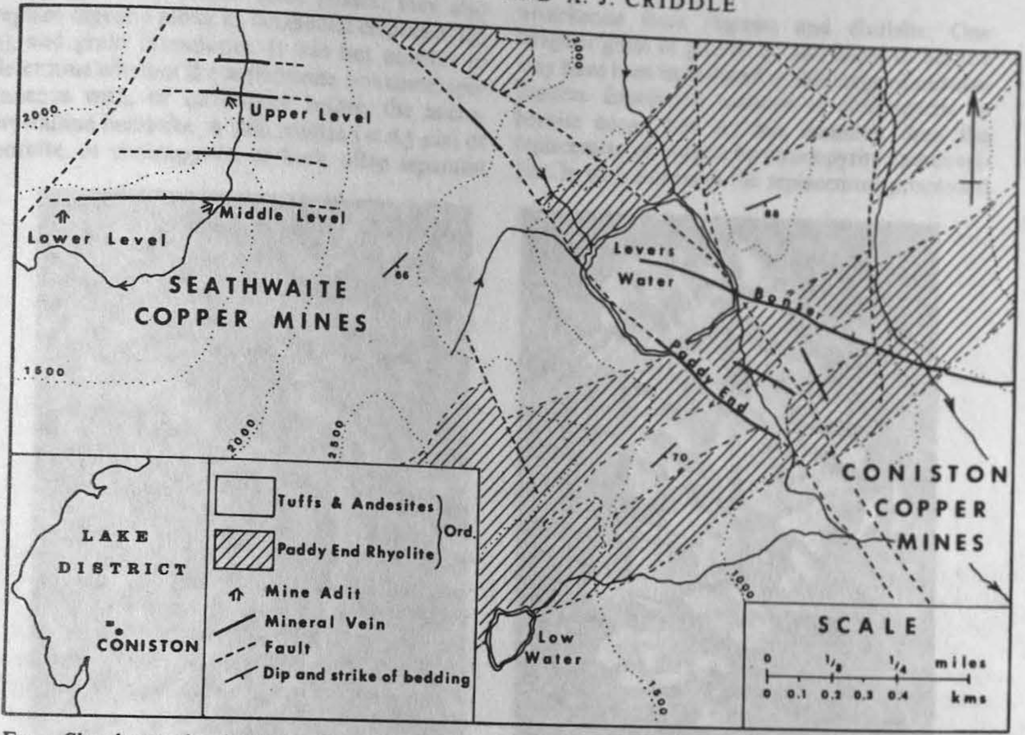
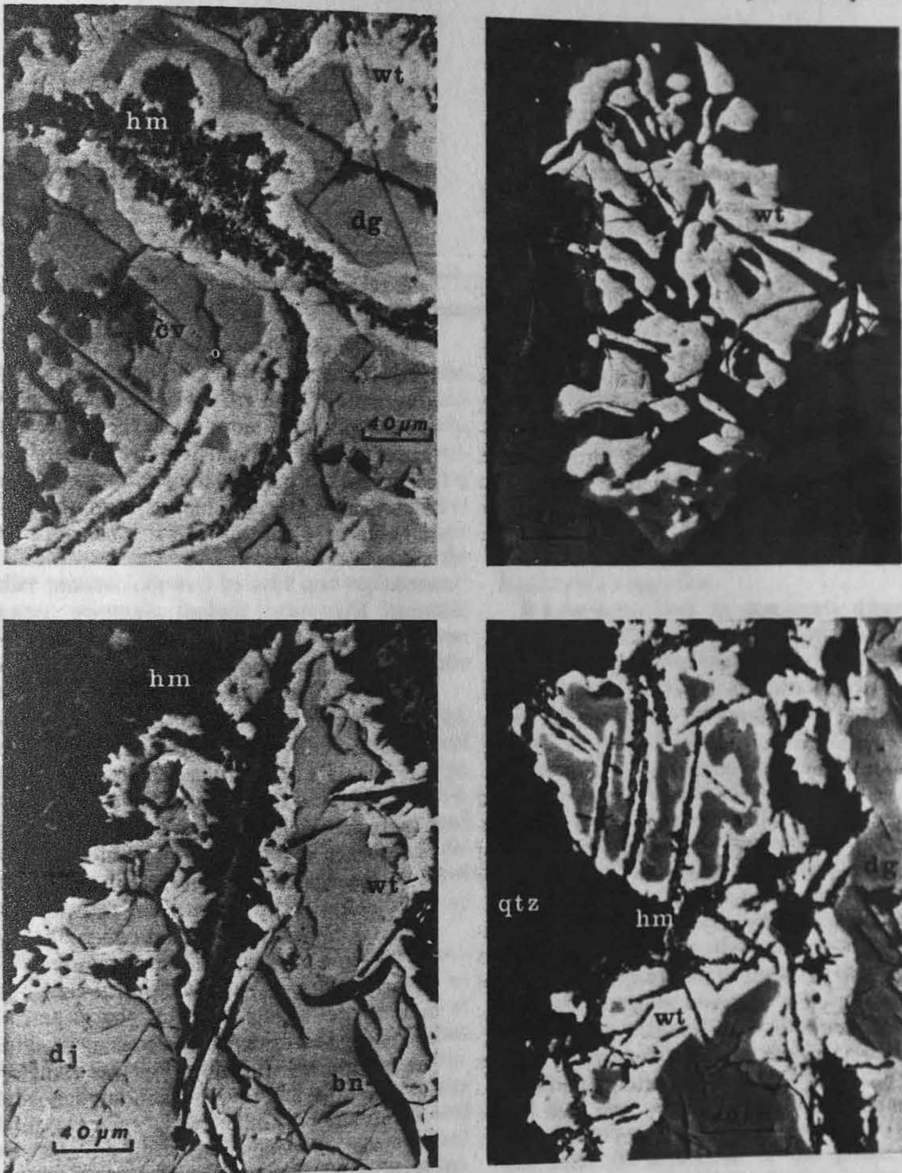


FIG. 1. Sketch map showing the location of Seathwaite and Coniston mines; the geology is based on Mitchell (1940 and 1963).

in the digenite and djurleïte (fig. 2). It is also found as graphic intergrowths with digenite and bornite (fig. 3). Descriptive and analytical data for Seathwaite wittichenite (BM 1977, 172), and for a specimen from Wittichen, Wolfach, Baden (Criddle and Stanley, 1979), are presented and compared later in this journal.

Paragenesis. Chalcopyrite-pyrite-arsenopyrite mineralization in the Lake District occupies normal faults with a predominantly E-W trend, which are assigned to earth movements associated with the Caledonian Orogeny (Strens, 1962; Dagger, 1977). This 'typical' mineral association, which is well developed at Coniston, is also seen at Seathwaite. However, this study has shown that the assemblage at Seathwaite is more varied and the paragenesis, particularly of the copper sulphides, more complex, than has been shown for the Coniston assemblage (Dagger, 1977).

The earliest mineralization at Seathwaite appears to have been of quartz with chlorite and minor amounts of hematite. The main sulphide assemblage was deposited after brecciation of these quartz-chlorite veins. In the ore-mineralized parts of the veins the quartz fragments are rarely more than a few cm across. Minor amounts of euhedral pyrite (< 0.8 mm), arsenopyrite (< 0.1 mm) and euhedral to subhedral cobaltite (< 0.5 mm) were introduced into the breccia before cementation by copper sulphides. Digenite and djurleïte are interpreted as the first formed copper sulphides. Both replace early quartz and hematite and, to a lesser extent, pyrite and arsenopyrite. Digenite and djurleïte were contiguous in none of the polished mounts in which both minerals were found. For this reason it was not possible to determine their age relationships with any certainty. Sillitoe and Clark (1969) suggest that digenite may be formed by the oxidation of djurleïte, and that further oxidation may lead to the formation of covelline and blaubleibender covelline. Both these minerals have replaced digenite at Seathwaite, but their position in the paragenetic sequence as a whole is uncertain. Digenite and djurleïte have been replaced by most of the later minerals: bornite replaces digenite extensively and, less commonly, forms sigmoidal replacement textures with djurleïte (fig. 4). Wittichenite occurs as discrete areas (0.2 mm) in graphic intergrowths with digenite and bornite (fig. 3), but is more commonly associated with microcrystalline hematite. Together they separate digenite and djurleïte from early quartz, and occupy fractures within these phases; they also replace digenite along its octahedral cleavages (fig. 5), and grain boundaries. It was not possible to determine whether the wittichenite was contemporaneous with, or introduced before, the microcrystalline hematite. A thin margin (< 0.5 μm) of bornite, or chalcopyrite, or both, often separates wittichenite from digenite and djurleïte. One irregular grain of gold (*c.* 20 μm) found in bornite may have been introduced at this stage of mineralization. Exsolution textures of chalcopyrite in bornite occur, but are less common than the replacement of bornite by chalcopyrite and covelline. In such instances the replacement proceeded



FIGS. 2–5: FIG. 2 (*top left*). Covelline replaced digenite along cleavages and fractures. Wittichenite and hematite also replace digenite. FIG. 3 (*top right*). Graphic intergrowth of wittichenite and digenite. FIG. 4 (*bottom left*). Djurleïte replaced by bornite and wittichenite. Wittichenite is separated from djurleïte by a thin margin of chalcopyrite (white) and bornite. Hematite and wittichenite are closely related. FIG. 5 (*bottom right*). Wittichenite and hematite replace digenite at grain boundaries and along structural planes.

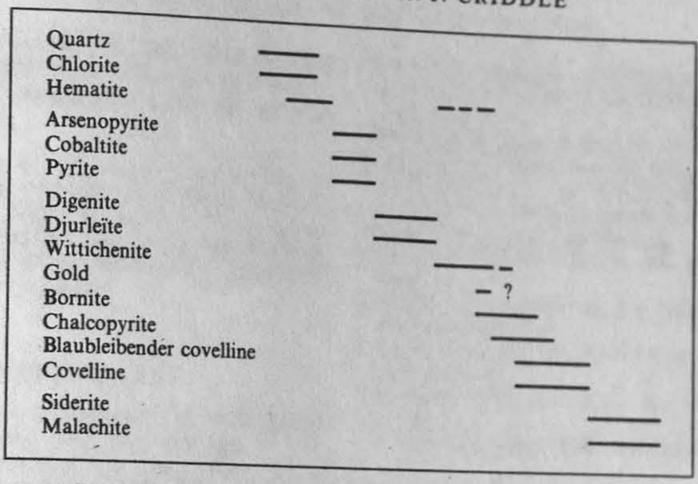


FIG. 6. Paragenetic relationships of vein minerals at Seathwaite.

along fractures and structural planes in the bornite. Covelline also defines cleavages in digenite and has sometimes replaced it more extensively. Similarly, blaubleibender covelline, in replacing digenite, utilized the host's structure, and, as with covelline, diffuse and more extensive replacements spread out from the earlier linear features. Many of these textures are characteristic of shrinkage of the earlier phases followed by infill and replacement.

Later minerals include botryoidal hematite, siderite, and small amounts of malachite. These observations are summarized in the paragenetic diagram (fig. 6).

Genesis. The major Coniston copper veins, Paddy End and Bonser, besides having the usual chalcopyrite-arsenopyrite-pyrite assemblage, carry small amounts of native bismuth and bismuthinite. In the Bonser vein, native bismuth and bismuthinite are more abundant in material derived from deep levels in magnetite-rich portions of the vein, whereas in the Paddy End vein they occur mainly as minute inclusions in chalcopyrite.

The origin of the copper mineralization at Coniston has been interpreted by Dagger (1977) as resulting from redistribution of trace amounts of copper and other elements from the Borrowdale Volcanic Series, the heat source being the underlying basement granite. Firman (1978) speculates that pre-Bala volcanic exhalations contributed 'formation waters', which were later recirculated when the Lower Devonian granites were intruded. Eastwood has suggested (in Dewey and Eastwood, 1925) that the veins at Seathwaite are probably continuations of the Coniston veins, but field evidence for this is not entirely convincing because, although the northernmost part of the Bonser vein swings towards the Seathwaite veins E-W trend, most of the Coniston veins have a NW-SE trend (fig. 1). There are, however, broad similarities in the paragenesis of both groups of veins and, although we have identified more copper sulphides in one stage of mineralization at Seathwaite than have yet been found at Coniston, the presence of wittichenite at Seathwaite and native bismuth and bismuthinite at Coniston offers some support for Eastwood's suggestion.

It is apparent from the paragenetic diagram (fig. 6) that the mineralization at Seathwaite was discontinuous, and consisted of three main episodes: an early quartz-chlorite and hematite stage, which was subsequently brecciated; an arsenopyrite, pyrite, and cobaltite stage, and finally the main copper-bismuth sulphide stage. The relatively superficial late oxidation assemblage may be considered to constitute a fourth episode.

There are similarities between this sequence and the sequence advocated, for Coniston, by Dagger (1977). He regarded the quartz-chlorite phase as a 'rock alteration' phenomenon rather than an episode in mineralization, and concluded (p. 201) that the sequence there consisted of three episodes: an early hematite phase; a pyrite-chalcopyrite-arsenopyrite-magnetite 'main' phase; and a 'carbonate' phase. However, he also suggested (p. 198) that the 'primary mineralization' was a single phase and that this involved 'sequential deposition of minerals and only minor replacement textures . . .'. The order of deposition of this phase, namely magnetite, arsenopyrite, pyrrhotine, pyrite, marcasite, chalcopyrite, blende, galena, bismuth, and bismuthinite is similar to that at Seathwaite where this mineralization is divided into two separate episodes and where there is ample textural evidence of replacement.

We conclude that the Coniston and Seathwaite deposits, which share many of the characteristics of the classical hydrothermal sequences, also share a common genesis.

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New data on wittichenite

A. J. CRIDDLE

Department of Mineralogy, British Museum (Natural History), Cromwell Road, London SW7 5BD

AND

C. J. STANLEY

Department of Geological Sciences, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET

SUMMARY. The wittichenite (BM 1977, 172) discovered in the course of a reflected light study of polished sections from the Seathwaite deposit, Cumbria (described earlier in this journal by Stanley and Criddle), is the first authenticated occurrence of the species in Great Britain; for this reason it was examined in detail and compared with a specimen (BM 1437) from Wittichen, the type locality. Chemical analyses, cell dimensions, visible-spectrum reflectances, quantitative colour values, and VHN's are provided. They are in agreement with previously published data for the species.

Specimen preparation. Specimens from both localities were mounted in epoxy resin and ground by hand on water-lubricated glass plates with 600-grade and 800-grade carborundum and 1200-grade alumina. Grinding was continued with 14 μm, 6 μm, and 3 μm diamond on water-lubricated Hyprocel laps on Engis machines. A thick paste of MgO in distilled water was used on a stationary cloth lap for the final stage of polishing, which was by hand. This was found preferable to the finer grades of diamond in that a 'perfect' polish was achieved in less than 30 seconds, thus reducing polishing relief induced by the extended polishing times needed for finishing with diamond.

Measurement procedure. Six specimens labelled as wittichenite, from Wittichen, in the BM (NH) collection were examined, but only one was found suitable for measurement. In this, and in the Seathwaite specimens, the areas measured were examined for freedom from inclusions and surface imperfections with a ×40 Nomarski objective. Three areas were selected for measurement on each of the Wittichen and Seathwaite mounts.

Measurements were made with a Zeiss Universal microscope equipped with ×16 air and ×16 oil objectives, immersion oil (Zeiss) $n_D = 1.5150$ at 23 °C and a SiC standard no. 232. This equipment is semi-automated. A step driven, wavelength scanning, line-interference filter and a digital voltmeter are 'on line' to a Hewlett Packard 9830 programmable calculator. An unpublished program written by G. S. Bearne was used to make measurements at 10 nm intervals from 400–700 nm and to derive from the measured reflectances the absorption coefficients, refractive indices, and quantitative colour values with respect to the CIE illuminants A, D_{65}, and C.

A modified Lanham stage was used to level and to interchange the specimens and the standard, which were focused in white light. As the precision of this apparatus was poor below 450 nm, at least two spectral scans were made for each grain measured and the results averaged. These data were plotted on a scale of $1\,\%\,R = 20$ nm, and the curves smoothed graphically. The smoothed values (Tables I and II) differ from the measured values by no more than 0.2 % (absolute) at any wavelength. The quantitative colour values, Table III, were derived from these data by the weighted-ordinate method. The ordinates used were weighted for the wavelength range commonly employed in ore microscopy, that is, 400–700 nm, and not for the range generally used in colorimetry of 380–770 nm. The two-dimensional colour-space coordinates (polar) were derived mathematically from the rectangular chromaticity coordinates. Table III includes colour values with respect to the two illuminants recommended by the CIE, A, and D_{65} and for the C illuminant used in the IMA/COM Quant. Data File.

Optical characteristics. In plane-polarized light (colour temperature *c.* 3000 °K), wittichenite from Seathwaite is white to creamy-white; there is no change in its colour in oil. Under the same conditions of illumination the wittichenite from Wittichen appeared greyish-white and to have a lower reflectance. Neither reflectance-pleochroism nor bireflectance were discernible. However, all the grains examined were weakly anisotropic; between crossed polars the rotation tints are varying shades of dark brown.

The spectral reflectance curves for the species, from both localities, are similar and are weakly dispersed. For this reason individual curves have not been plotted; instead, the extreme *R*-values, in air and in oil, for each wavelength were selected, tabulated (Table IV), and plotted (fig. 1). It will be seen that the data for Seathwaite material are in good agreement with those obtained from the topotype specimen. Both are in excellent agreement with Caye and Pasdeloup's data quoted in the IMA/COM card 1.9760 (1977), for the species (from Butte, Montana, USA).

The complete reflectance data for each grain (Tables I and II) reveal that the R_2 curves for grain 1 from Seathwaite and grains 4 and 6 from Wittichen cross the corresponding R_1 curves at *c.*420 nm in air. In oil, R_2 crosses R_1 at *c.*400 nm for the Seathwaite grain 1 as it does for grain 6 from Wittichen. The trend of these curves is shown for the wavelength range 400–500 nm for both media (fig. 1). In the absence of oriented sections we cannot explain the consistent crossover at *c.*420 nm.

The reflectance curves and tables show that the difference in colour and brightness between the Seathwaite and Wittichen wittichenites, noted

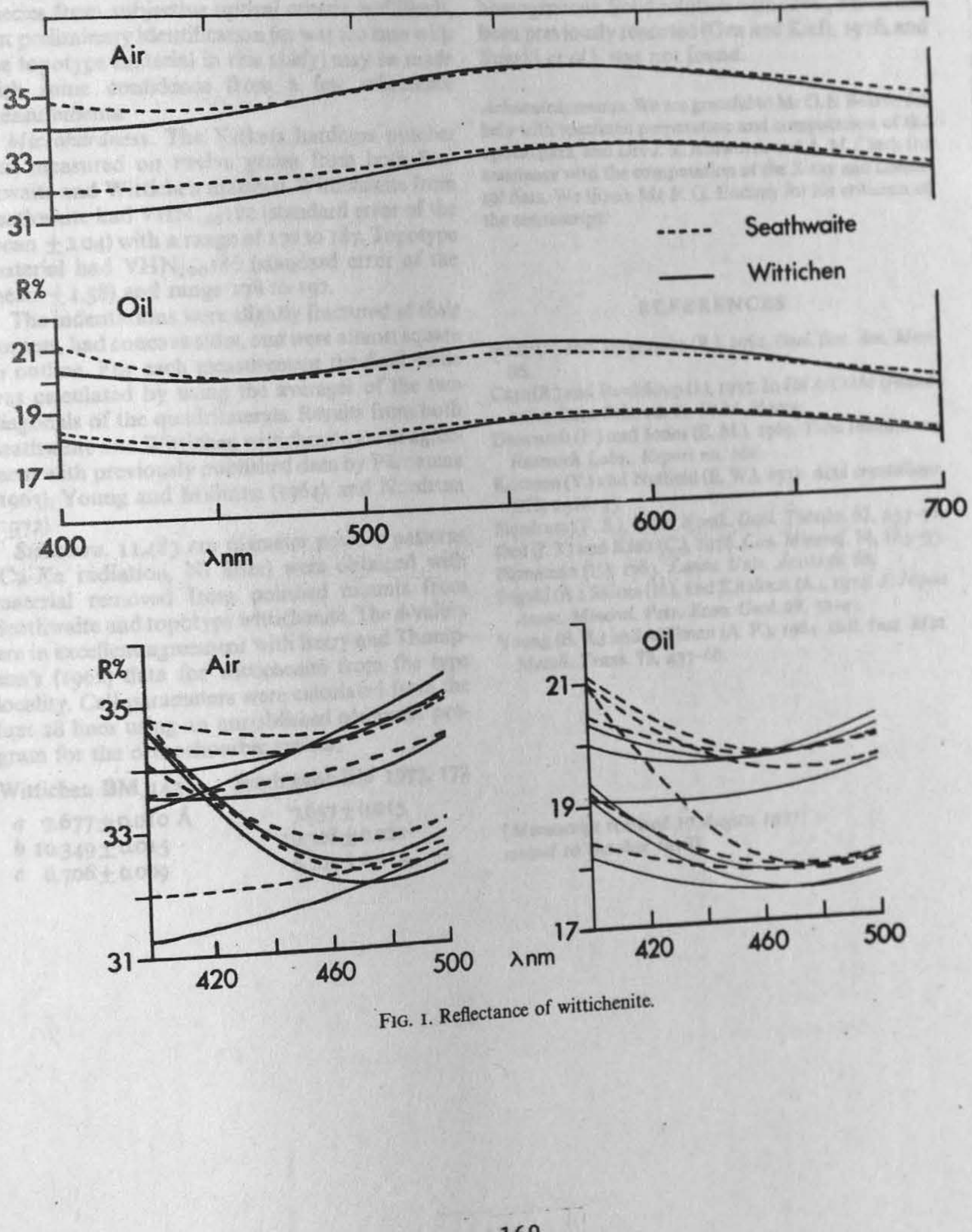

FIG. 1. Reflectance of wittichenite.

earlier, is not real. It is a result of the eyes' poor memory for brightness and colour, particularly where, as in this case, the associated minerals in the two mounts are different. In the Seathwaite specimens many of the associated minerals, including bornite, digenite, djurleïte, hematite, and covelline, are more strongly saturated, differ in hue and, in general, have lower brightness levels than has wittichenite. Hence, the wittichenite appears white to creamy-white, and to have a relatively high reflectance. In comparison, in the Wittichen mount, it appears greyish-white and not as highly reflecting. This is because it is associated with other copper bismuth and bismuth sulphides, which are similar in hue and saturation, but have higher reflectances. For these reasons, identification of the species from subjective optical criteria is difficult, but preliminary identification (as was the case with the topotype material in this study) may be made with some confidence from a few reflectance measurements.

Microhardness. The Vickers hardness number was measured on twelve grains from both Seathwaite and Wittichen material. Wittichenite from Seathwaite had VHN_{100}180 (standard error of the mean ±2.04) with a range of 170 to 187. Topotype material had VHN_{100}186 (standard error of the mean ±1.58) and range 178 to 197.

The indentations were slightly fractured at their corners, had concave sides, and were almost square in outline. For each measurement the final value was calculated by using the averages of the two diagonals of the quadrilaterals. Results from both Seathwaite and Wittichen wittichenite are in agreement with previously published data by Pärnamaa (1963), Young and Millman (1964), and Nordrum (1972).

Structure. 11.483 cm diameter powder patterns (Cu-$K\alpha$ radiation, Ni filter) were obtained with material removed from polished mounts from Seathwaite and topotype wittichenite. The *d*-values are in excellent agreement with Berry and Thompson's (1962) data for wittichenite from the type locality. Cell parameters were calculated from the first 28 lines using an unpublished computer program for the orthorhombic system:

	Wittichen BM 1437	Seathwaite BM 1977, 172
a	7.677±0.010 Å	7.657±0.015
b	10.349±0.015	10.308±0.022
c	6.706±0.009	6.707±0.013

Chemistry. Six areas of wittichenite on the Seathwaite sections and seven on the Wittichen section were analysed by electron probe. In both cases three of the analyses were on scribed areas previously used for reflectance measurements. A Cambridge Microscan 5 operated at 20 kV was used, the radiations measured being Bi-$L\alpha$, Cu-$K\alpha$, S-$K\alpha$ and using standards Bi_2S_3, Cu, and FeS_2. The results (Table VI) were corrected using a computer program devised by Duncumb and Jones (1969).

The average compositions Cu 38.0; Bi 42.8; S 18.3% for Seathwaite and Cu 37.7; Bi 43.4; S 18.7% for Wittichen material compare well with published data (Sugaki *et al.* 1974; Kocman and Nuffield, 1973) and the stoichiometric composition. Wittichenite from both localities is chemically homogeneous. Solid solution with silver, which has been previously reported (Oen and Kieft, 1976, and Sugaki *et al.*), was not found.

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Table I

Reflectance data (Air)

	Seathwaite						Wittichen					
Grains -	1		2		3		4		5		6	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	33.62	34.77	34.83	34.10	34.38	32.02	33.36	34.65	34.02	31.31	33.56	34.58
410	33.65	34.22	34.73	33.80	34.34	32.04	33.51	34.15	34.03	31.37	33.54	34.03
420	33.68	33.68	34.64	33.54	34.30	32.09	33.67	33.68	34.05	31.45	33.52	33.53
430	33.71	33.22	34.57	33.27	34.30	32.11	33.85	33.23	34.08	31.55	33.51	33.00
440	33.75	32.82	34.53	33.03	34.30	32.16	34.03	32.86	34.14	31.67	33.51	32.57
450	33.81	32.51	34.50	32.87	34.31	32.23	34.25	32.60	34.22	31.78	33.53	32.28
460	33.88	32.33	34.53	32.76	34.37	32.30	34.50	32.46	34.35	31.91	33.60	32.12
470	33.98	32.26	34.58	32.75	34.45	32.39	34.73	32.45	34.50	32.04	33.72	32.06
480	34.10	32.27	34.67	32.79	34.61	32.41	34.92	32.50	34.67	32.18	33.88	32.05
490	34.23	32.35	34.82	32.88	34.73	32.50	35.12	32.62	34.88	32.36	34.08	32.12
500	34.37	32.46	34.98	33.01	34.90	32.67	35.31	32.77	35.06	32.55	34.27	32.24
510	34.50	32.57	35.17	33.14	35.09	32.80	35.47	32.92	35.23	32.73	34.44	32.42
520	34.60	32.69	35.31	33.26	35.24	33.00	35.60	33.06	35.38	32.91	34.58	32.59
530	34.69	32.80	35.40	33.37	35.40	33.12	35.70	33.22	35.49	33.06	34.69	32.76
540	34.80	32.91	35.47	33.47	35.49	33.28	35.77	33.38	35.56	33.19	34.77	32.92
550	34.88	33.00	35.55	33.55	35.51	33.32	35.83	33.50	35.59	33.34	34.82	33.04
560	34.95	33.09	35.58	33.61	35.59	33.40	35.82	33.60	35.62	33.44	34.86	33.14
570	34.99	33.17	35.60	33.66	35.58	33.46	35.78	33.67	35.62	33.52	34.87	33.21
580	35.01	33.22	35.61	33.71	35.54	33.47	35.74	33.70	35.59	33.56	34.87	33.25
590	35.01	33.24	35.58	33.72	35.50	33.46	35.65	33.70	35.55	33.56	34.84	33.27
600	35.00	33.24	35.55	33.71	35.50	33.41	35.56	33.66	35.46	33.53	34.80	33.26
610	34.96	33.20	35.50	33.64	35.42	33.38	35.44	33.58	35.37	33.47	34.73	33.22
620	34.90	33.14	35.43	33.56	35.33	33.30	35.33	33.48	35.24	33.40	34.64	33.14
630	34.85	33.07	35.34	33.48	35.13	33.20	35.20	33.36	35.11	33.31	34.54	33.06
640	34.79	33.02	35.25	33.37	35.01	33.13	35.17	33.22	34.98	33.19	34.42	32.94
650	34.73	32.94	35.16	33.26	34.98	33.00	34.93	33.06	34.84	33.06	34.30	32.82
660	34.65	32.86	35.05	33.14	34.88	32.82	34.77	32.91	34.72	32.92	34.18	32.68
670	34.56	32.77	34.94	33.02	34.80	32.71	34.63	32.73	34.58	32.75	34.04	32.56
680	34.47	32.66	34.83	32.90	34.72	32.61	34.47	32.59	34.44	32.58	33.92	32.43
690	34.37	32.57	34.78	32.79	34.64	32.49	34.32	32.42	34.30	32.43	33.79	32.27
700	34.25	32.47	34.63	32.68	34.53	32.38	34.14	32.24	34.18	32.27	33.67	32.13

Table II

Reflectance data (Oil)

	Seathwaite						Wittichen					
Grains -	1		2		3		4		5		6	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	21.00	21.04	21.15	19.25	20.52	18.42	20.08	19.38	20.36	18.20	19.16	19.14
410	20.70	20.45	20.78	18.95	20.37	18.38	19.89	18.98	20.18	18.04	19.14	18.81
420	20.37	19.85	20.47	18.67	20.19	18.28	19.77	18.61	20.03	17.89	19.11	18.48
430	20.08	19.23	20.20	18.40	20.00	18.12	19.70	18.32	19.90	17.76	19.10	18.18
440	19.85	18.68	20.00	18.22	19.90	18.03	19.70	18.10	19.80	17.66	19.12	17.94
450	19.67	18.27	19.89	18.07	19.87	17.94	19.75	17.95	19.73	17.60	19.15	17.74
460	19.56	18.05	19.84	18.00	19.81	17.88	19.85	17.85	19.70	17.56	19.21	17.62
470	19.49	17.92	19.83	17.97	19.78	17.81	19.95	17.88	19.75	17.54	19.24	17.55
480	19.49	17.90	19.86	17.97	19.80	17.83	20.10	17.93	19.84	17.56	19.32	17.55
490	19.55	17.94	19.92	18.04	19.91	17.88	20.23	18.01	19.97	17.64	19.43	17.61
500	19.66	18.00	20.04	18.15	20.03	17.98	20.38	18.11	20.10	17.77	19.58	17.71
510	19.77	18.08	20.14	18.28	20.12	18.10	20.50	18.24	20.24	17.93	19.73	17.83
520	19.87	18.17	20.25	18.38	20.21	18.23	20.65	18.38	20.34	18.08	19.88	17.96
530	19.96	18.25	20.32	18.47	20.21	18.39	20.70	18.51	20.38	18.23	19.97	18.08
540	20.04	18.33	20.35	18.53	20.23	18.50	20.75	18.62	20.42	18.35	20.02	18.17
550	20.08	18.39	20.36	18.57	20.29	18.50	20.75	18.70	20.44	18.43	20.04	18.25
560	20.13	18.44	20.36	18.61	20.31	18.54	20.75	18.74	20.44	18.50	20.05	18.34
570	20.14	18.47	20.36	18.64	20.32	18.62	20.70	18.74	20.43	18.52	20.05	18.39
580	20.16	18.49	20.35	18.65	20.31	18.63	20.63	18.73	20.38	18.53	20.04	18.42
590	20.15	18.48	20.31	18.63	20.30	18.60	20.53	18.70	20.33	18.52	20.00	18.40
600	20.13	18.47	20.25	18.57	20.22	18.55	20.40	18.63	20.25	18.50	19.93	18.38
610	20.08	18.43	20.17	18.50	20.12	18.48	20.27	18.54	20.16	18.44	19.84	18.33
620	20.03	18.38	20.08	18.41	20.01	18.39	20.12	18.44	20.06	18.36	19.74	18.25
630	19.95	18.31	20.00	18.33	19.90	18.31	19.99	18.33	19.95	18.28	19.65	18.18
640	19.87	18.23	19.91	18.23	19.81	18.19	19.85	18.21	19.83	18.18	19.56	18.09
650	19.80	18.14	19.81	18.14	19.72	18.11	19.72	18.08	19.69	18.08	19.45	17.98
660	19.73	18.05	19.73	18.05	19.60	18.02	19.58	17.93	19.56	17.97	19.35	17.88
670	19.63	17.97	19.63	17.97	19.50	17.91	19.46	17.80	19.44	17.84	19.24	17.77
680	19.54	17.87	19.54	17.87	19.38	17.82	19.32	17.68	19.31	17.72	19.13	17.64
690	19.44	17.79	19.44	17.79	19.30	17.70	19.20	17.52	19.17	17.56	19.02	17.54
700	19.35	17.69	19.35	17.69	19.21	17.61	19.03	17.37	19.05	17.43	18.92	17.44

Table III Quantitative Colour Values

		AIR					OIL				
		x	y	λ_D	P_e%	Y	x	y	λ_D	P_e%	Y
SEATHWAITE											
A	R_1	0.4483-0.4489	0.4094-0.4098	576-579	1.9-2.2	34.5-35.4	0.4470-0.4481	0.4088-0.4094	560-576	0.8-1.3	20.0-20.2
	R_2	0.4484-0.4489	0.4082-0.4096	578-582	1.1-2.3	33.0-33.5	0.4475-0.4485	0.4076-0.4096	518-577	0.0-2.1	18.4-18.5
D_{65}	R_1	0.3146-0.3151	0.3323-0.3329	569-572	1.4-1.7	34.8-35.4	0.3132-0.3141	0.3307-0.3314	561-575	0.7-0.9	20.0-20.2
	R_2	0.3142-0.3152	0.3330-0.3310	574-582	0.7-1.8	33.0-33.5	0.3130-0.3149	0.3279-0.3322	-534-572	0.5-1.5	18.3-18.5
C	R_1	0.3120-0.3125	0.3194-0.3201	570-573	1.4-1.6	34.8-35.4	0.3106-0.3115	0.3178-0.3185	562-576	0.7-0.8	20.0-20.2
	R_2	0.3116-0.3127	0.3172-0.3201	572-585	0.6-1.7	33.0-33.5	0.3103-0.3123	0.3150-0.3194	-542-573	0.6-1.4	18.3-18.5
WITTICHEN											
A	R_1	0.4480-0.4485	0.4099-0.4106	573-576	2.1-2.4	34.7-35.6	0.4463-0.4480	0.4102-0.4113	561-573	1.4-2.5	19.9-20.5
	R_2	0.4486-0.4499	0.4086-0.4101	579-582	1.7-3.4	33.0-33.4	0.4480-0.4491	0.4090-0.4101	574-581	2.1-3.2	18.2-18.6
D_{65}	R_1	0.3146-0.3149	0.3332-0.3343	565-569	1.8-2.1	34.7-35.6	0.3135-0.3149	0.3327-0.3344	558-567	1.3-2.0	19.9-20.5
	R_2	0.3147-0.3165	0.3308-0.3344	572-579	1.1-2.6	32.9-33.4	0.3147-0.3162	0.3313-0.3336	570-578	1.4-2.3	18.2-18.5
C	R_1	0.3121-0.3124	0.3204-0.3215	566-570	1.7-2.0	34.7-35.6	0.3110-0.3123	0.3198-0.3215	559-567	1.2-1.9	19.9-20.5
	R_2	0.3121-0.3139	0.3179-0.3216	573-581	1.0-2.5	32.9-33.4	0.3121-0.3136	0.3185-0.3209	571-580	1.3-2.2	18.2-18.5

The values are relative to the CIE illuminants A, D_{65} and C, having colour temperatures of 3300°K, 6500°K and 6750°K respectively. The rectangular coordinates are x and y from which were derived the polar coordinates λ_D, the dominant wavelength, and P_e%, the excitation purity. Y is the 'luminance'. As the colour values were so similar for all the grains measured the range of values is shown rather than individual grain values.

Table IV Reflectance Data

	Seathwaite				Wittichen			
	AIR		OIL		AIR		OIL	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2
400	34.8	32.0	21.2	18.4	34.0	31.3	20.4	18.2
420	34.6	32.1	20.5	18.3	34.1	31.5	20.0	17.9
440	34.5	32.2	20.0	18.0	34.1	31.7	19.8	17.7
460	34.5	32.3	19.8	17.9	34.5	31.9	19.9	17.6
470	*34.6*	*32.3*	*19.9*	*17.9*	*34.7*	*32.0*	*20.0*	*17.6*
480	34.7	32.3	19.9	17.8	34.9	32.1	20.1	17.6
500	35.0	32.5	20.0	18.0	35.3	32.3	20.4	17.7
520	35.3	32.7	20.3	18.2	35.6	32.6	20.7	18.0
540	35.5	32.9	20.4	18.3	35.8	32.9	20.8	18.2
546	*35.6*	*33.0*	*20.4*	*18.3*	*35.8*	*33.0*	*20.8*	*18.2*
560	35.6	33.1	20.4	18.4	35.8	33.1	20.8	18.3
580	35.6	33.2	20.4	18.5	35.7	33.3	20.6	18.4
589	*35.6*	*33.2*	*20.4*	*18.5*	*35.7*	*33.3*	*20.5*	*18.4*
600	35.6	33.2	20.3	18.5	35.6	33.3	20.3	18.4
620	35.4	33.1	20.1	18.4	35.3	33.1	20.1	18.3
640	35.3	33.0	19.9	18.2	35.1	32.9	19.9	18.1
650	*36.2*	*32.9*	*19.8*	*18.1*	*35.0*	*32.8*	*19.7*	*18.0*
660	35.1	32.8	19.7	18.0	34.8	32.7	19.6	17.9
680	34.8	32.6	19.5	17.8	34.5	32.4	19.3	17.7
700	34.6	32.4	19.4	17.6	34.2	32.1	19.0	17.4

These values are the R maxima and minima from the three groups of measurements made on specimens from both localities. (Tables I and II). They include graphically interpolated values for the 4 COM wavelengths *470*, *546*, *589* and *650* nm.

Table VI Chemical analyses

	Seathwaite						Wittichen						
				1	2	3	4	5	6				
Cu	37.80	38.11	37.37	38.26	38.18	38.32	37.77	37.58	37.83	37.41	37.48	37.71	37.85
Bi	43.17	42.90	43.16	42.01	42.70	42.93	43.06	43.76	43.46	43.47	43.38	43.24	43.73
S	18.49	18.37	18.50	18.06	17.96	17.94	19.06	19.07	19.02	18.16	18.23	18.51	19.11
TOTAL	99.46	99.38	99.03	98.33	98.84	99.19	99.89	100.41	100.31	99.04	99.09	99.46	100.69

Numbers 1-6 correspond to the areas measured in the reflectance study.

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Cobalt-, nickel-, and iron-bearing sulpharsenides from the North of England

R. A. IXER, C. J. STANLEY, AND D. J. VAUGHAN

Department of Geological Sciences, University of Aston in Birmingham, Birmingham B4 7ET

SUMMARY. Within the Alston Orefield of the North Pennines, glaucodot and gersdorffite have been found in samples from Tynebottom Mine, Garrigill, and zoned gersdorffite has been found from Nenthead and the Great Sulphur Vein. At Scar Crag in the English Lake District, glaucodot and alloclase (the first reported occurrence in the United Kingdom) occur associated with arsenopyrite and minor cobaltite and skutterudite. The mineralogy and parageneses of these associations have been studied by ore microscopy, X-ray powder photography, and electron probe microanalysis.

Electron probe microanalysis shows a considerable range in nickel content in the sulpharsenides from the Alston Orefield with a relatively constant Co:Fe ratio. Samples from Scar Crag contain no nickel but exhibit almost a complete range of Co:Fe ratios from FeAsS to CoAsS. The compositions of the Alston Orefield sulpharsenides, in particular, show them to be metastable phases when compared with data from synthetic studies. At Tynebottom Mine, glaucodot and gersdorffite overgrow arsenical marcasite, and at Nenthead and the Great Sulphur Vein, early pyrite framboids or euhedra act as cores to zoned gersdorffite crystals. The Scar Crag sulpharsenides occur in a quartz-chlorite-apatite vein with the glaucodot and alloclase as overgrowths on arsenopyrite.

In the case of the Scar Crag association, consideration of the compositions of coexisting phases, together with precise determinations of the arsenic content of the arsenopyrites, has permitted speculation regarding temperatures and sulphur activities during ore formation. Estimated ranges are T c. 400 °C–300 °C and $a_{S_2} \approx 10^{-9}$ -10^{-11} bar. The occurrence of the sulpharsenides in the Alston Orefield correlates with further geochemical differences compared to other Pennine ores, differences that have been linked to higher temperatures of formation and a magmatic contribution to the ore-forming fluid. The Scar Crag mineralization may be related to a postulated stock intrusion beneath Causey Pike and the geographical proximity of the Alston and Scar Crag occurrences does suggest the possibility of a genetic link.

SULPHARSENIDE minerals of cobalt, nickel, and iron have been found in two distinct associations within the Alston Block area of the North Pennines; cobalt and iron-bearing sulpharsenides have also been found in ore samples from Scar Crag in the English Lake District. The compositions, mineral properties, associations, and parageneses of these newly reported phases are presented here, together with some speculations as to the conditions of formation of the assemblages.

At Tynebottom Mine, Garrigill [NY 739 418], glaucodot and gersdorffite have been found in samples collected from dump materials. The occurrence of cobalt-bearing minerals from Tynebottom Mine confirms the suggestion by Dunham (1948) of the presence of an 'unknown cobalt arsenide or cobalt sulphide', which was made on the basis of abundant erythrite around the mine. A second association, which contains zoned crystals of gersdorffite, occurs both in material collected from Nenthead [NY 790 436] and from the Great Sulphur Vein [NY 740 390]. The mineralization at Scar Crag [NY 2060 2070] in the Lake District contains glaucodot and alloclase associated with arsenopyrite and minor amounts of cobaltite and skutterudite. This is the first authenticated occurrence of alloclase in the United Kingdom. Samples collected from surface exposures and obtained from the Kingsbury Collection at the British Museum have been studied in this work.

The geological setting of the mineral veins of the Alston Block and their general mineralogy has been discussed in detail by Dunham (1948). The Scar Crag Vein (also known as the 'Cobalt Vein') outcrops above the footpath from Braithwaite village to Sail and Scar Crag in Long Comb, about one kilometre to the west of Causey Pike. Strens (1962) considered that the vein, which trends a few degrees east of north, was emplaced along a pre-Bala tear fault in Mosser-Kirkstile slates of the Skiddaw Slates Group. Although minor amounts of cobalt- and nickel-bearing phases have been found at Coniston (Russell, 1925) and at Dale Head (by C. J. S.), the over-all assemblages are different from those at Scar Crag, which appears to be a unique association for the Lake District. Unsuccessful attempts to extract cobalt at Scar Crag have been recorded by Postlethwaite (1913).

Experimental methods. Samples have been studied using reflected light microscopy and selected areas analysed by electron microprobe. The instrument used was a Cambridge Microscan V employing an accelerating voltage of 15 kV. Standards used were synthetic sulphides and sulpharsenides and the results were corrected by standard procedures. Certain samples were also examined by X-ray powder (Debye-Scherrer) photography using Co radiation. Vein material from Scar Crag was also examined in thin section.

Mineral data. At Tynebottom Mine, glaucodot and gersdorffite overgrowths on arsenical marcasite occur within a quartz, calcite, and ankerite gangue. The arsenical marcasite forms 1-2 cm by 0.2 cm laths, which are randomly oriented or collected into sheaf-like aggregates or rarely into large (2-5 cm) anhedra (see fig. 1). In oil immersion, it has a distinct green-white to pink-brown reflection pleochroism and a strong, green to brown anisotropy. The laths show a fine diamond-shaped

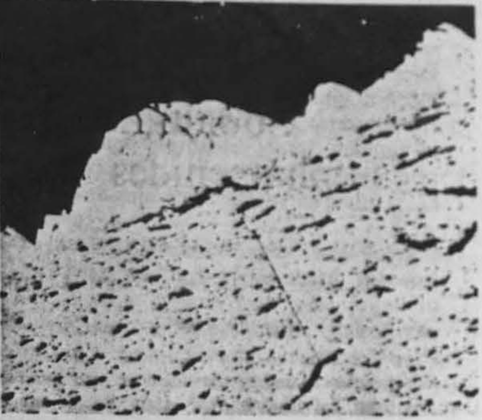

FIG. 1. Photomicrograph of a polished section showing euhedral-subhedral sulpharsenide overgrowths on lath crystal of arsenical marcasite, Tynebottom Mine, Garrigill.

TABLE I. *Representative electron microprobe analyses of cobalt, nickel, and iron-bearing sulpharsenides* (All data in wt.%.)

Locality/Mineral Species	Fe	Co	Ni	As	S	Total
Alston Block (Tynebottom Mine)						
Arsenical marcasite	39.83	3.34	1.24	8.60	46.67	99.68
	39.77	3.75	1.14	8.68	46.44	99.79
	44.19	0.88	0.12	4.13	50.55	99.87
Gersdorffite	4.86	11.45	19.28	46.70	20.02	102.30
	3.35	11.88	21.39	44.84	19.57	101.04
	2.36	7.03	24.49	45.95	18.82	98.65
Glaucodot	12.04	22.03	2.22	45.69	20.64	102.62
	9.86	21.06	5.80	43.98	21.93	102.62
	11.29	23.68	1.71	42.27	21.59	100.54
	11.24	24.27	1.56	40.41	23.92	101.41
Lake District (Scar Crag)						
Arsenopyrite	34.7	0.3	—	44.6	19.7	99.3
	35.0	0.3	—	45.4	20.1	100.8
	34.2	0.4	—	46.7	19.1	100.4
Alloclase	4.8	32.0	—	46.6	18.0	101.5
	4.9	32.0	—	46.4	17.3	100.6
	4.8	30.9	—	46.3	17.4	99.4
	5.9	29.5	—	47.3	16.9	99.6
	6.4	29.8	—	45.7	17.8	99.7
	6.1	29.5	—	47.4	16.9	99.9
	6.8	29.4	—	45.9	18.9	101.0
	5.6	30.1	—	47.3	18.4	101.5
	5.6	30.4	—	47.5	17.7	101.2
	6.7	28.2	—	48.1	16.9	99.9
	8.0	27.1	—	48.3	16.8	100.2
Glaucodot	11.9	23.61	—	46.2	19.4	101.1
	15.8	19.4	—	46.3	19.1	100.6
	13.4	22.3	—	45.8	18.8	100.3
	12.8	23.2	—	46.2	19.1	101.3
	24.0	10.6	—	45.4	19.1	99.1
	24.5	10.7	—	46.1	17.9	99.2
	22.4	12.8	—	46.7	17.2	99.1
Cobaltian Arsenopyrite	28.2	5.9	—	47.0	18.7	99.8
Cobaltite	2.0	33.6	—	44.7	19.0	99.3
Skutterudite	2.7	19.5	—	77.2	1.7	101.1

cleavage in addition to later fracturing and individual marcasite rhombs are composed of a complex intergrowth of small (< 5 μm) domains. Compared to normal marcasite it has a lower reflectivity and the yellow component of the reflection pleochroism is absent. Electron microprobe analysis (Table I) shows the marcasite commonly contains in excess of 8 wt.% arsenic as well as 3-4 wt.% cobalt and *c.* 1 wt.% nickel. Along the width of the marcasite laths, oriented tabular aggregates of pyrite or pyritohedra (5-20 μm diameter) occur. The pyrite itself encloses small pyrrhotine (< 5 μm) inclusions.

The cobalt-, nickel-, and iron-bearing sulpharsenides at Tynebottom form subhedral to euhedral overgrowths (up to 40 μm in width) on the edges of fractured marcasite or heal internal fractures. The overgrowths have two, or sometimes three, optically distinct phases, which have been identified by electron microprobe analysis. The relationships between these phases and the distribution of Co, Ni, Fe, As, and S between them are illustrated in fig. 2. The outermost phase has been identified as gersdorffite by electron microprobe analysis (see Table I). It displays a good cubic cleavage, cubic habit and is pink-yellow in colour under the ore microscope. It is isotropic to weakly anisotropic. The analytical data (Table I) show dominant nickel (*c.* 17-24 wt.%) with lesser cobalt (*c.* 7-12 wt.%) and minor iron (*c.* 2-6 wt.%). The phase within this has been identified as glaucodot by electron microprobe analysis (and X-ray powder diffraction). It contains dominant cobalt (*c.* 19-24 wt.%) with lesser iron (*c.* 9-12 wt.%) and minor amounts of nickel (*c.* 1-6 wt.%). This glaucodot exhibits slight pink to yellow-pink reflection pleochroism and moderate anisotropy. Both phases take a good polish and have reflectivities a little below that of pyrite on qualitative observation.

A thin zone, adjacent to the enclosed arsenical marcasite, appears an optically distinct third phase in some parts of the sections as it has a lower reflectivity. The electron microprobe data, however, show that this phase has the composition of gersdorffite (fig. 2, Table I). Frequently, the sulpharsenide overgrowths display optical continuity with the enclosed marcasite. Minor amounts of euhedral gersdorffite (*c.* 10 μm diameter) also occur associated with anhedral chalcopyrite grains (*c.* 20 μm diameter).

In the material collected from the Great Sulphur Vein and from workings at Nenthead, euhedral zoned gersdorffite crystals have been found in quartz in association with anhedral chalcopyrite and pyrite. The gersdorffite was identified initially on the basis of its optical properties in comparison with the Tynebottom Mine material. Electron microprobe analysis showed the presence of major nickel, sulphur, and arsenic with some cobalt and iron, but it was not possible to obtain quantitative data for these small grains. Gersdorffite occurs as small (5-10 μm) discrete, lilac-white euhedral crystals within vein quartz and calcite, and within mineralized shaley limestones. Associated opaque minerals are chalcopyrite, galena, pyrite, and marcasite. The gersdorffite euhedra display cubic habit and cleavage (triangular polishing pits), and exhibit faint zoning characterized by colour differences (lilac to pink) and differences in reflectivity and hardness. The zoning is difficult to see in freshly polished material but the colour differences between zones gradually become enhanced. The zone boundaries follow the crystal outlines and frequently more than one (*c.* 2-3 μm wide) zone is present. The zoning is too fine in scale to enable compositional differences between zones to be determined by microprobe analysis. Small pyrite framboids or euhedra act as cores to many gersdorffite crystals and the gersdorffite itself is commonly enclosed and replaced by galena and chalcopyrite.

At Scar Crag, cobalt-iron sulpharsenide minerals occur with arsenopyrite in a quartz-chlorite-apatite vein. Quartz is by far the most dominant

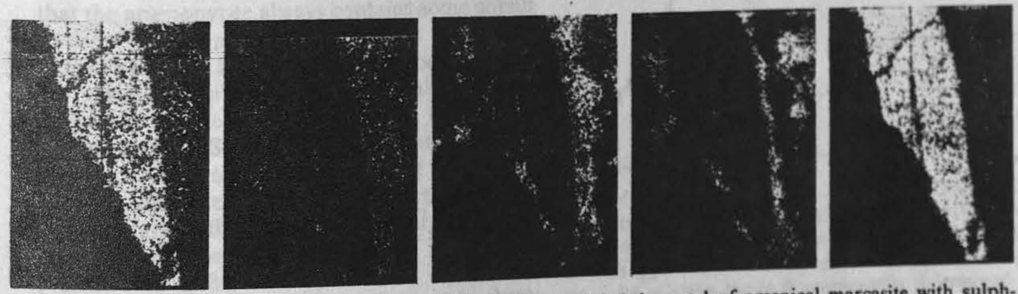

FIG. 2. Electron microprobe X-ray scanning micrographs of a bladed crystal of arsenical marcasite with sulpharsenide overgrowths (*bottom*), Tynebottom Mine, Garrigill: (*a*) sulphur K_α; (*b*) arsenic K_α; (*c*) cobalt K_α; (*d*) nickel K_α; (*e*) iron K_α.

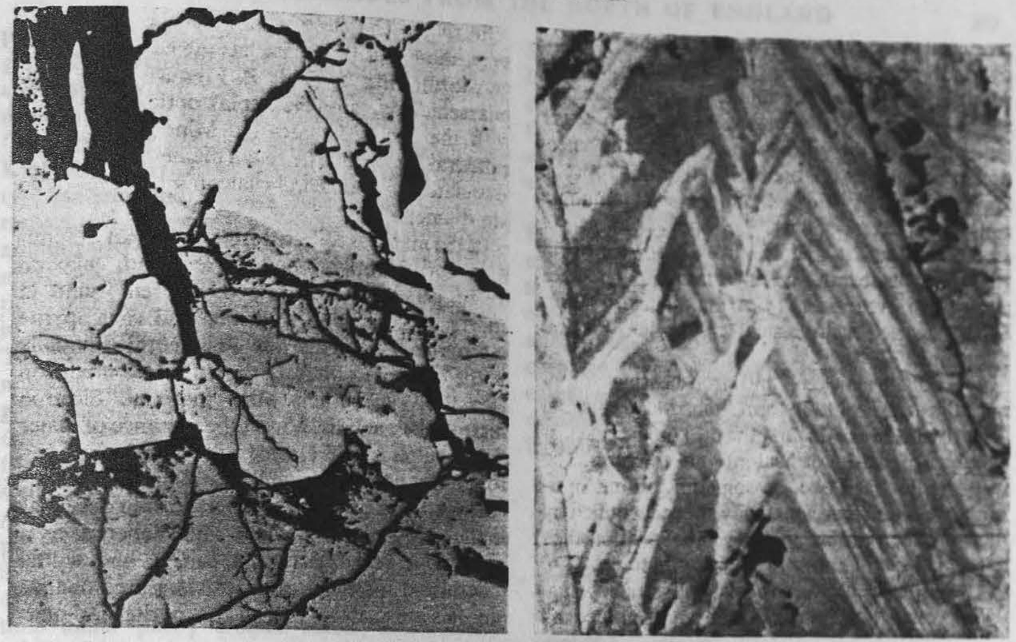

FIG. 3. Photomicrographs of polished sections of material from Scar Crag: (*a, left*) Arsenopyrite (*bottom*) overgrown by alloclase with cobaltite euhedra developed along a fracture in alloclase. (*b, right*) Zoning in glaucodot shown by etching with saturated ferric chloride solution (high-cobalt glaucodot is less etched than low-cobalt glaucodot and cobaltian arsenopyrite).

vein mineral; early quartz is often euhedral and with a zoned arrangement of inclusions. Rutile occurs within quartz either as radiating bunches of fine needles (< 100 μm in length) or as subhedral grains (< 30 μm). Small amounts of tourmaline showing blue-brown pleochroism occur as subhedral to euhedral grains (< 400 μm) associated with early quartz. Abundant apatite occurs as large euhedra (< 5 cm in some specimens) growing inwards from the vein margins, and chlorite is also common. Arsenopyrite is the most abundant opaque mineral present, occurring as large euhedral and subhedral grains and aggregates (< 3 mm). Electron microprobe analysis (Table I) shows that the arsenopyrite always contains some cobalt (usually < 1 %) and slight zoning is evident in polished section. This zonation could be related to the variations in S:As ratio but this was not observed in electron microprobe data, and Kretschmar and Scott (1976) have pointed out that 'optically zoned arsenopyrites are not necessarily compositionally zoned'. The arsenopyrite is overgrown by glaucodot or, more commonly, alloclase. Electron microprobe data for both phases are presented in Table I. In contrast to the Alston area sulpharsenides, no nickel is present in these minerals and there is a much greater variation in the Fe:Co ratio, which was relatively constant in the former samples (Table I, fig. 4).

The identification of glaucodot and alloclase at Scar Crag has been substantiated by X-ray powder

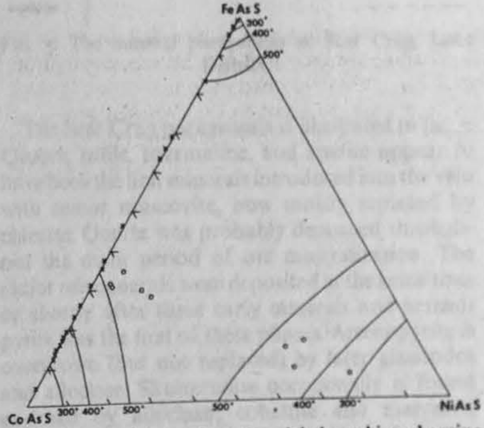

FIG. 4. Compositions of cobalt-, nickel-, and iron-bearing sulpharsenides from northern England plotted (in atomic per cent) on the ternary diagram FeAsS-CoAsS-NiAsS (x Scar Crag phases; o Tynebottom phases). Also shown are the solid solution limits experimentally determined by Klemm (1965).

photography. The X-ray powder data obtained for glaucodot are closely comparable to published data and distinctly different to data obtained for the more cobalt-rich alloclase. Comparison of the data for Scar Crag alloclase with that published by Kingston (1971) and by Petruk *et al.* (1971) for the type material and samples from Cobalt, Ontario, respectively, support the identification. Although, as illustrated by our analysis, alloclase is a generally more cobalt-rich sulpharsenide than glaucodot, there is no evidence of a clear break in composition in the CoAsS–FeAsS solid solution series (fig. 4). The distinction between glaucodot and alloclase must be made on the basis of crystal structure, glaucodot being of orthorhombic space group *Cmmm* (Ferguson, 1946), whereas alloclase from the type locality is now known to be monoclinic, of space group $P2_1$ (Scott and Nowacki, 1976). Although alloclase is not easily distinguished in polished section, it does have slightly lower polishing hardness and reflectivity than arsenopyrite and exhibits purple/mauve-greenish olive anisotropic tints under partly crossed nicols; arsenopyrite exhibits blue and orange tints whereas the colours exhibited by glaucodot are much less intense greys and browns.

As well as anhedral overgrowths (< 500 μm) on arsenopyrite, alloclase occasionally forms (< 100 μm) subhedra. It also sometimes encloses grains of skutterudite (< 20 μm) as confirmed by microprobe analysis (Table I). Cobaltite, also confirmed by electron microprobe (Table I) occurs as small euhedra (< 50 μm) at the outer margin of the alloclase, at the boundary between alloclase and arsenopyrite or along fractures in these two minerals. Other minerals observed are: marcasite, which rarely overgrows alloclase; native bismuth, which occurs as inclusions in arsenopyrite and early quartz; bismuthinite, which occurs along fractures in arsenopyrite and alloclase and at grain boundaries; and a few small (< 20 μm) molybdenite fibres.

Certain of the Scar Crag specimens exhibit a fine zonal texture with individual zones having compositions of cobaltian arsenopyrite, glaucodot, and alloclase. This faint zonation is best seen under partly crossed nicols and is enhanced by etching. Although previous studies of the mineralization at Scar Crag have resulted in reports of scheelite (Kingsbury and Hartley, 1957) and löllingite (Strens, 1962), neither of these minerals was found in the present study, despite considerable searching.

Mineral parageneses. At the Tynebottom Mine, the earliest phases are pyrite with very minor associated pyrrhotine. These are succeeded by the arsenical marcasite, which is in turn overgrown by the sulpharsenides—gersdorffite and glaucodot. Some euhedral gersdorffite is also associated with later chalcopyrite and very minor arsenopyrite occurs within the carbonate gangue. Oxidation of the pyrite to limonite and of the gersdorffite to erythrite has occurred as a result of weathering, especially along cleavages.

The paragenesis at Nenthead and the Great Sulphur Vein is of early pyrite framboids or euhedra acting as cores to gersdorffite crystals, which have in turn been enclosed and replaced by galena and chalcopyrite. Weathering has resulted in the alteration of chalcopyrite to covelline, blaubleibender covelline, and limonite along cleavages and crystal edges; of galena to anglesite and covelline or cerussite and chalcosine; and of gersdorffite to limonite.

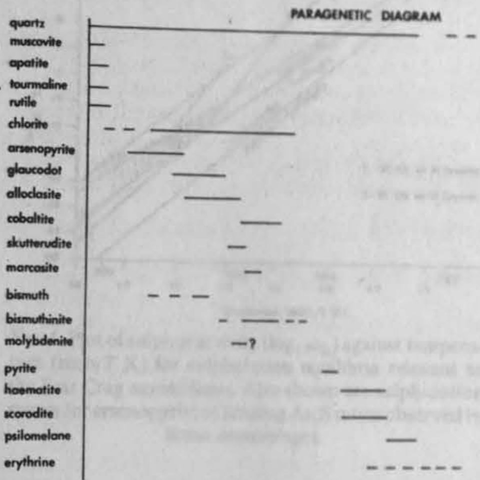

FIG. 5. The mineral paragenesis at Scar Crag, Lake District.

The Scar Crag paragenesis is illustrated in fig. 5. Quartz, rutile, tourmaline, and apatite appear to have been the first minerals introduced into the vein with minor muscovite, now mostly replaced by chlorite. Quartz was probably deposited throughout the main period of ore mineralization. The major ore minerals were deposited at the same time or shortly after these early minerals and arsenopyrite was the first of these phases. Arsenopyrite is overgrown (but not replaced) by later glaucodot and alloclase. Skutterudite occasionally is found enclosed by alloclase; cobaltite and marcasite formed later than alloclase. Native bismuth occurs within arsenopyrite and early quartz, bismuthinite is a slightly later phase. Minor molybdenite and pyrite occur as late minerals in the primary assemblage. There has been extensive later replacement of arsenopyrite by scorodite and some replacement by hematite. Psilomelane is found as a coating on joint planes and erythrite has resulted from weathering of the cobaltiferous sulpharsenides.

Discussion. Very little data are available on phase relations in the ternary system FeAsS-CoAsS-NiAsS (or its constituent binary systems). Klemm (1965) has investigated equilibrium solid solution limits in the dry FeAsS-CoAsS-NiAsS system as a function of temperature and his results are shown in fig. 4, together with the sulpharsenide compositions determined in this work. According to these data, most of the sulpharsenides found in this work should form only above 300 °C and many only above 500°. A few analyses represent compositions that cannot be synthesized in the dry system. Estimates of the temperatures of mineralization in the Alston orefield (from fluid inclusion and isotope studies) indicate appreciably lower temperatures than 300 °C (*c*. 100-200 °C) (Sawkins, 1966; Smith, 1974). The sulpharsenide assemblages from the Alston orefield are certainly metastable, like the bravoites that are a significant minor feature of the mineralization of the South Pennines (Ixer, 1978). Klemm (1965) suggested widespread metastability of glaucodot by comparison of his experimental work with analyses from the literature.

The arsenopyrite in the mineral assemblage at Scar Crag can be employed as a geothermometer through determination of S:As ratios provided an independent estimate can be made of sulphur activity during ore formation. This technique, based on the work of Kretschmar and Scott (1976), also requires that the arsenopyrite be from an equilibrium a_{S_2}-buffered assemblage and contains a combined minor element content $< 1\%$. Since the Scar Crag arsenopyrite generally only contains $< 0.5\%$ Co, the latter criterion is fulfilled. The question of equilibrium is much more difficult to assess, but it would seem worth while to apply the technique and then critically evaluate the results. Accurate determination of the wt.% As in the Scar Crag arsenopyrite samples is also essential and two methods have been employed here. Careful measurement of the position of the d_{131} line in X-ray powder diffraction data enables the determinative curve of Kretschmar and Scott (1976) to be used (the equation Atomic% As $= 866.67\ d_{131} - 1381.2$ defines this curve). The measured d_{131} values gave a range of 1.630-1.631 Å which leads to a range in at.% As $= 32.42$-31.55. These results are in good agreement with those obtained by the second method, electron microprobe analysis using synthetic arsenopyrite as a standard (if pure arsenic is used as a standard, results are up to 2% different due to differences in As coordination and bonding between element and sulpharsenide). The a_{S_2} during the main phase of sulpharsenide formation can be approximately estimated by the formation of native bismuth and bismuthinite at this time (fig. 5). In fig. 6, the bismuth-bismuthinite sulphidation curve (Barton and Skinner, 1967) is plotted on a diagram showing variation of log a_{S_2} with temperature; also plotted are the limits of temperature and sulphur activity defined by the range of As content in Scar Crag arsenopyrite. Sulphidation curves for certain Fe-As-S phases are also shown along with the curve for the sulphidation of pyrrhotine to pyrite.

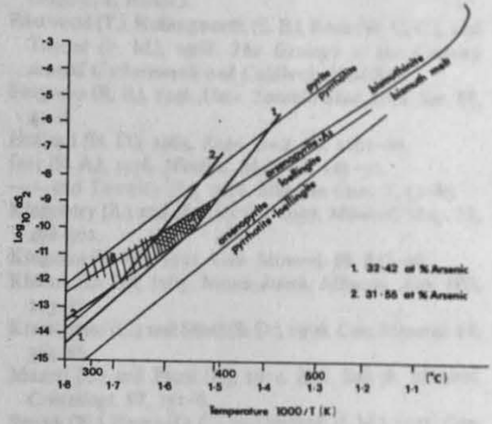

FIG. 6. Plot of sulphur activity ($\log_{10}a_{S_2}$) against temperature ($1000/T$ K) for sulphidation equilibria relevant to the Scar Crag assemblages. Also shown are sulphidation curves for arsenopyrite of limiting As:S ratios observed in those assemblages.

The early sulpharsenide assemblage appears to have been in equilibrium with bismuth and to have formed under the temperature (*c*. 400 °C) and a_{S_2} (*c*. 10^{-9} atm) conditions defined by the field 'A' in fig. 6. Later assemblages see the appearance of bismuthinite and cobaltite (which Maurel and Picot, 1973, relate to increasing S:As ratio). This could correspond to an increase in a_{S_2} or, more likely, just a drop in temperature. The eventual appearance of pyrite ties in with falling temperature and conditions closer to those shown by field 'B' (*T c*. 300 °C, a_{S_2} *c*. 10^{-12} atm). Although arsenopyrites of the composition range determined could coexist with bismuth at much lower values of a_{S_2} and somewhat lower temperature, this seems unlikely in view of the subsequent appearance of bismuthinite, cobaltite, and pyrite. The conditions of ore formation indicated here are well within the 'main-line' ore fluid environment outlined by Holland (1965) and other workers. The only comparable vein in the Lake District occurs in the Carrock Fell Tungsten deposit where Shepherd *et al*. (1973) obtained temperatures of 295 °C (assuming 800 bar pressure) from fluid inclusions in mineralized quartz.

A factor of importance in the occurrence of these sulpharsenides in the Alston orefield is their complete absence from samples studied from the Derbyshire orefield of the South Pennines (Ixer and Townley, 1978). Other notable mineralogical differences between the two orefields include the presence of pyrrhotine in the Alston ores as a characteristic and early sulphide but its rarity in the South Pennines, and the occurrence within only the Alston galenas of a number of small (< 2 μm) crystallographically orientated inclusions, which probably account for the high silver and arsenic values reported by Small (1977). This correlates with other geochemical differences shown by the Alston orefield, such as a marked enrichment of rare-earth elements in fluorite (Smith, 1974), which has been suggested to indicate a magmatic contribution to the ore-forming fluid (Rogers, 1978). Fluid inclusion data from the Alston ores also indicate higher temperatures of formation and greater potassium content than the other Pennine orefields (Smith, 1974; Sawkins, 1966; Rogers, 1978).

The origin of the Scar Crag mineralization could be linked to the possible existence of a stock-like intrusion beneath Causey Pike (Rose, 1955). The slates in this area have been altered to a lighter and harder rock with minute dark spots and this lithology, termed Blakefell Mudstone (Eastwood *et al.*, 1931), has been interpreted as the metamorphic aureole of the supposed intrusion. Although there are certainly differences in the temperatures of sulpharsenide mineralization in the Alston orefield and at Scar Crag, and probably differences in age, their geographical proximity does suggest a possible genetic link.

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VOLUME II

MINERALOGICAL STUDIES OF COPPER, LEAD, ZINC AND COBALT MINERALIZATION IN THE ENGLISH LAKE DISTRICT

(2 volumes)

by

Christopher John Stanley

A thesis submitted for the degree of Doctor of Philosophy

The University of Aston in Birmingham

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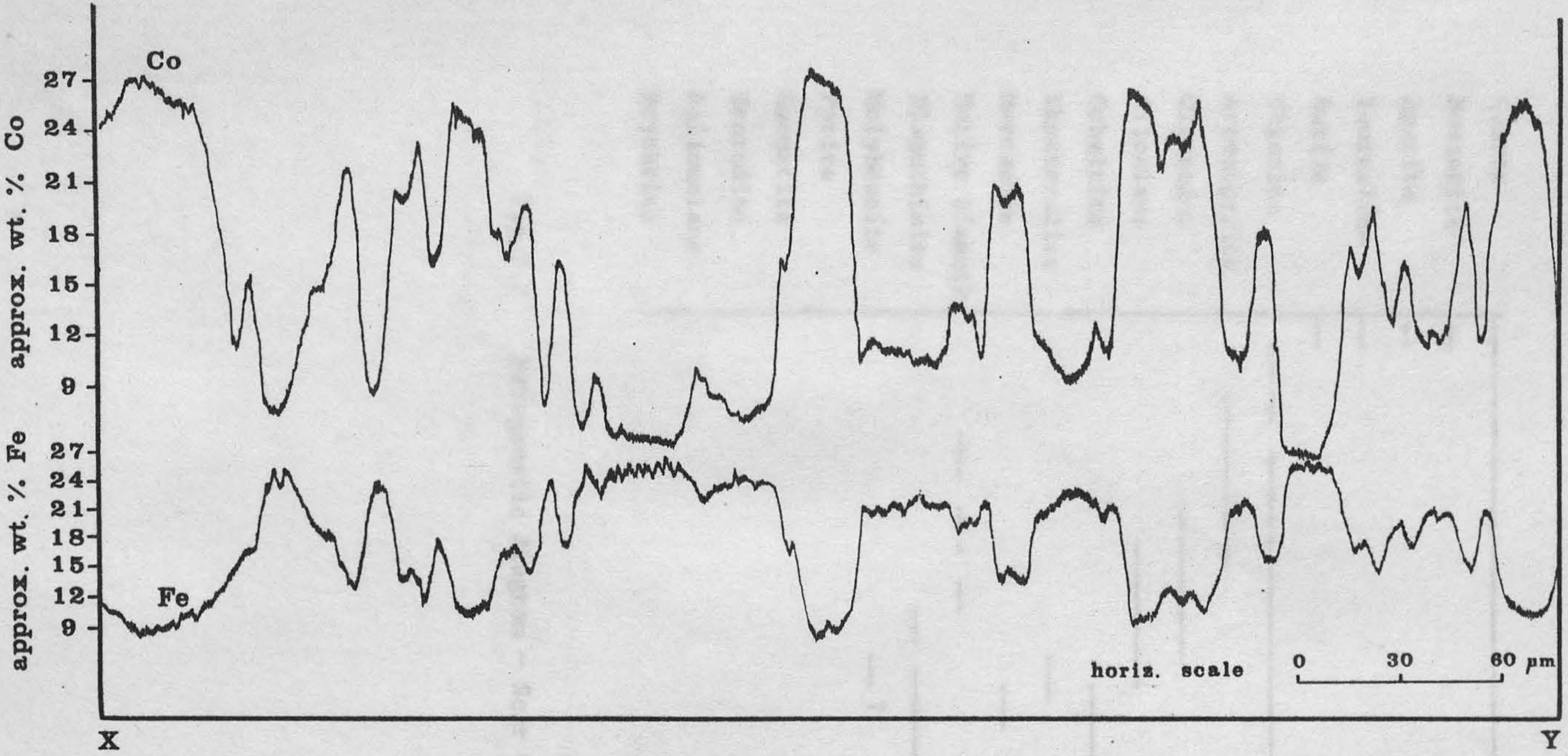

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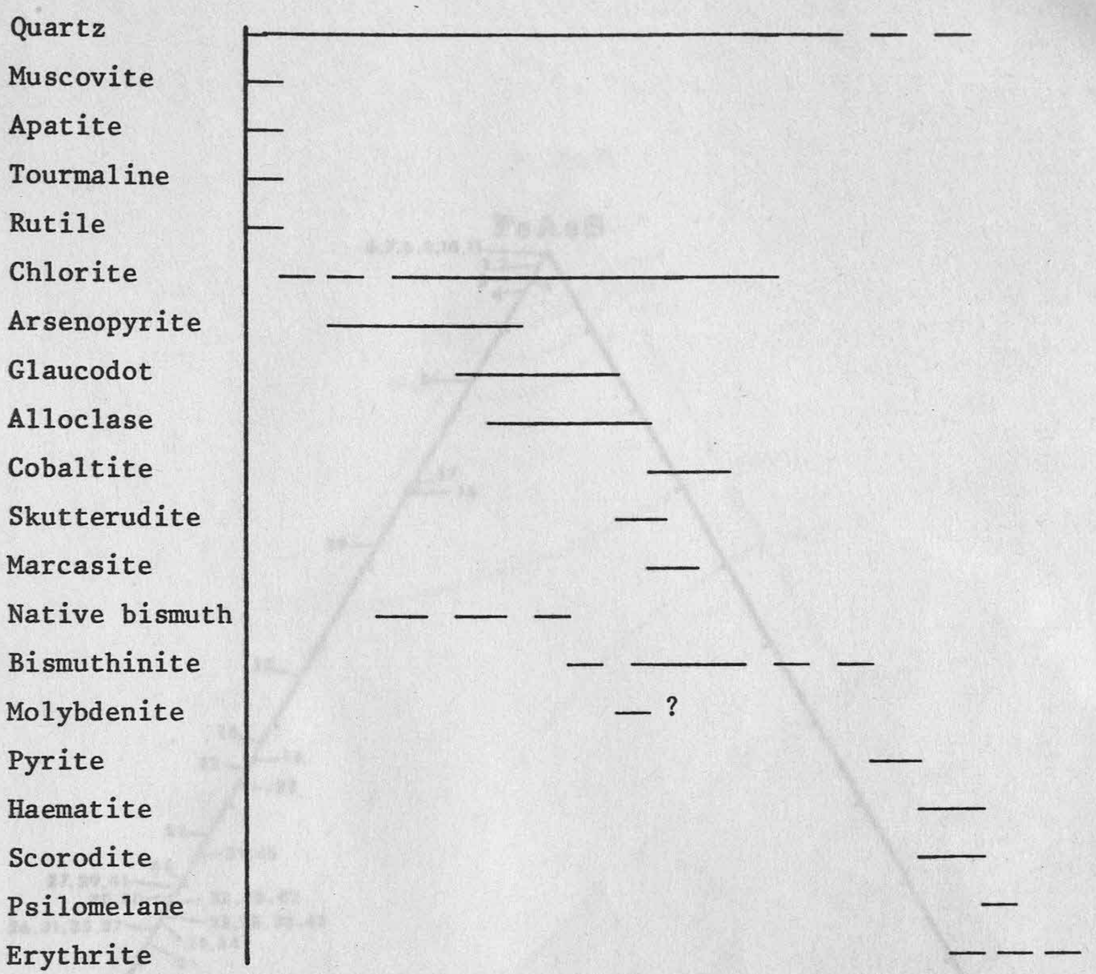

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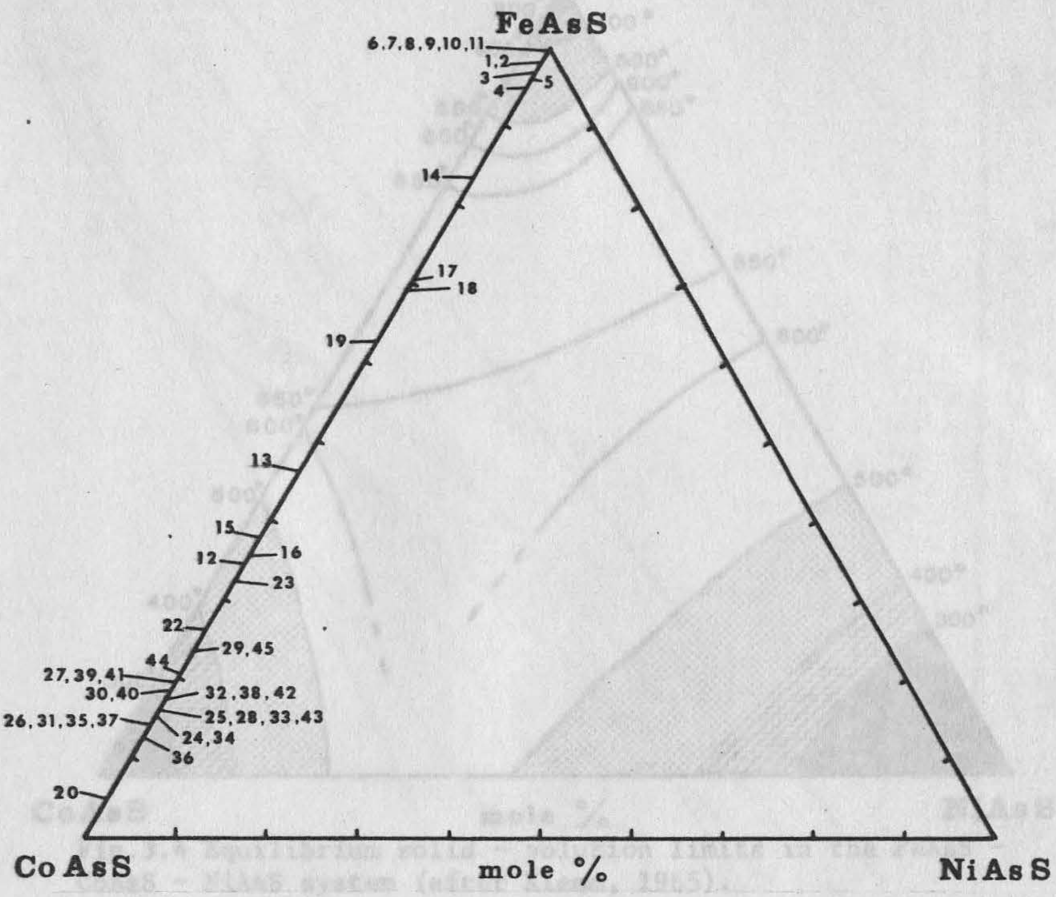

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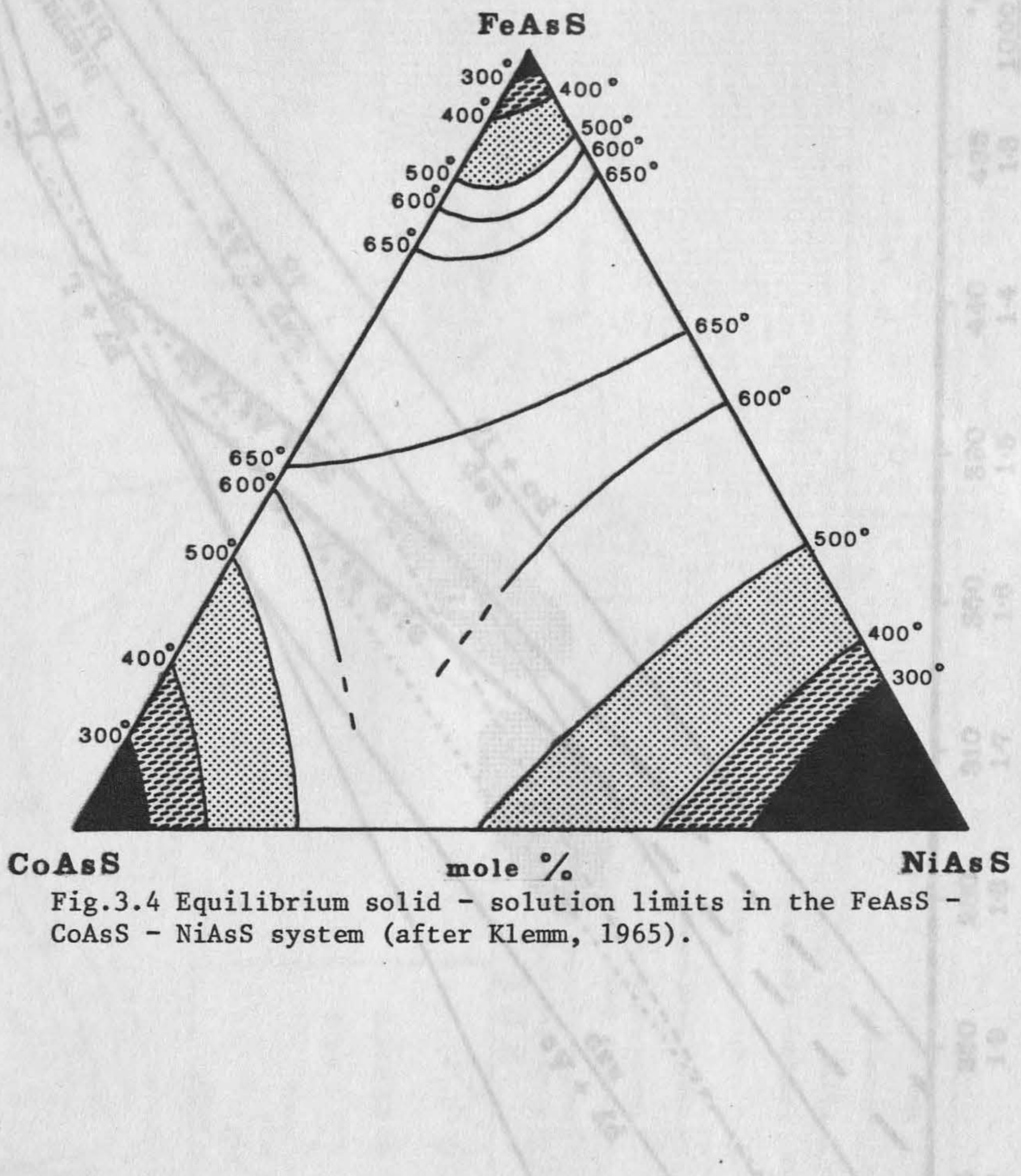

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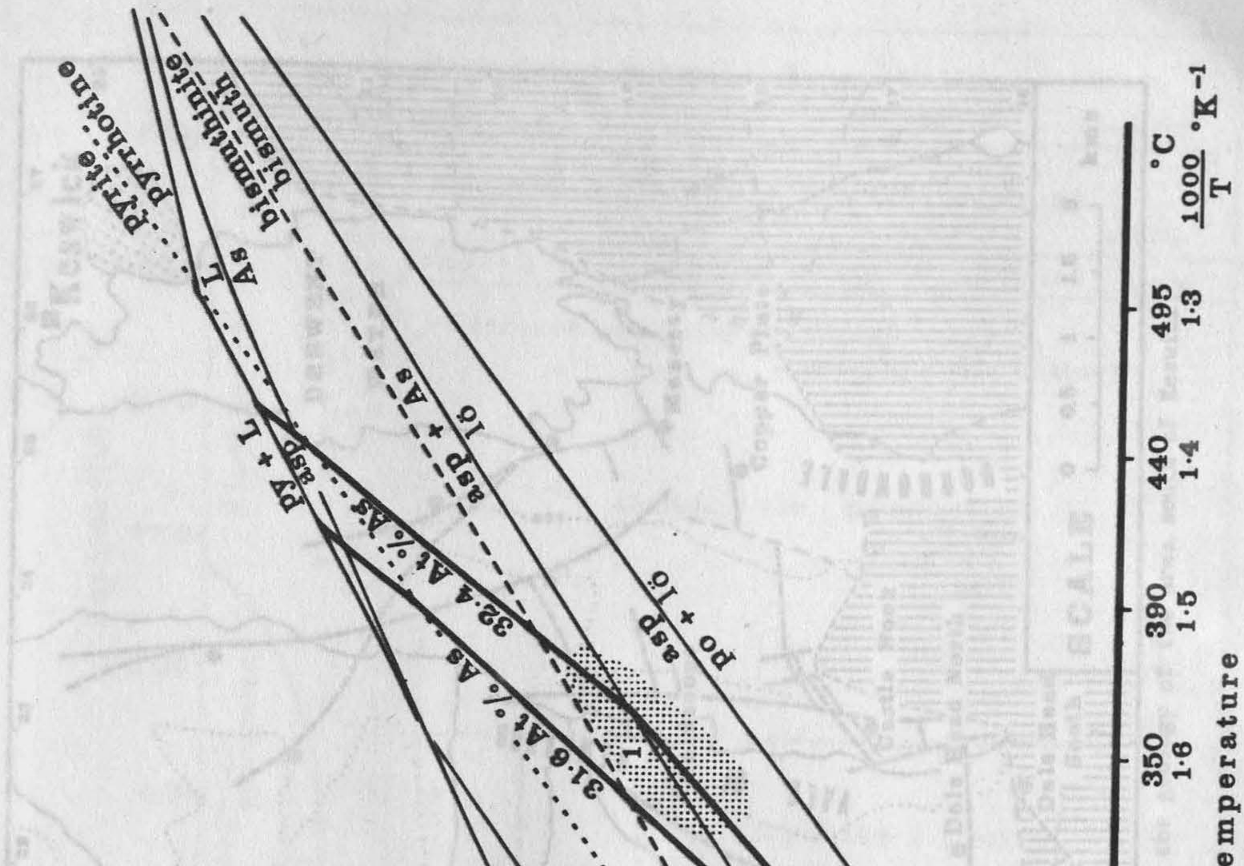

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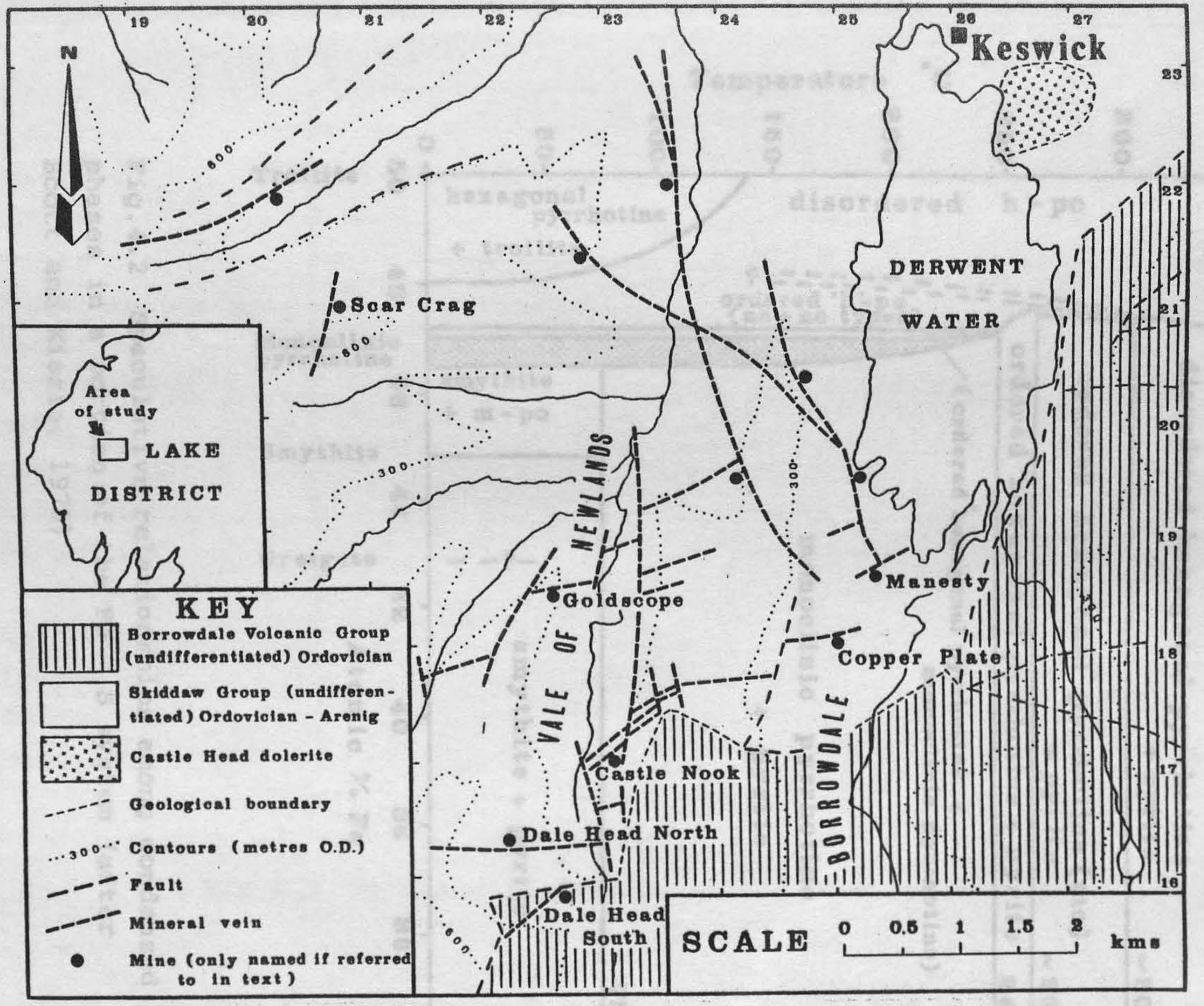

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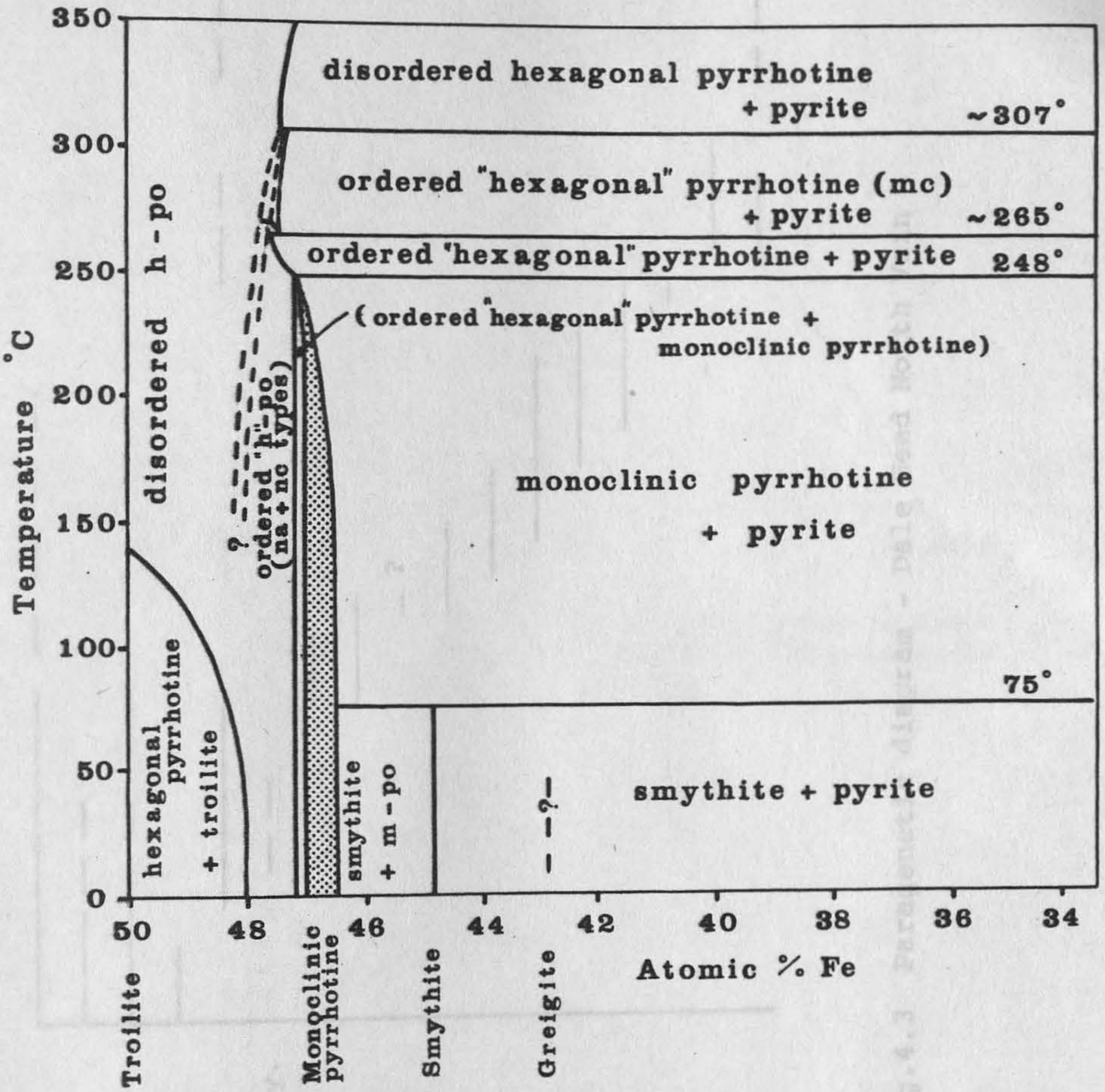

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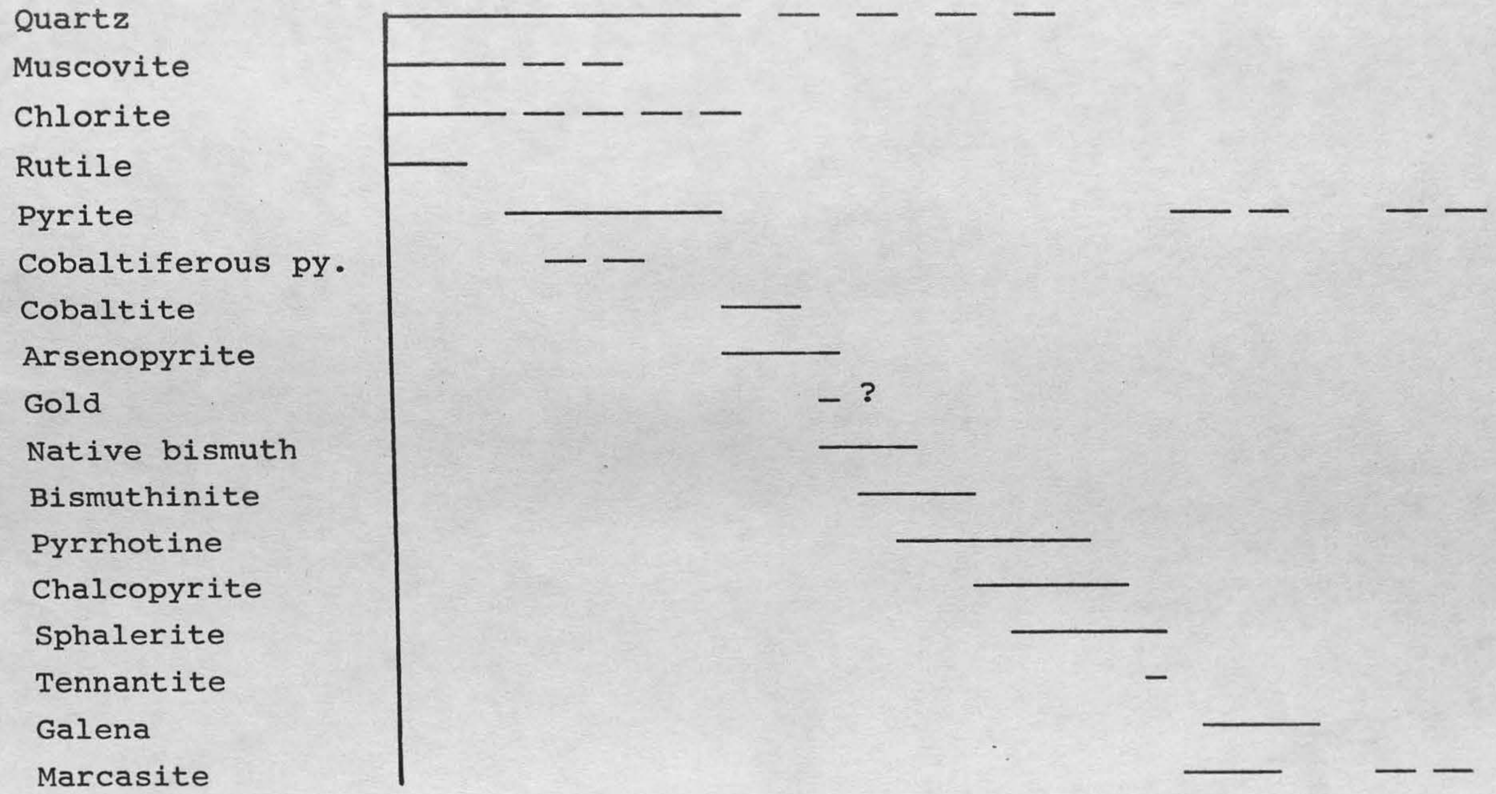

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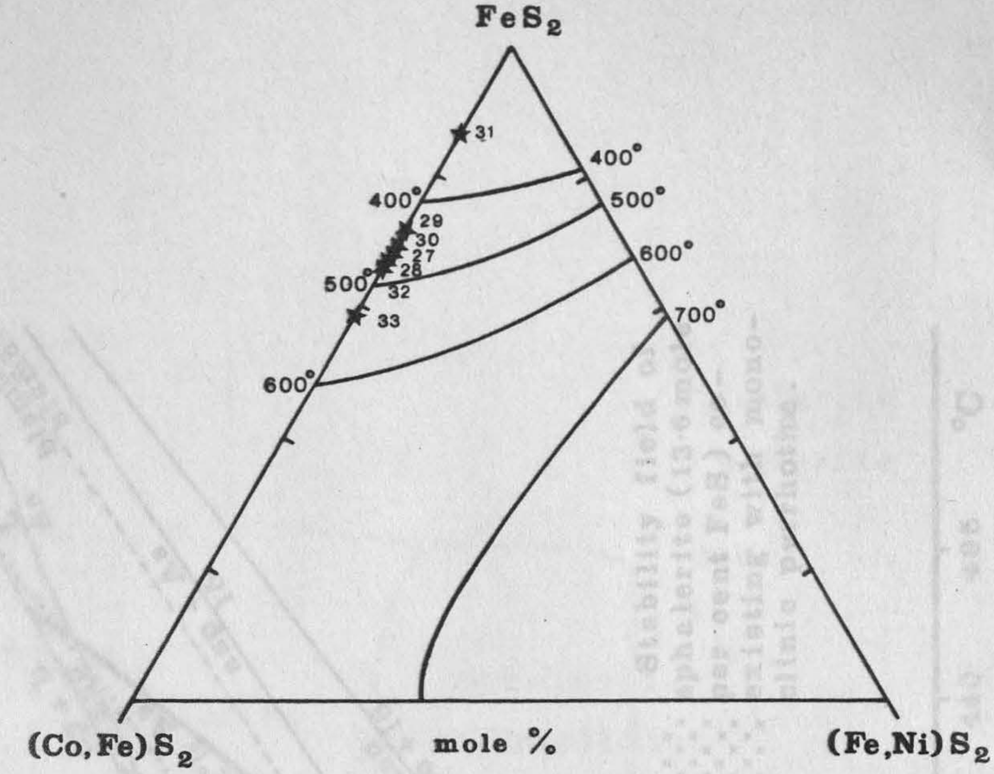

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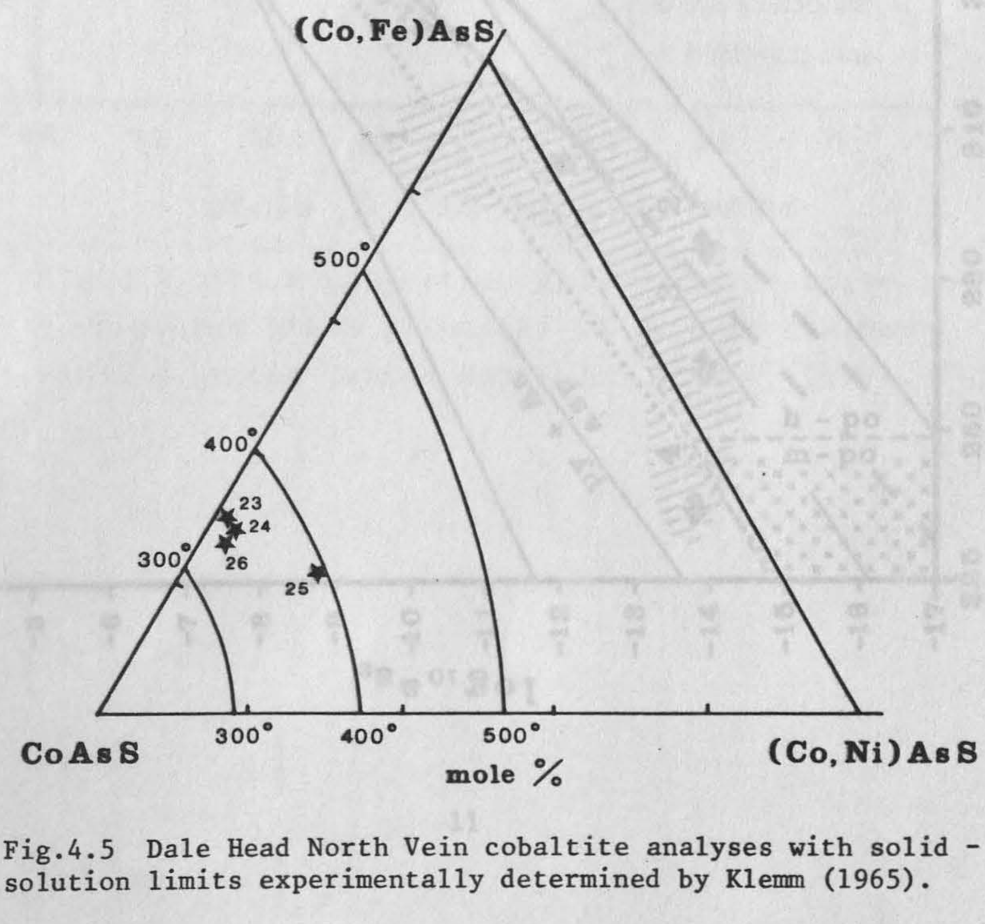

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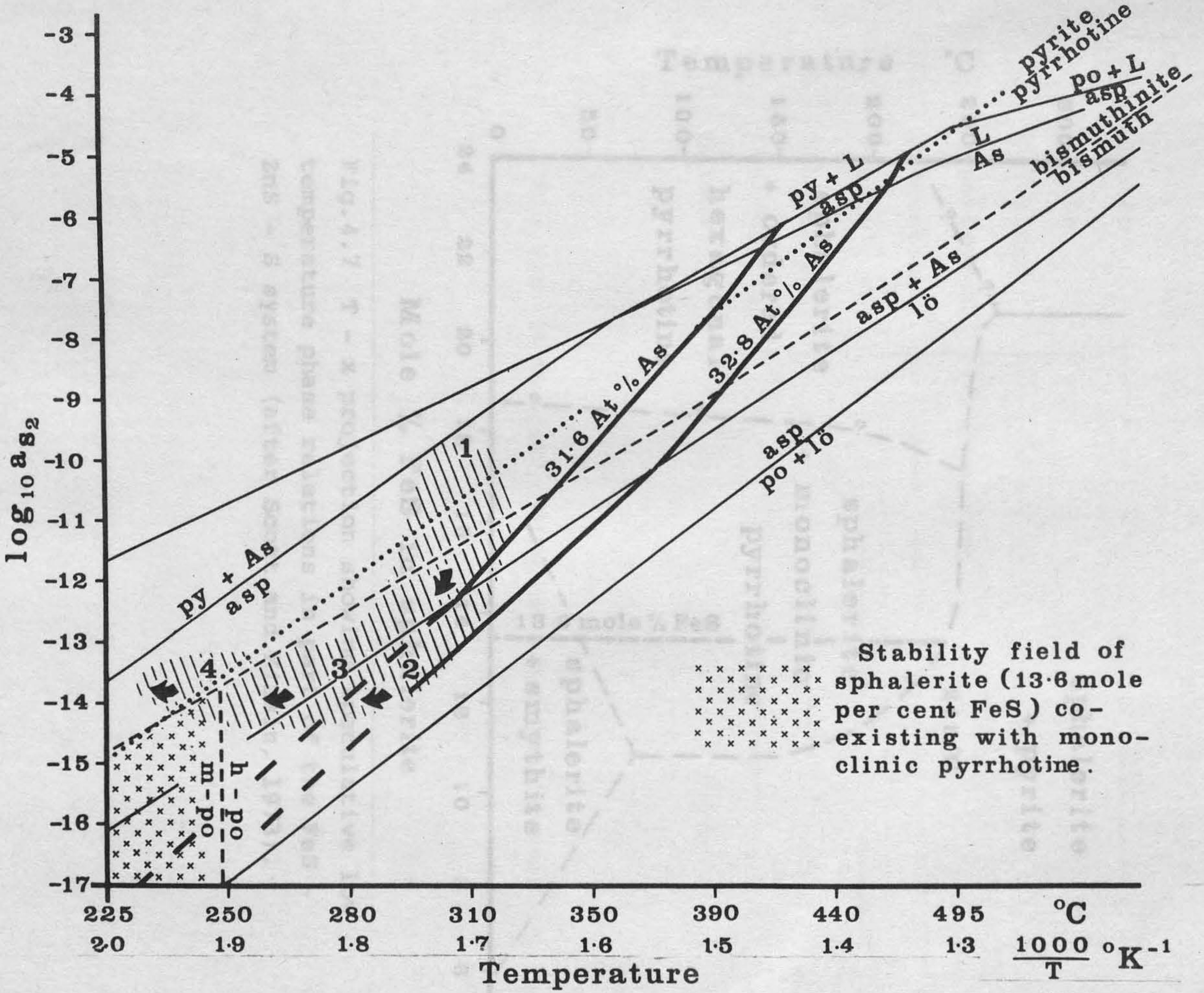

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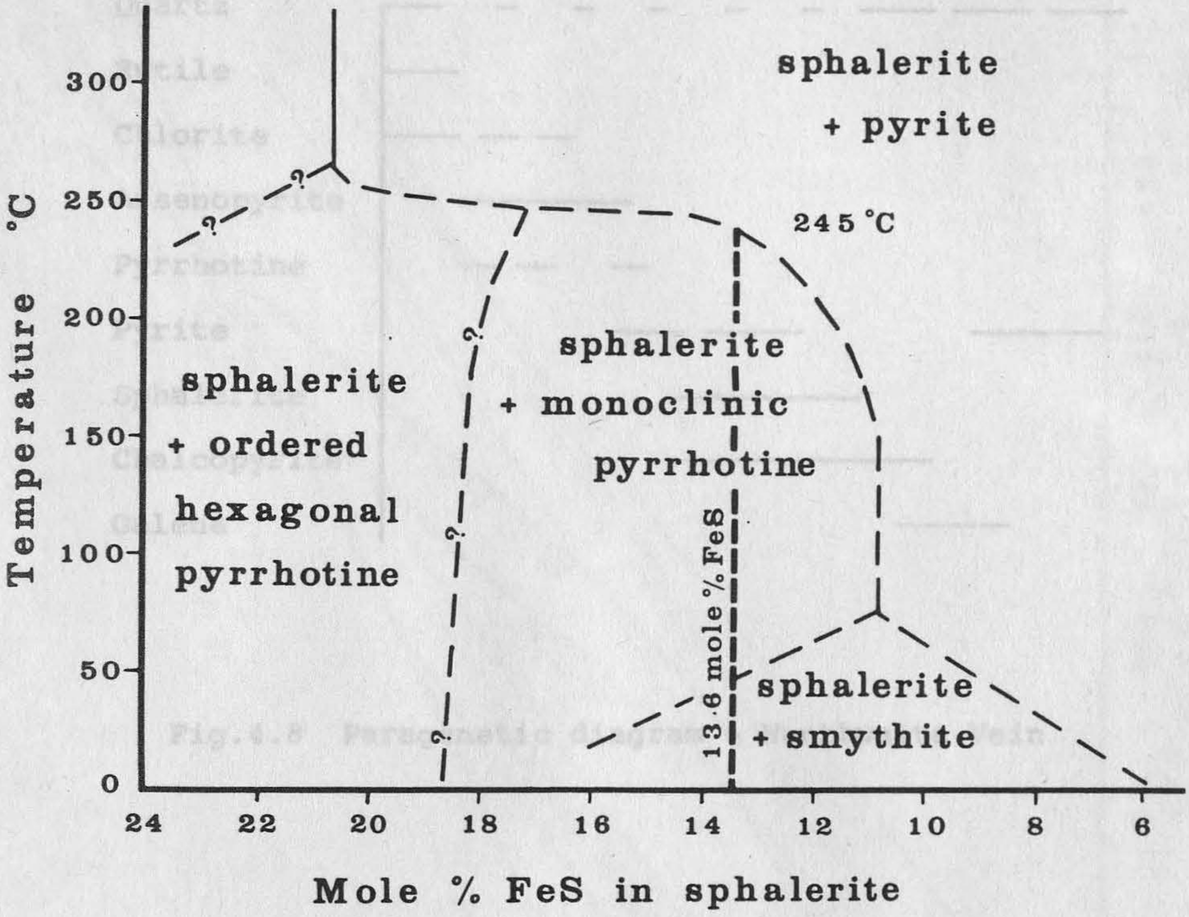

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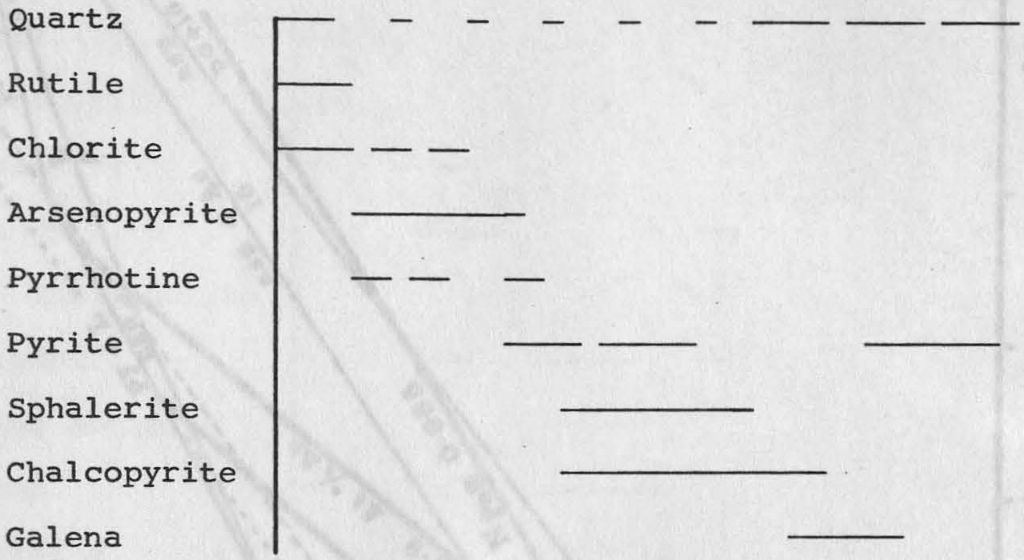
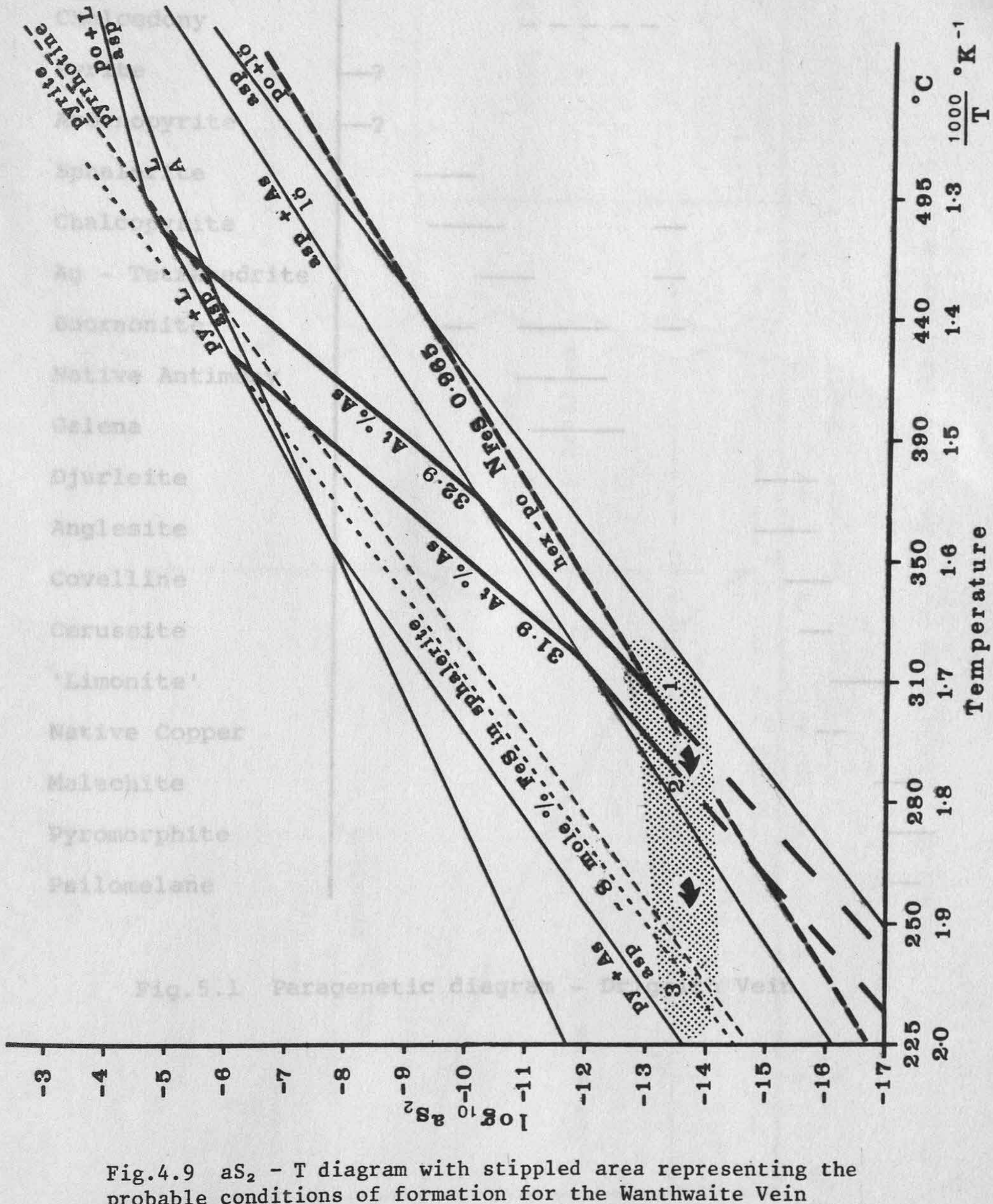


Fig.4.8 Paragenetic diagram - Wanthwaite Vein



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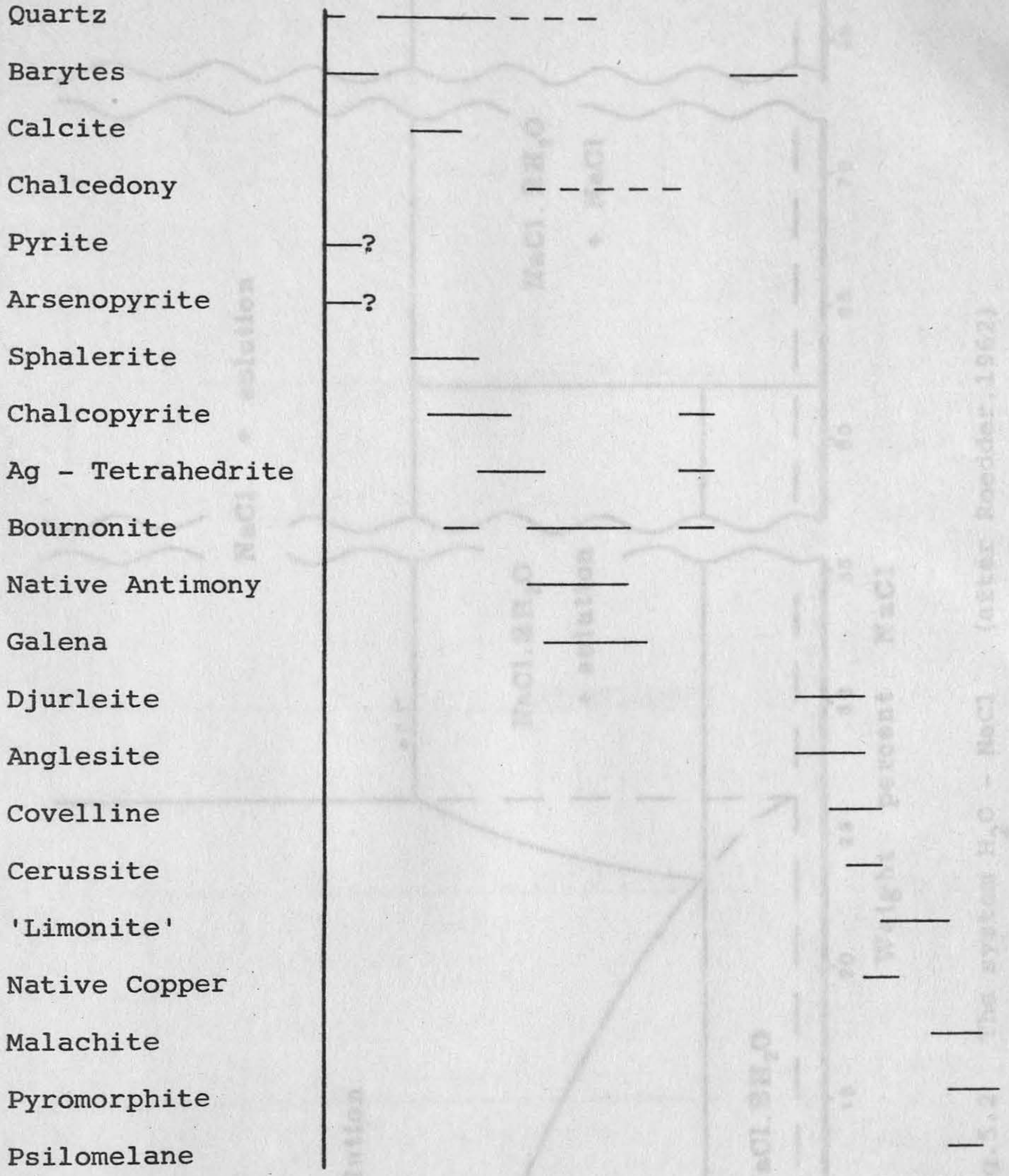

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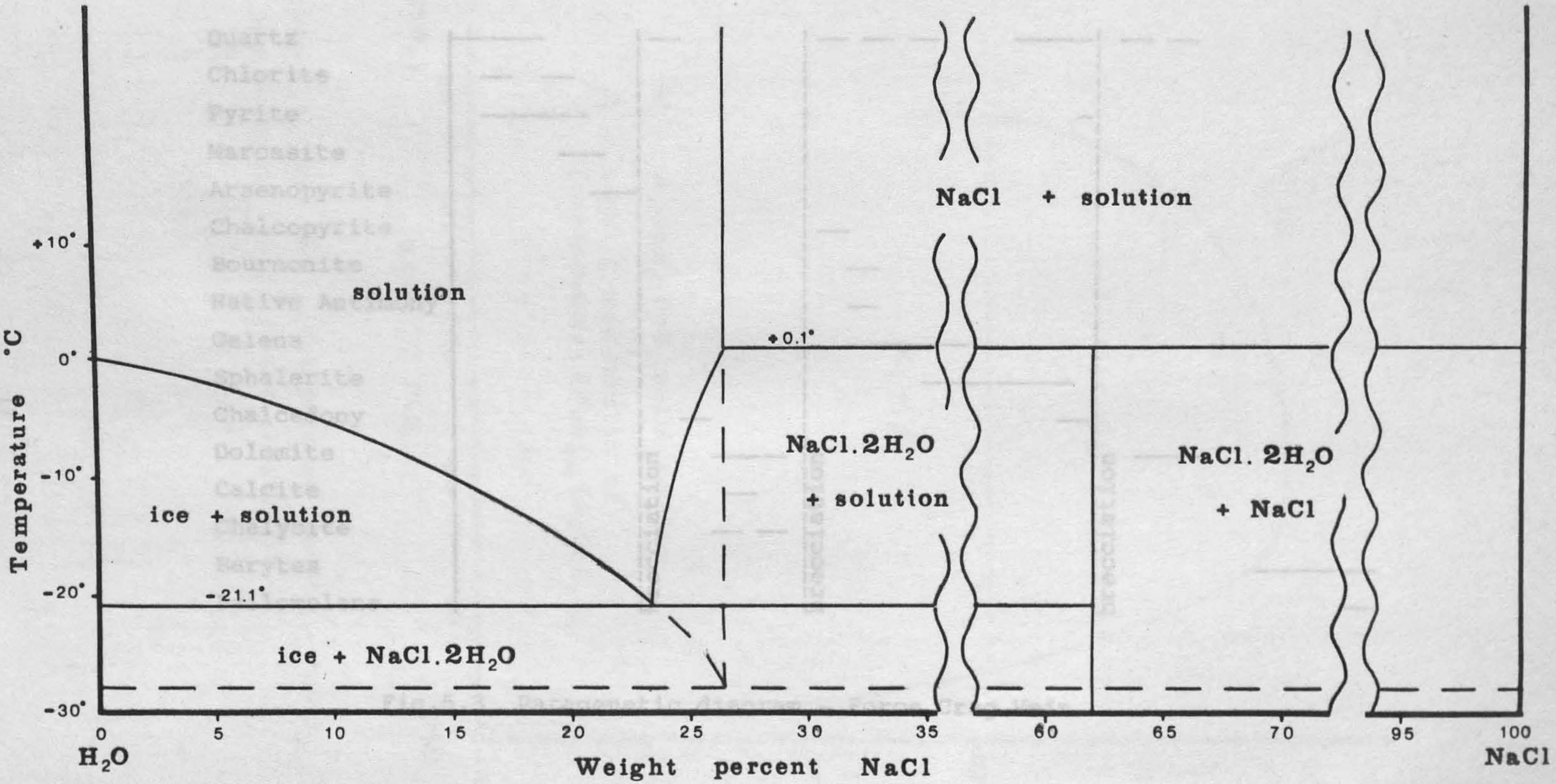

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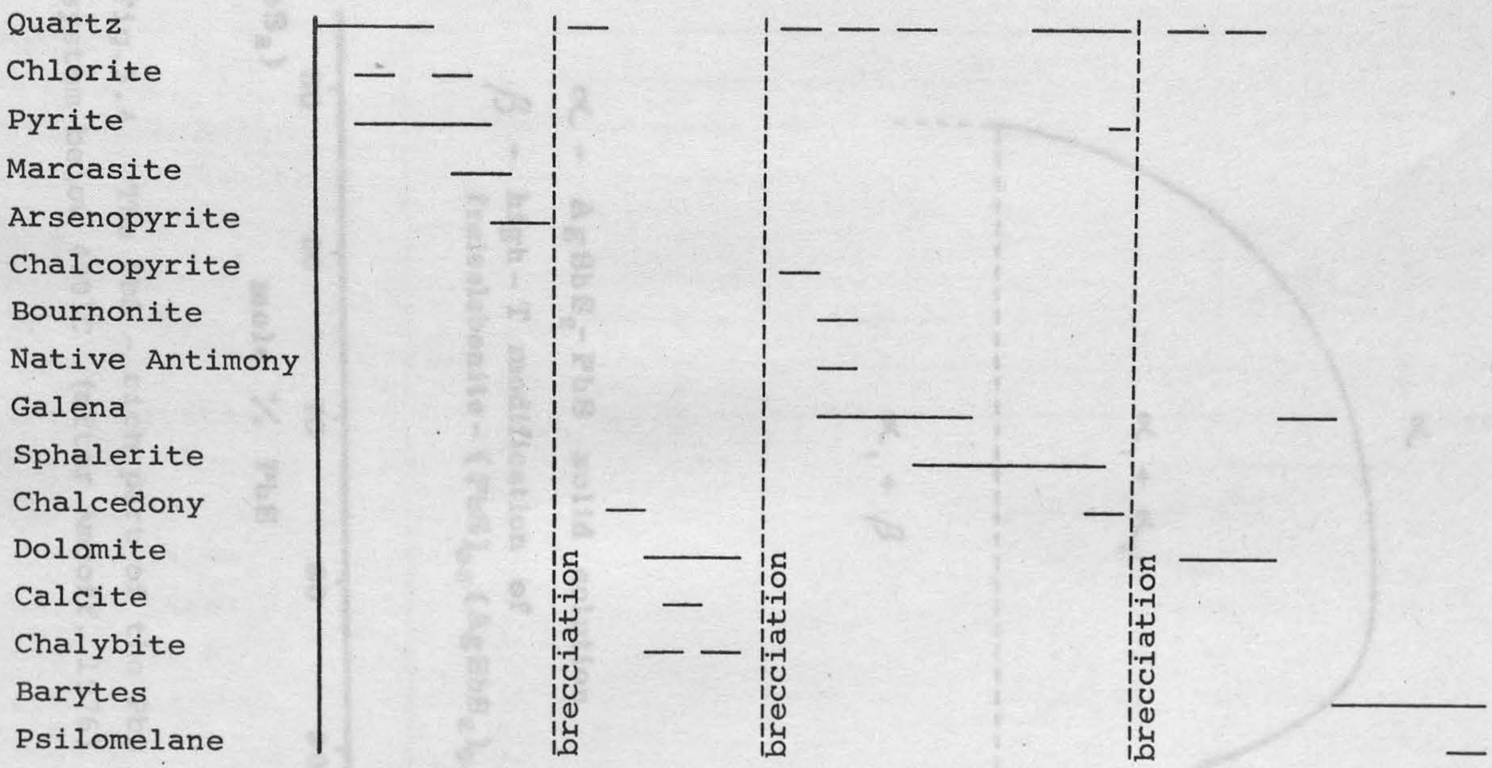

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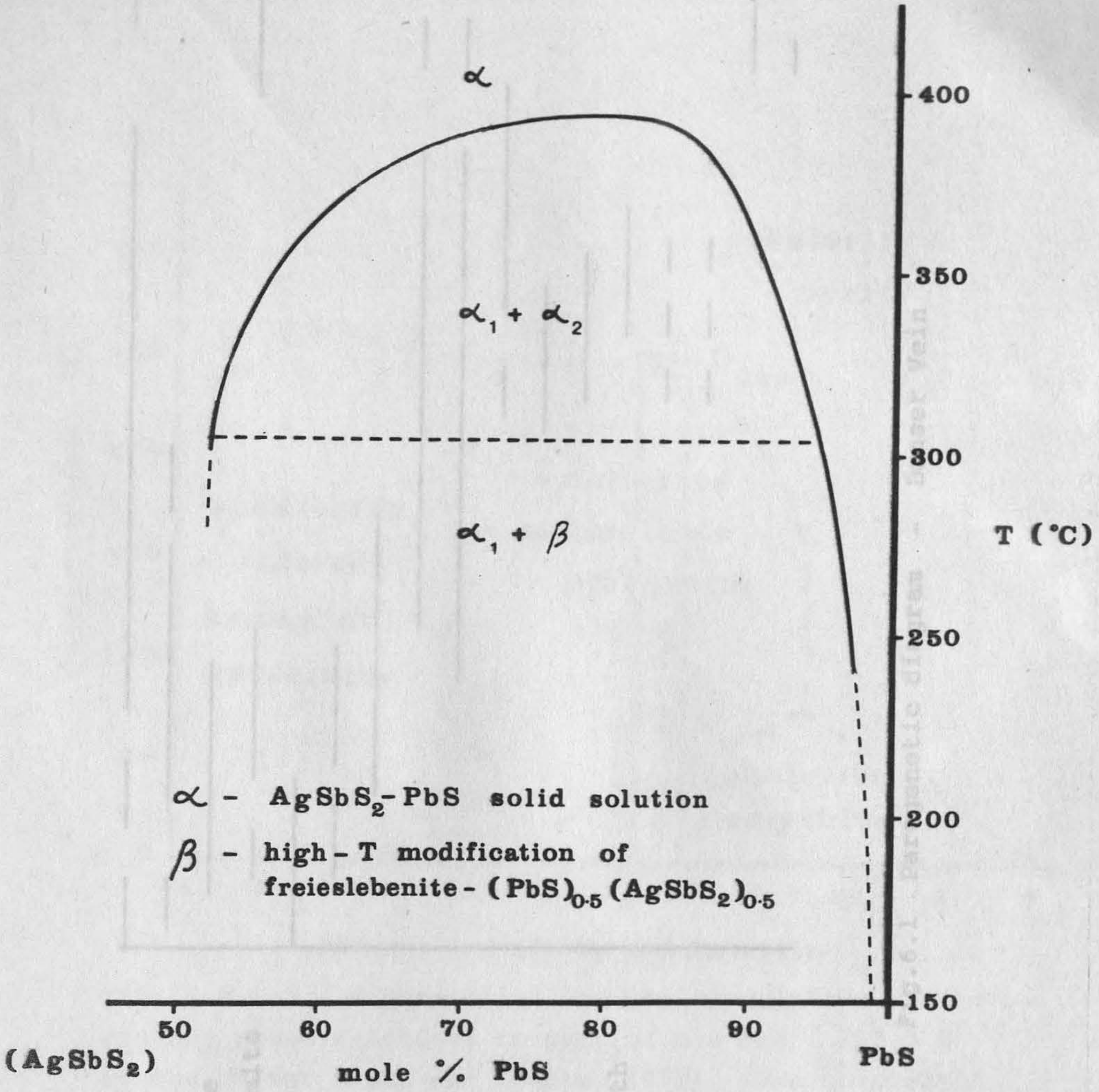

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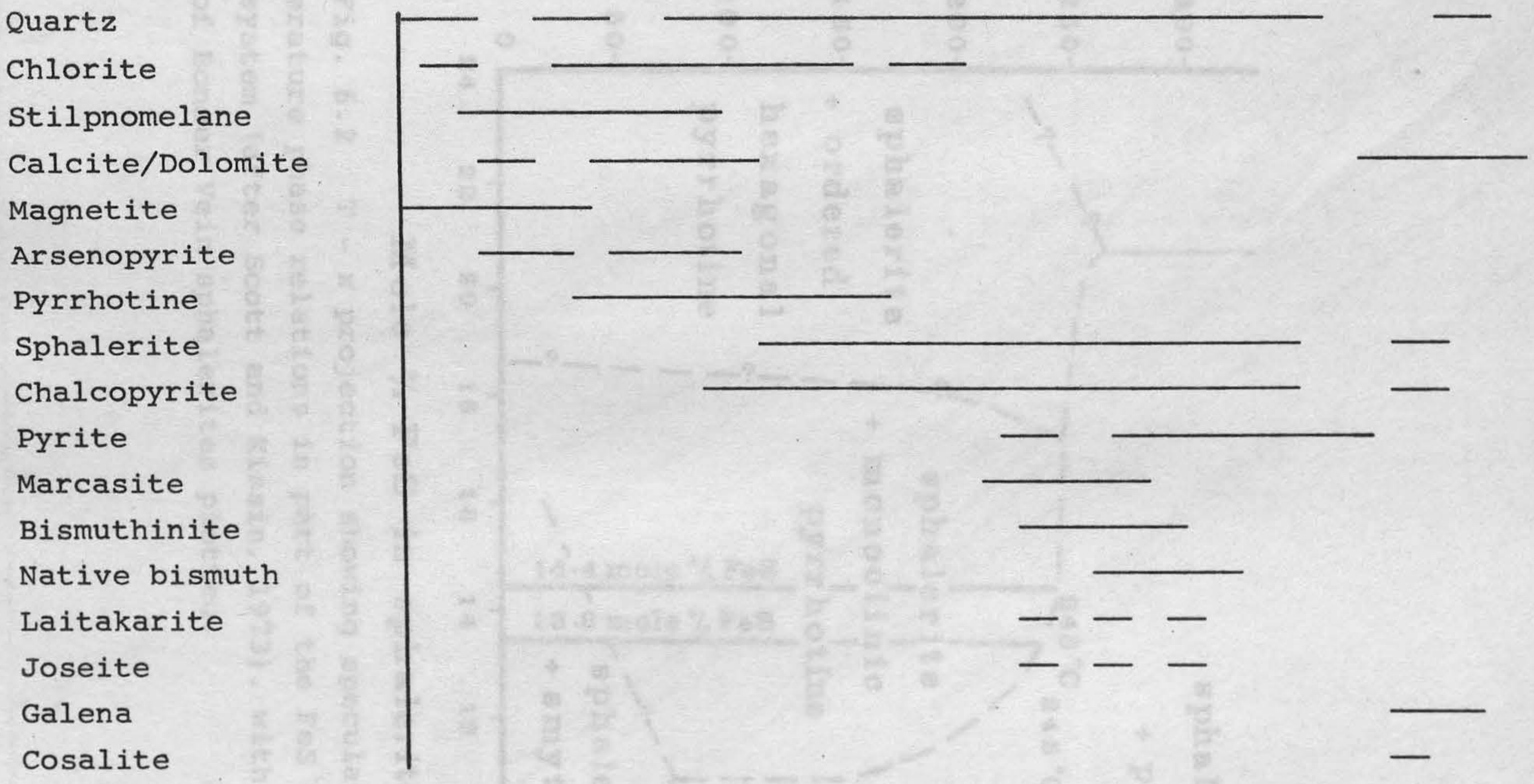

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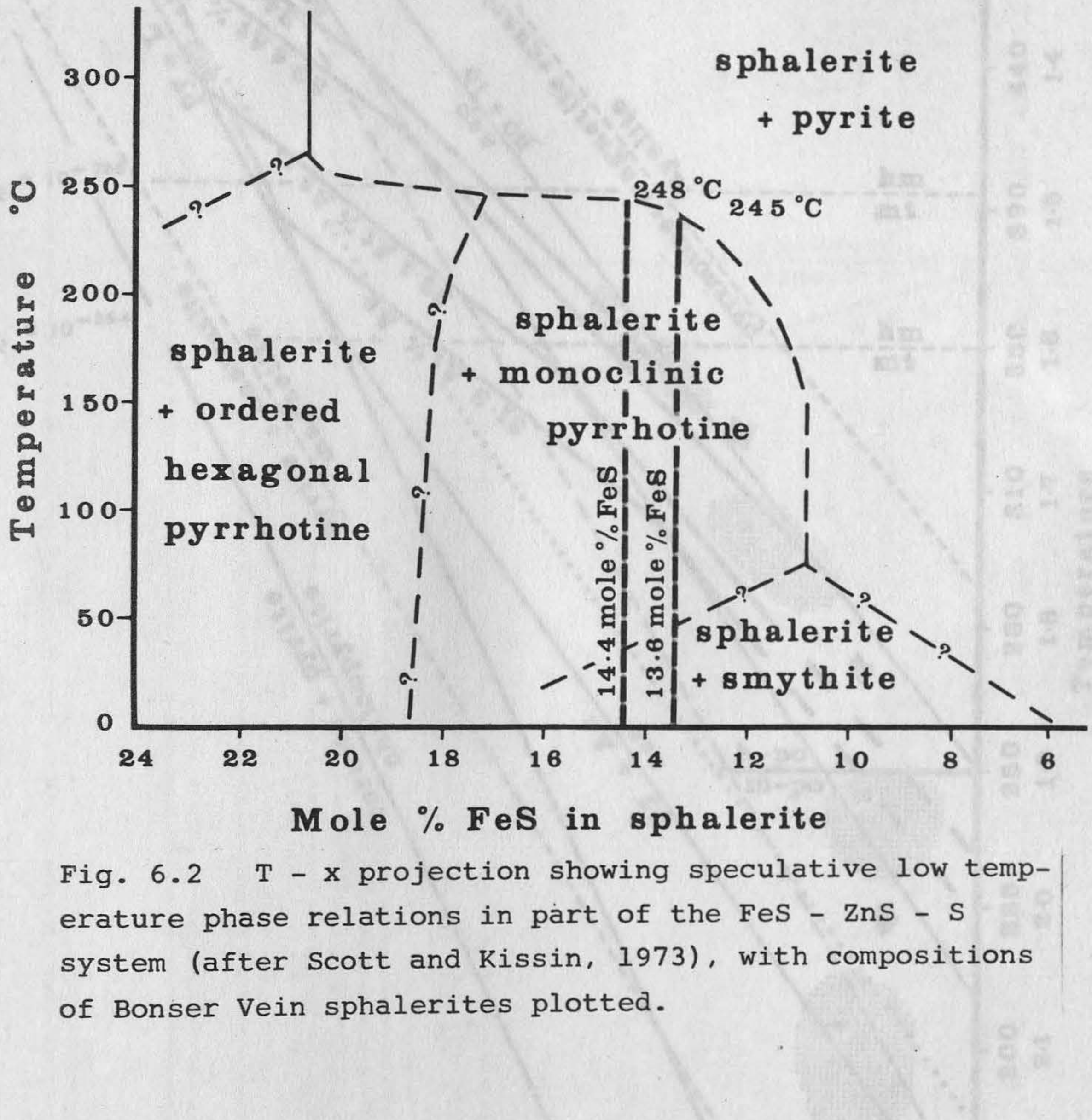


Fig. 6.2 T - x projection showing speculative low temperature phase relations in part of the FeS - ZnS - S system (after Scott and Kissin, 1973), with compositions of Bonser Vein sphalerites plotted.

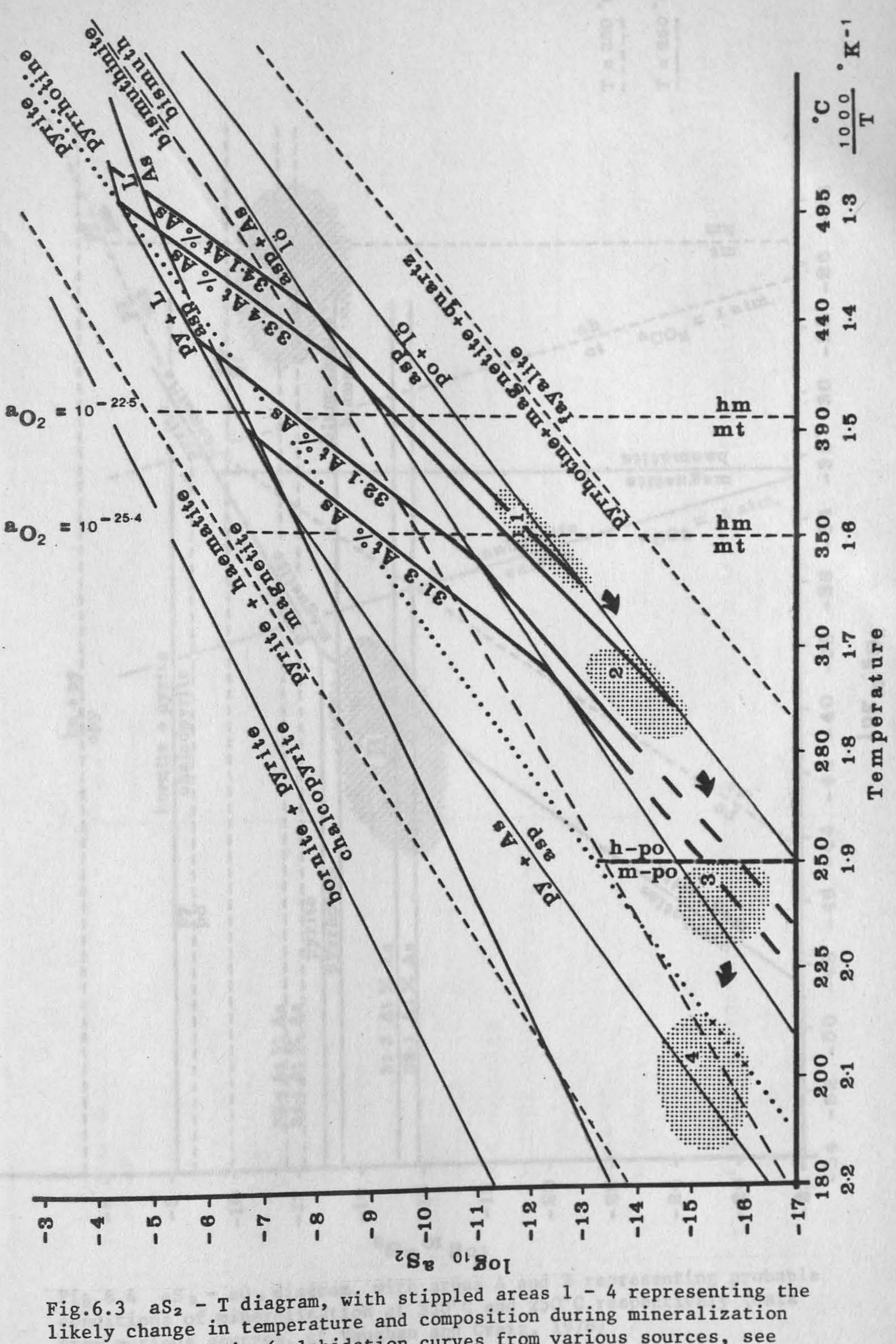


Fig.6.3 aS_2 - T diagram, with stippled areas 1 - 4 representing the likely change in temperature and composition during mineralization of the Bonser Vein (sulphidation curves from various sources, see Barton and Skinner, 1967, and Vaughan and Craig, 1978).

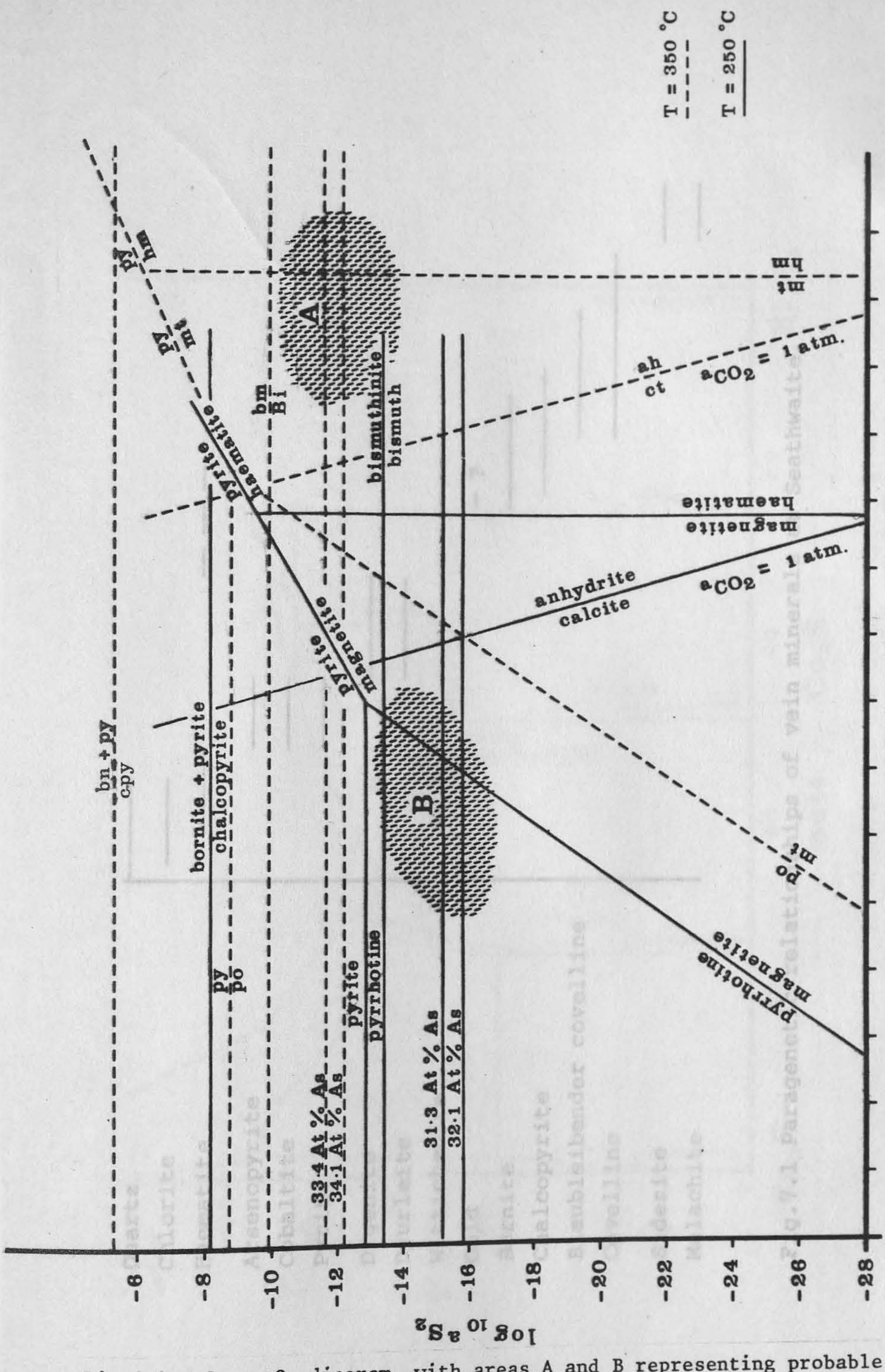


Fig.6.4 aS_2 - aO_2 diagram, with areas A and B representing probable conditions of mineralization at 350°C and 250°C respectively (data from various sources, cf.Vaughan and Craig, 1978)

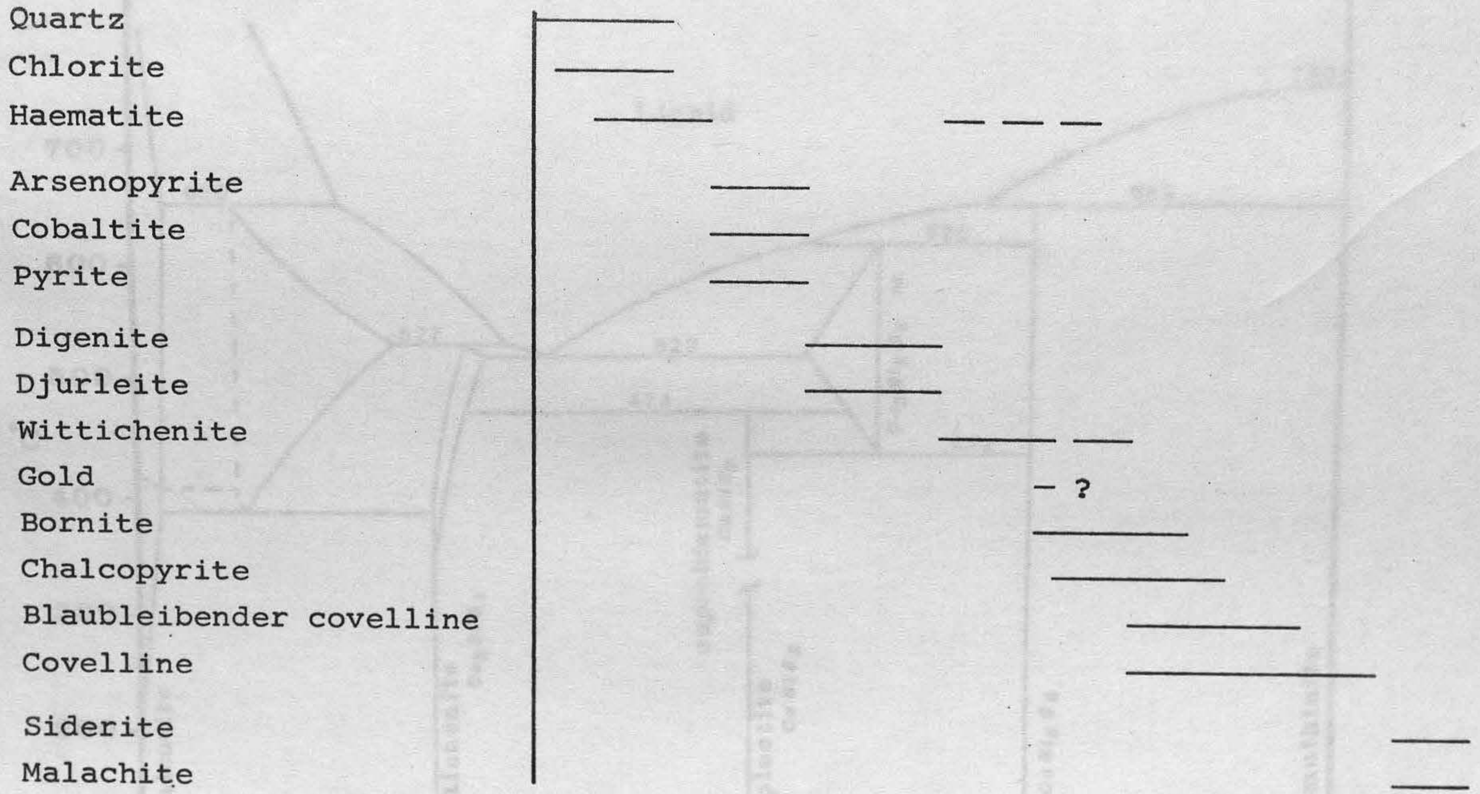


Fig.7.1 Paragenetic relationships of vein minerals at Seathwaite.

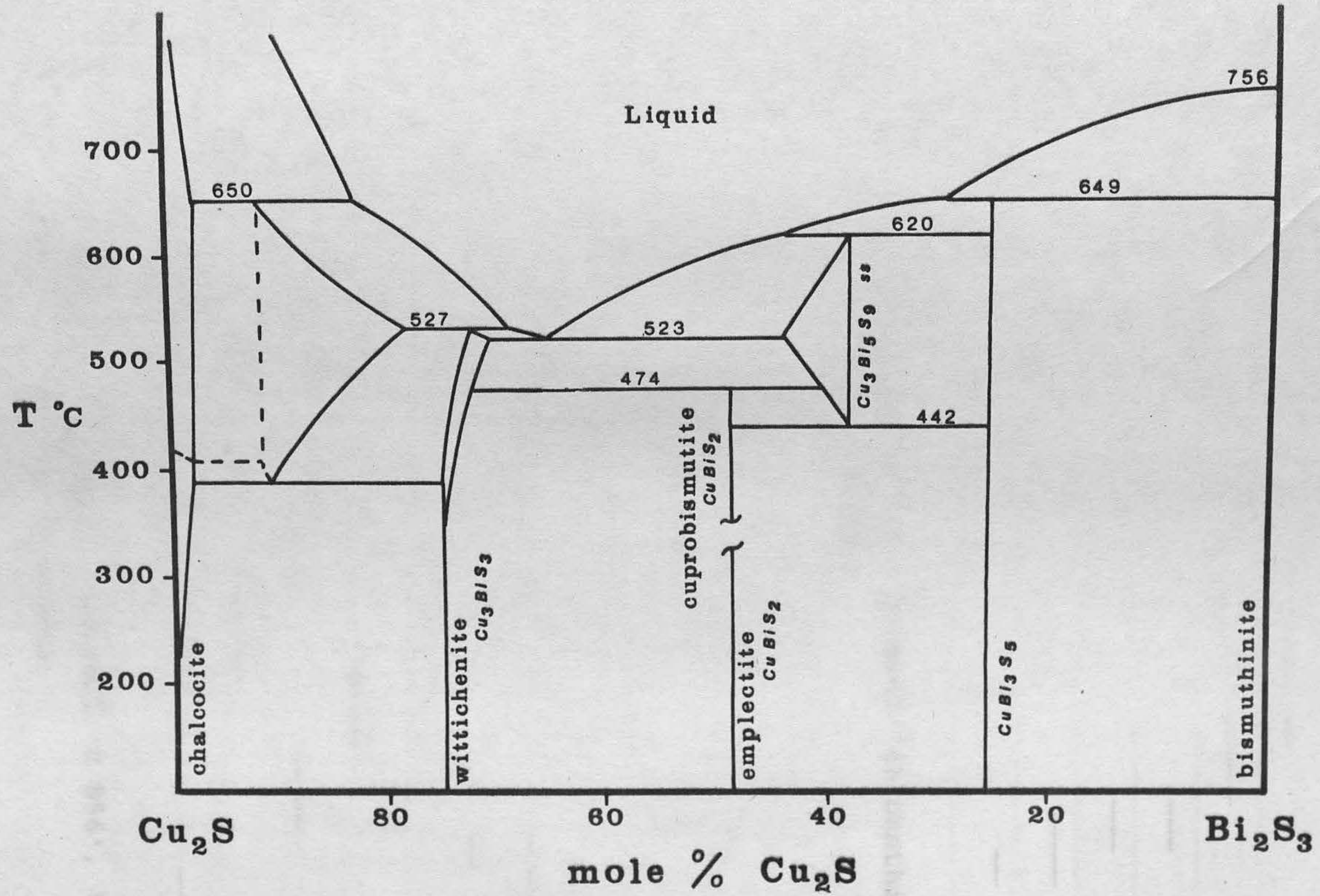


Fig.7.2 Phase diagram of the Cu_2S - Bi_2S_3 system (after Sugaki et al.,1974)

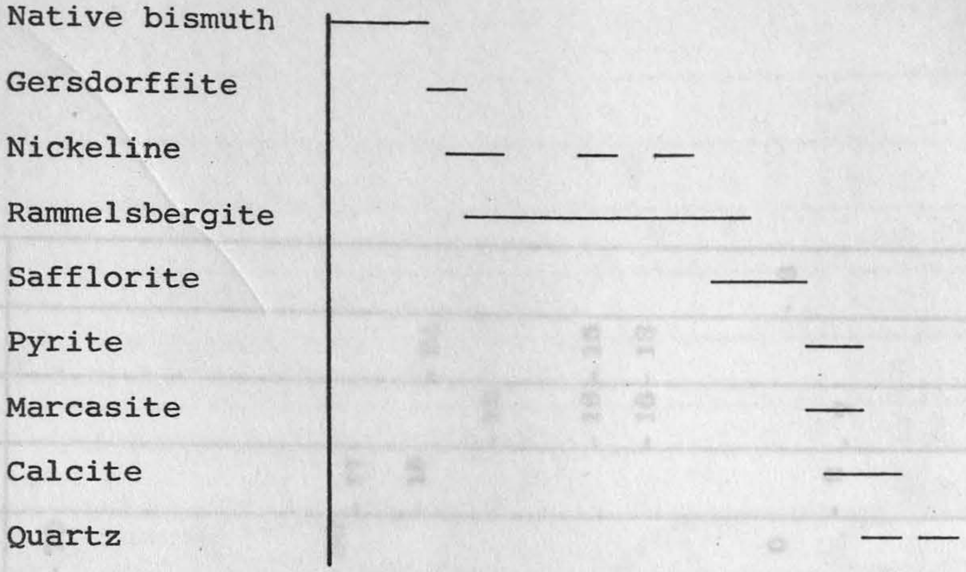


Fig.8.1 Paragenetic diagram - Russell 'chloanthite with native bismuth' specimen.

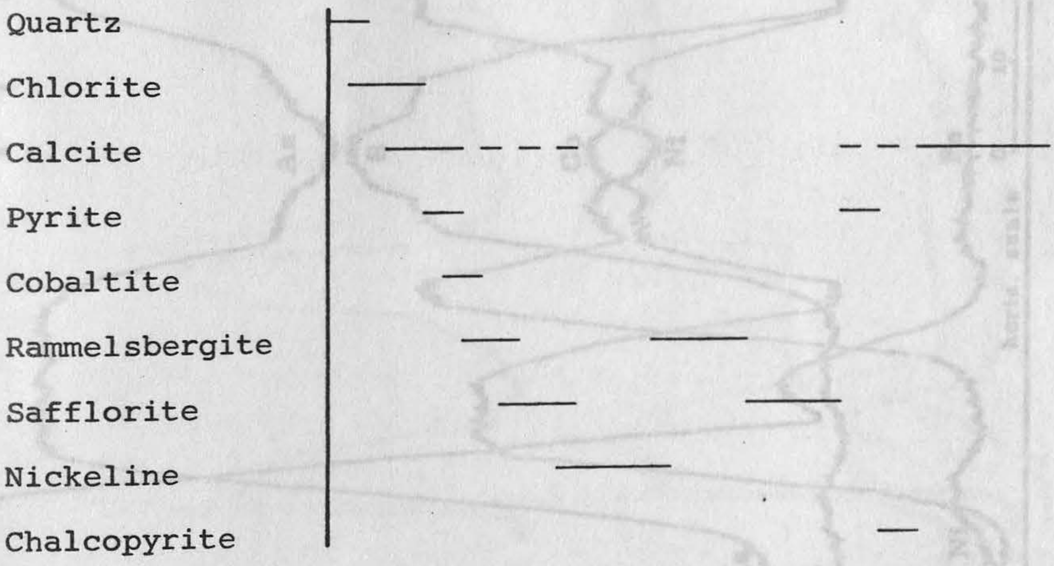


Fig.8.2 Paragenetic diagram - Russell 'R 856', 'R 857', 'R 577', and 'erythrite' specimens.

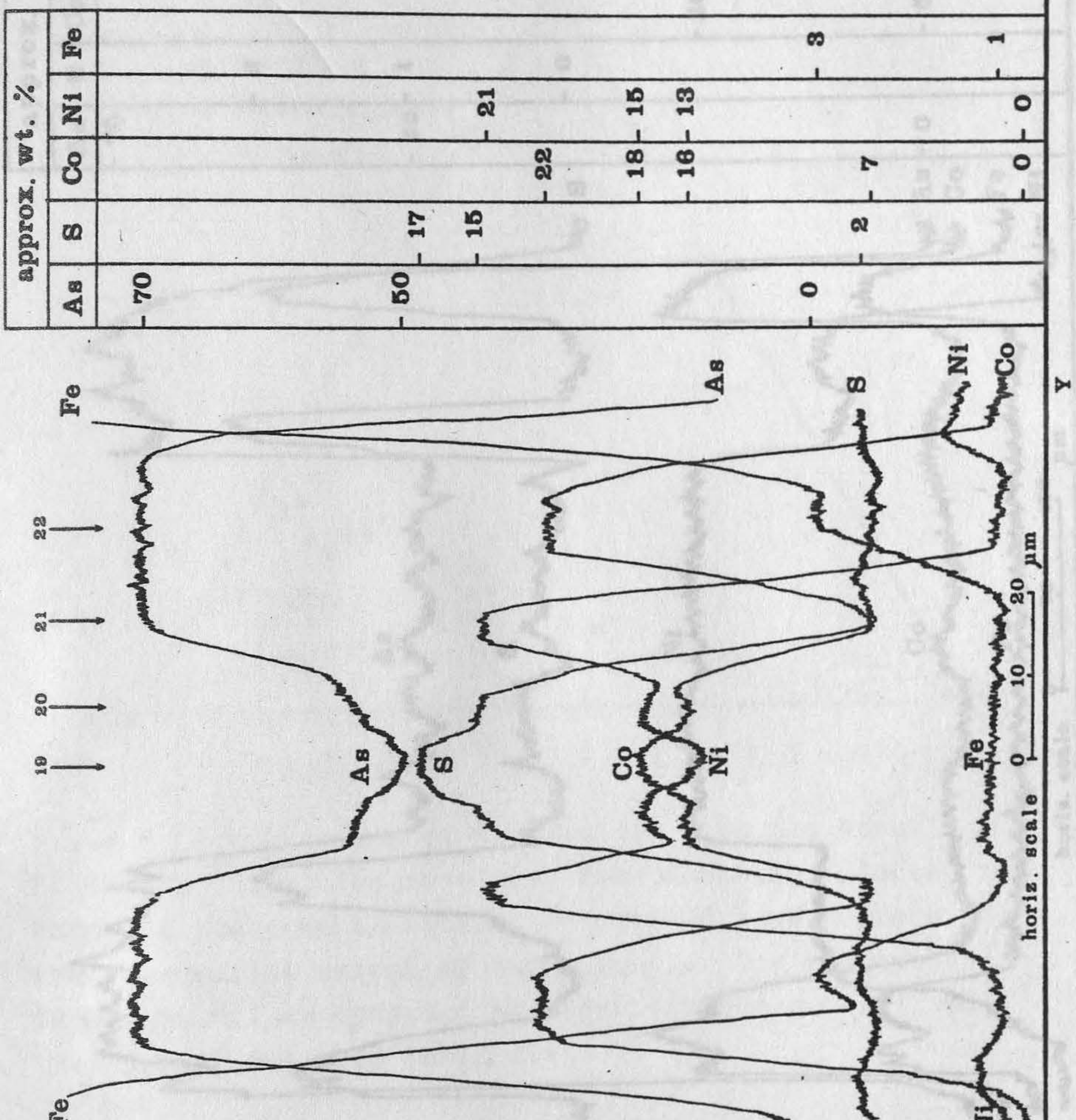


Fig.8.3 Electron microprobe line profile across a grain with central cobaltite overgrown by rammelsbergite and safflorite (see Plate 31). The numbered arrows refer to individual analyses (see Table 8.1).

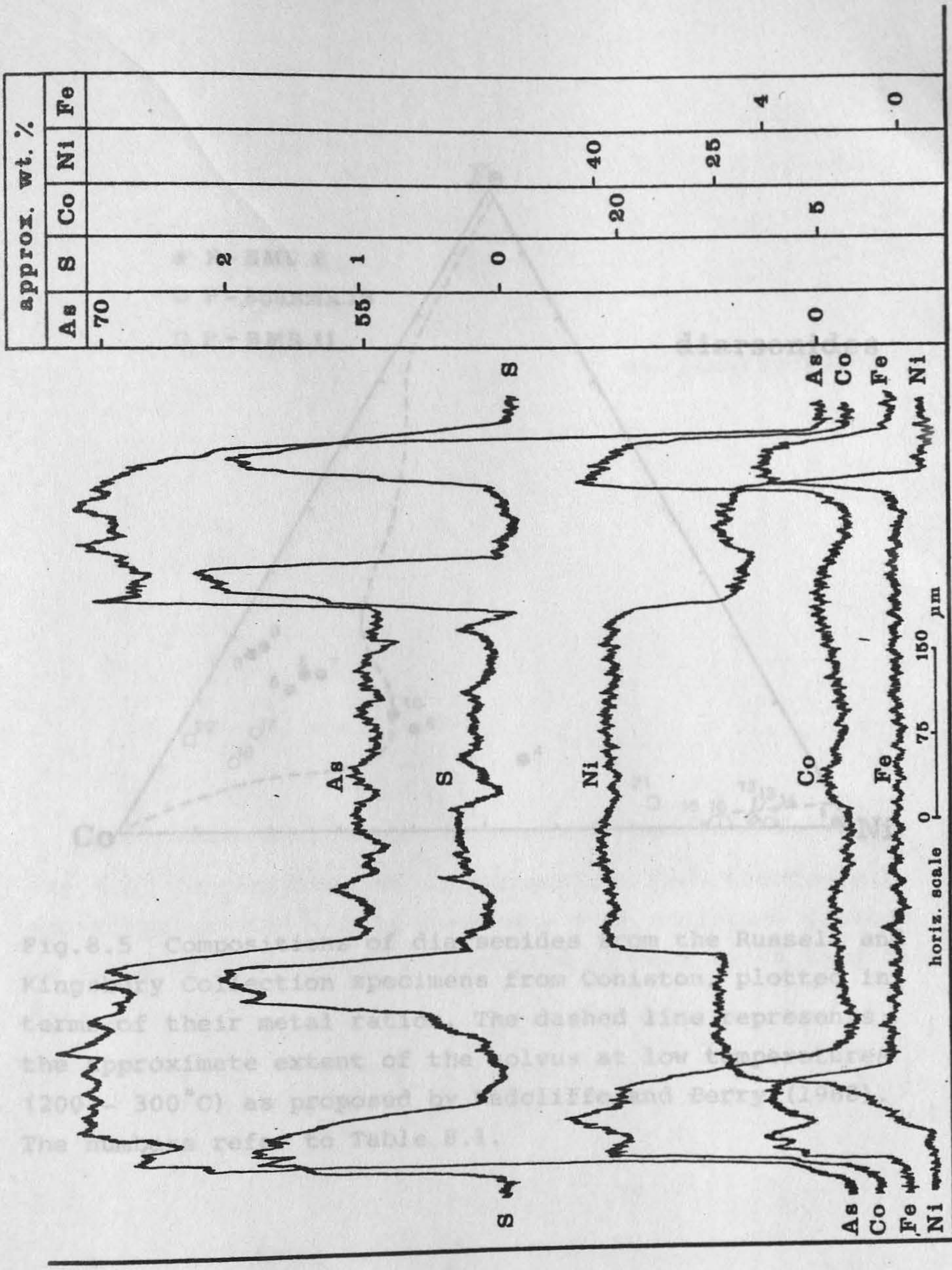


Fig.8.4 Electron microprobe line profile across a grain with nickeline in the centre surrounded by rammelsbergite (with a significant sulphur content adjacent to nickeline), and with safflorite at the margin. X - Y refers to Plate 17.

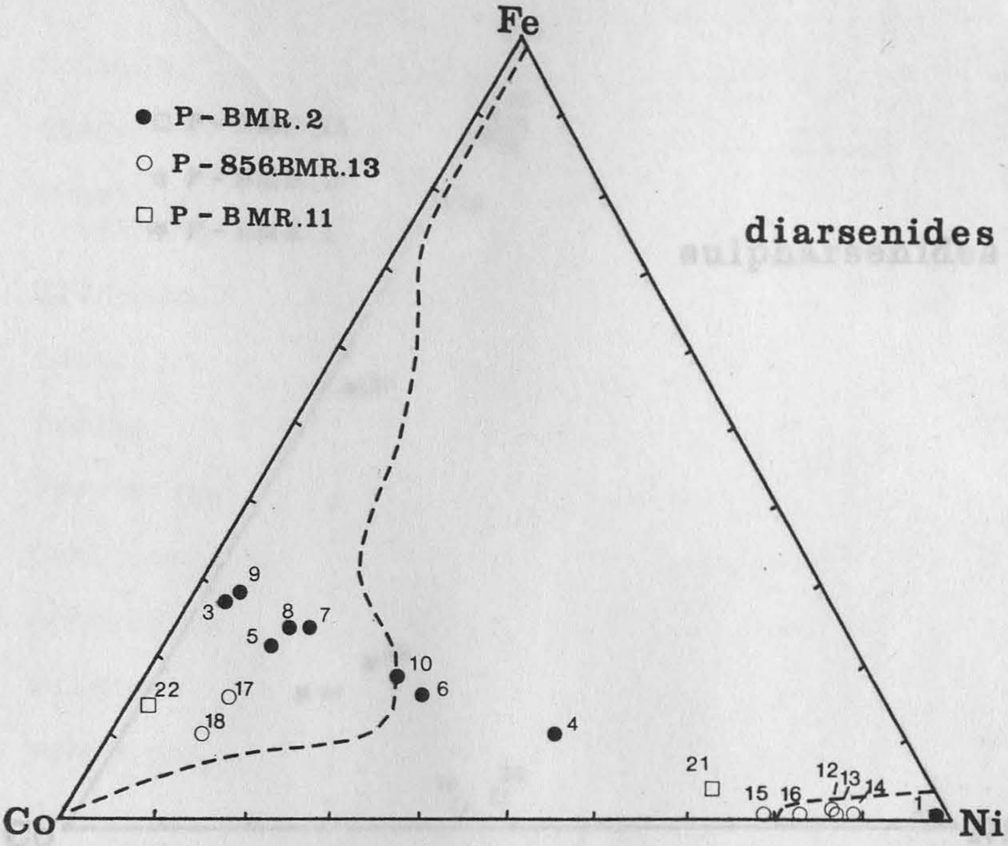


Fig.8.5 Compositions of diarsenides from the Russell and Kingsbury Collection specimens from Coniston, plotted in terms of their metal ratios. The dashed line represents the approximate extent of the solvus at low temperatures (200 - 300°C) as proposed by Radcliffe and Berry (1968). The numbers refer to Table 8.1.

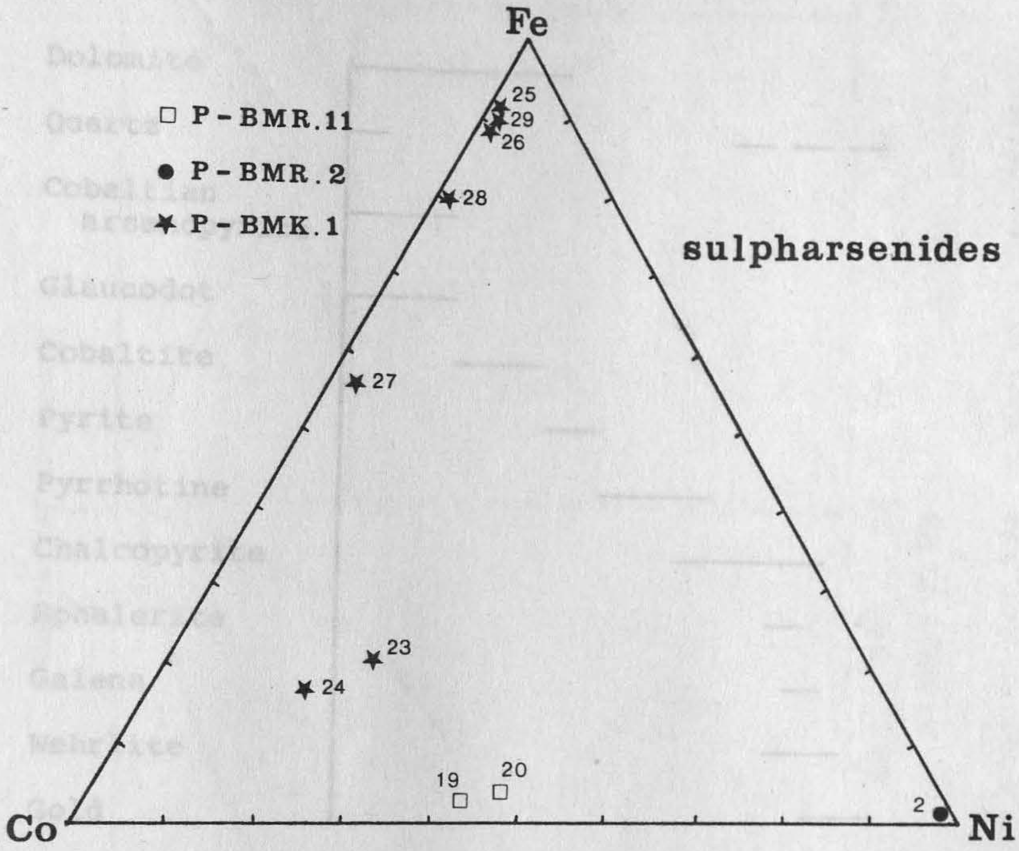


Fig.8.6 Compositions of sulpharsenides from the Russell and Kingsbury Collection specimens from Coniston, plotted in terms of their metal ratios. The numbers refer to Table 8.1.

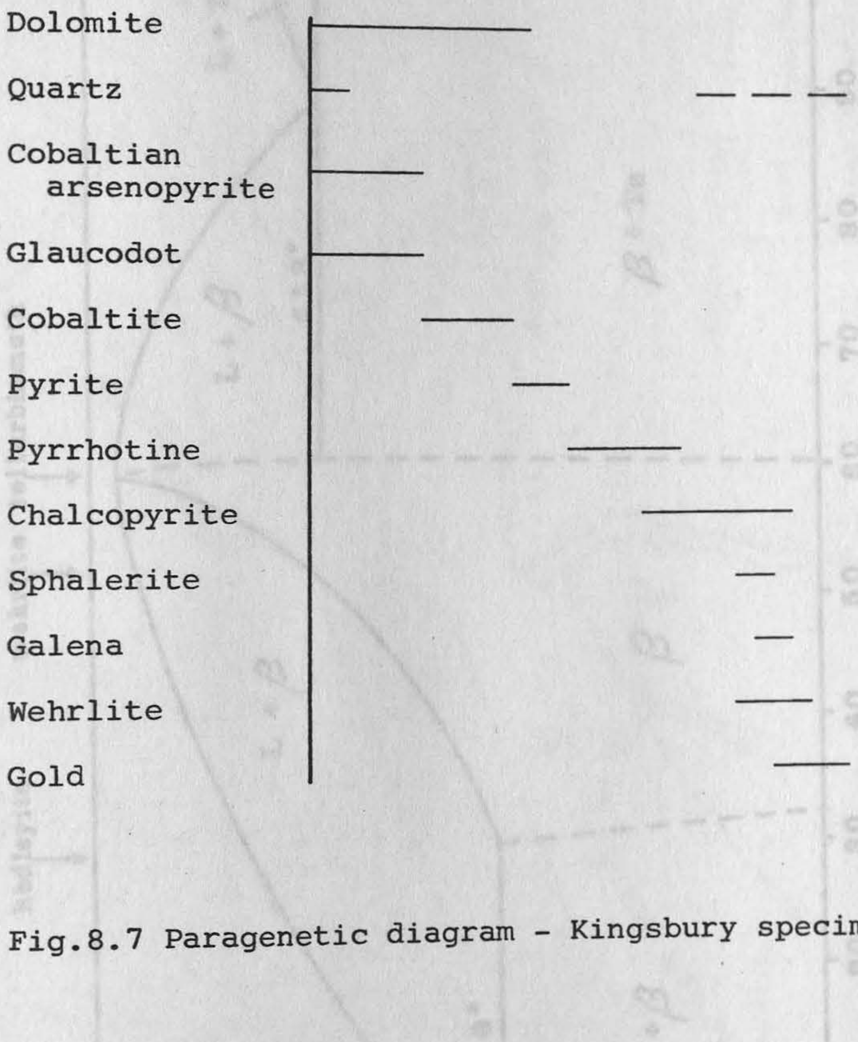


Fig.8.7 Paragenetic diagram - Kingsbury specimens.

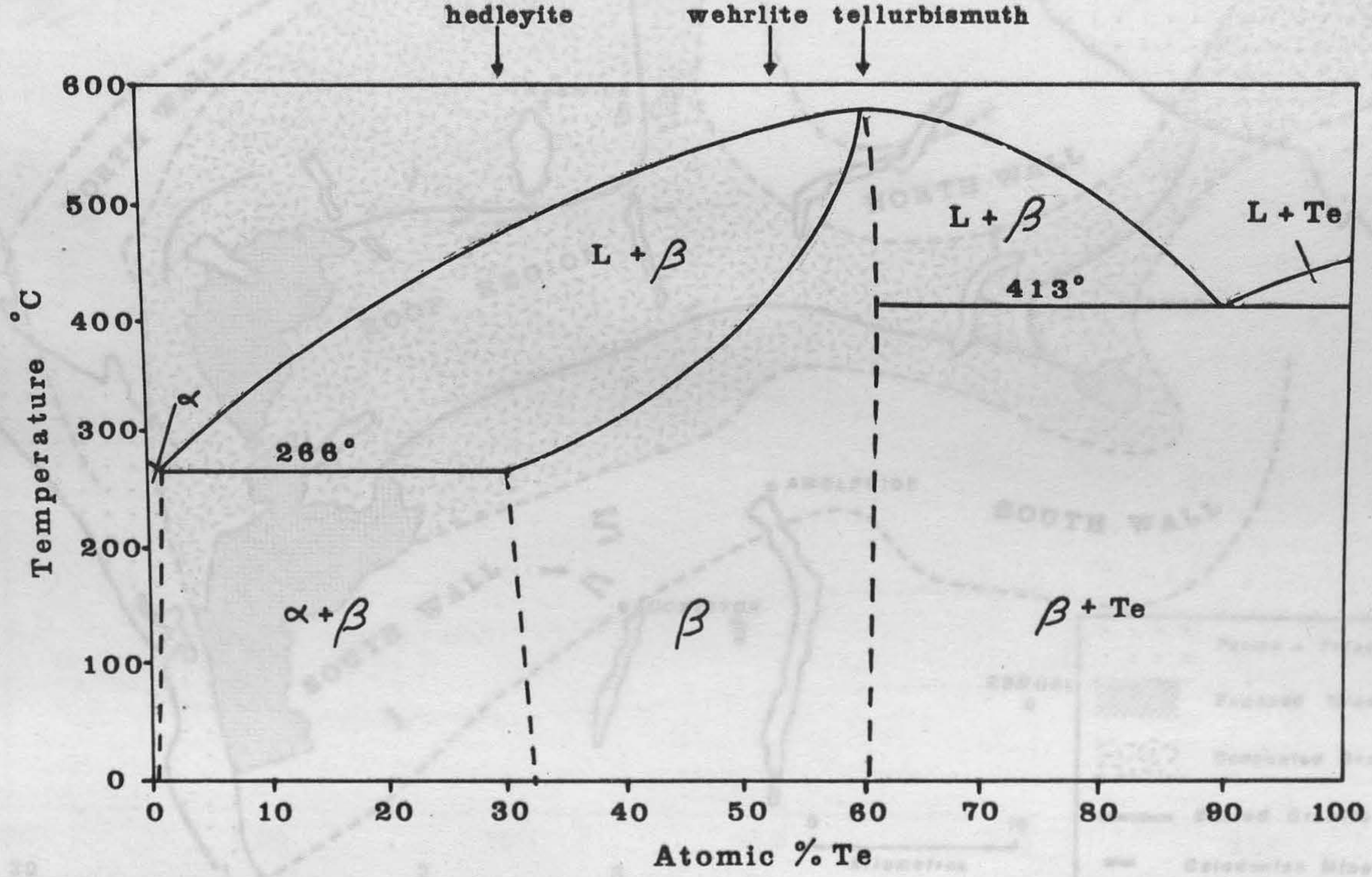


Fig.8.8 Equilibrium diagram for the system Bi - Te (after Brown and Lewis, 1962).

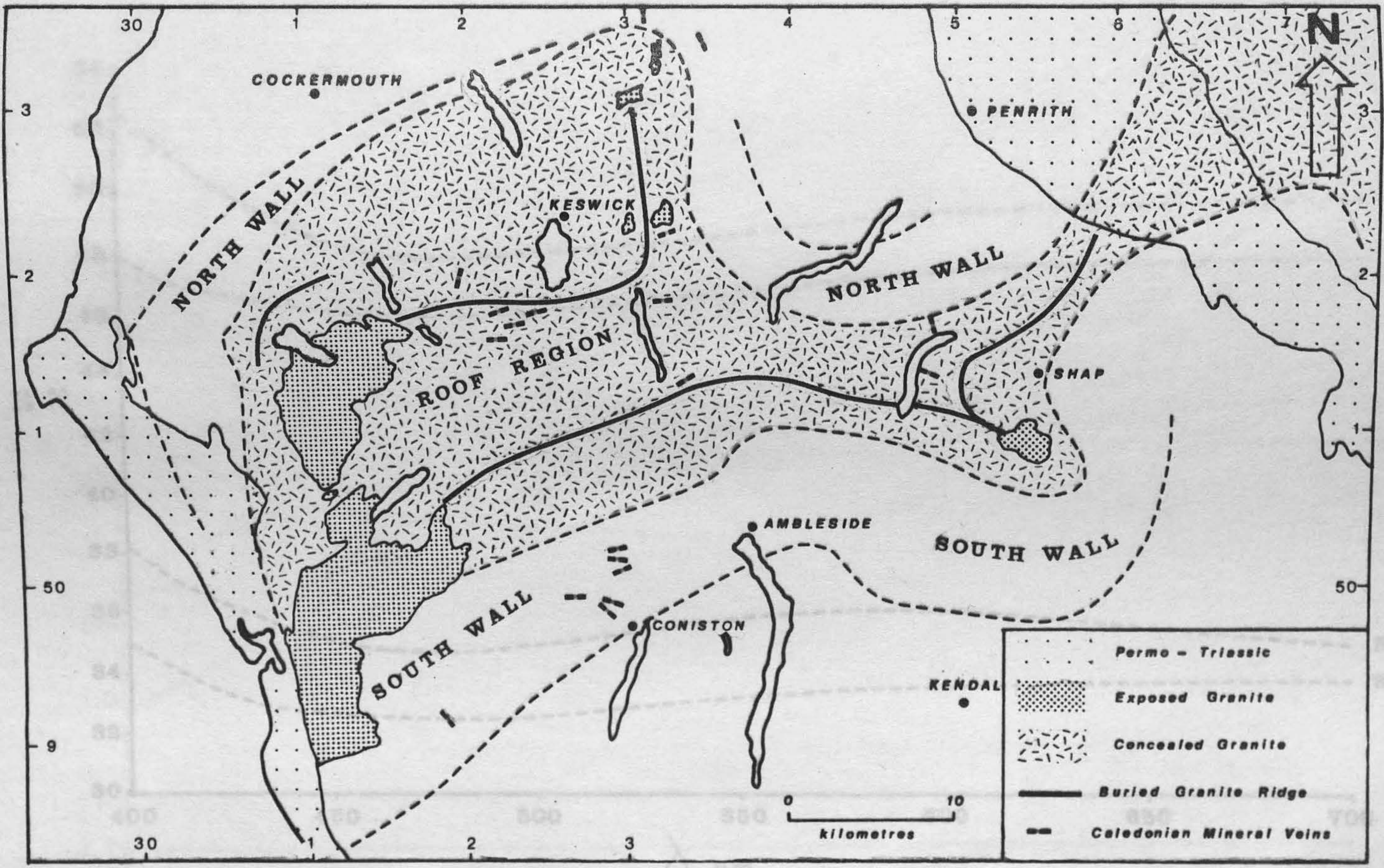


Fig.9.1 Map of the Lake District illustrating the relationship of the Lower Devonian or 'Caledonian' mineral veins to the composite granite batholith of Bott (1974)

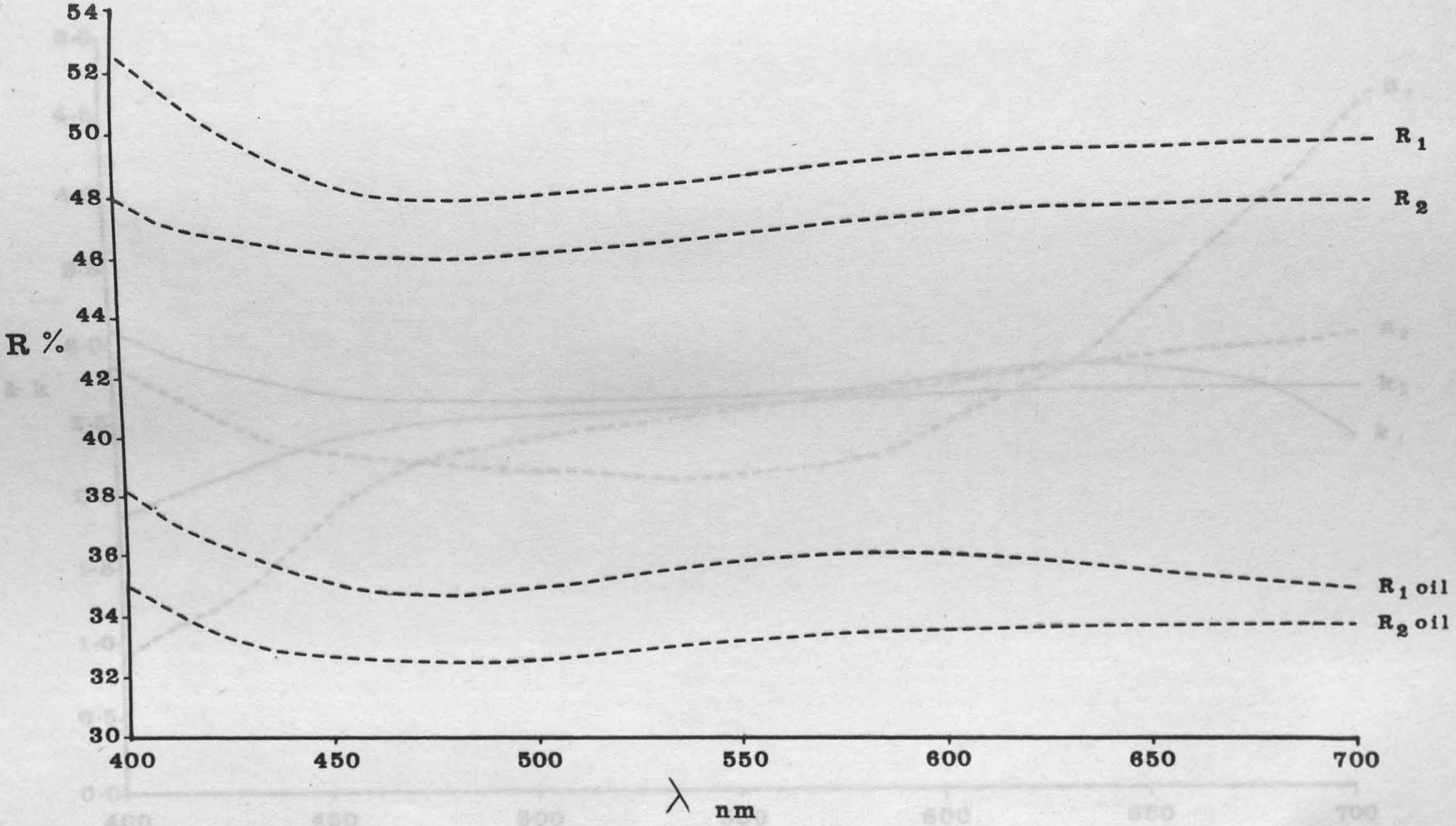


Fig.AII.1 Reflectance of alloclase (curves smoothed graphically)

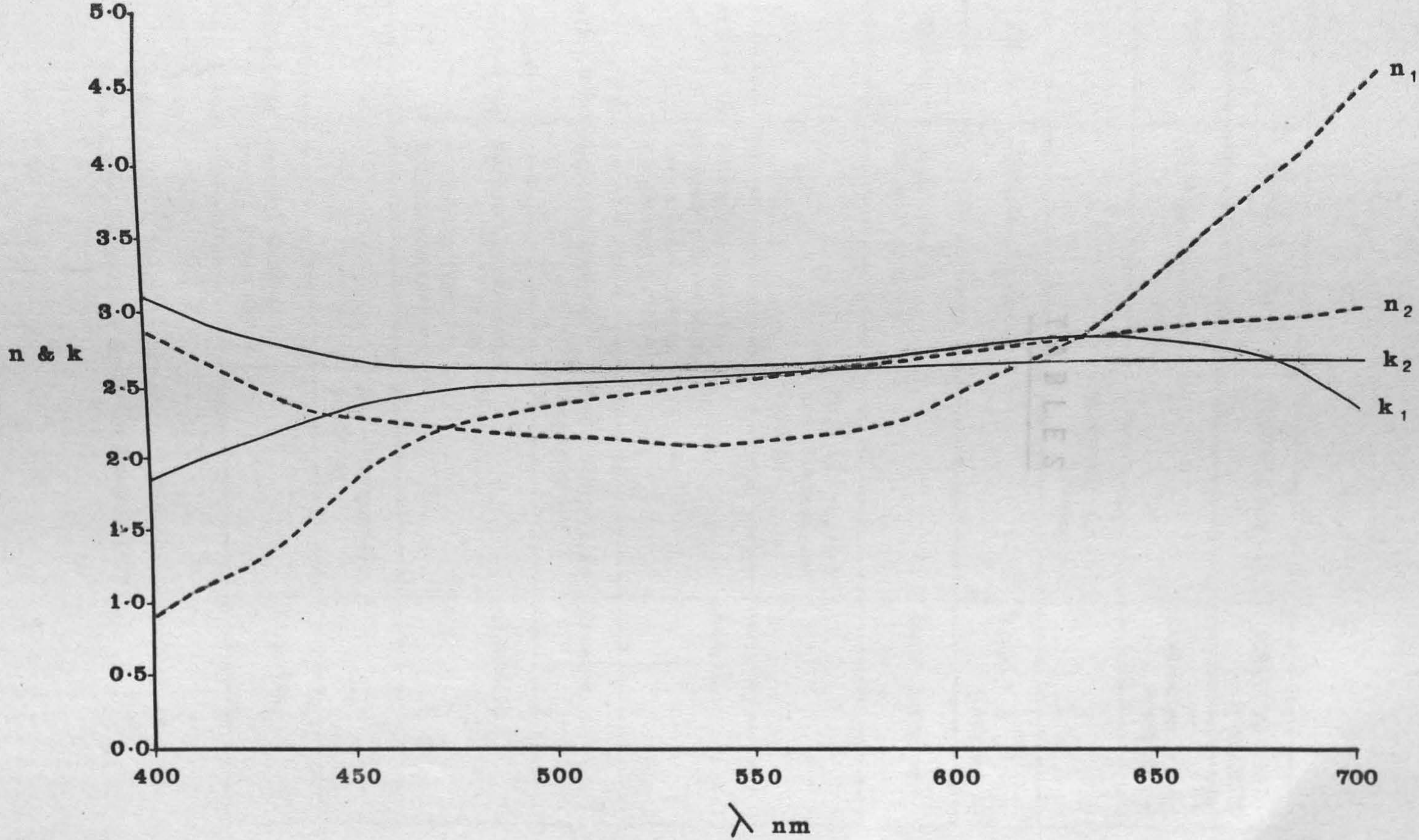


Fig.AII.2 n and k values for alloclase (curves smoothed graphically)

TABLES

AGE	MAGMATIC ACTIVITY	TECTONIC ACTIVITY	STRATIGRAPHIC POSITION
~295 Ma	Olivine dolerite dykes		Stephanian - Westphalian
		Hercynian earth movements	
~345 Ma	Cockermouth Lavas		Dinantian (Courceyan)
~395 Ma	Shap Granite Skiddaw Granite		Lower Devonian
		Main end - Silurian cleavage and folding	
421 ± 8 Ma	Stockdale Rhyolite Ennerdale Granophyre Carrock Granophyre Harestones Felsite		Ashgill
429 ± 9 Ma	Eskdale Granite	Pre - Ashgillian compression	Caradoc
458 ± 9 Ma	Borrowdale Volcanic Group St John's (Threlkeld) Microgranite		Llandeilo
		Pre - Borrowdale faulting	
468 ± 10Ma	Carrock Gabbro Eycott Group Lavas		Llanvirn

TABLE 2.1 Possible sequence of magmatic events in the Lake District (largely based on Rundle, 1979).

TABLE 3.1 Electron microprobe data - Scar Crag Vein

	Spec. No	Composition (wt%)					(atomic%)				Comments
		Co	Fe	As	S	Total	Co	Fe	As	S	
1	K.6.4	0.9	33.6	47.6	19.3	101.4	1.0	32.6	34.2	32.2	Arsenopyrite
2	"	0.9	33.0	47.4	18.6	99.9	1.0	32.6	34.6	31.9	"
3	K.6.5	1.1	33.0	47.1	18.8	100.0	1.3	32.2	34.6	31.9	"
4	BMKi.K.6.1	1.6	32.7	46.7	19.4	100.4	1.3	31.8	33.8	33.1	"
5	78K.6.13	0.8	32.7	47.2	18.7	99.4	0.7	32.4	34.8	32.4	"
6	78K.6.3i	0.3	34.7	45.3	20.5	100.8	0.3	33.2	32.2	34.2	"
7	"	0.9	33.6	44.9	19.4	98.8	0.7	33.1	33.1	33.1	"
8	"	0.3	34.7	44.6	19.7	99.3	0.3	33.9	32.4	33.5	" (using Asp 200)
9	"	0.3	35.0	45.4	20.1	100.8	0.3	33.6	32.5	33.6	" (using Asp 200)
10	78K.6.3ii	0.4	34.2	46.7	19.1	100.4	0.4	33.3	33.9	32.4	"
11	K.6.6	0.3	33.3	46.5	18.6	98.7	0.3	33.1	34.5	32.2	"
12	K.6.5	23.6	11.9	46.2	19.4	101.1	21.9	11.6	33.6	32.9	Glaucodot
13	"	19.4	15.8	46.3	19.1	100.6	17.9	15.6	33.9	32.6	"
14	"	5.9	28.2	47.0	18.7	99.8	5.7	27.7	34.3	32.3	Cobaltian arsenopyrite
15	78K.6.13	22.3	13.4	45.8	18.8	100.3	20.8	13.2	33.7	32.3	Glaucodot
16	"	23.2	12.8	46.2	19.1	101.3	21.5	12.5	33.7	32.3	"
17	"	10.6	24.0	45.4	19.1	99.1	10.0	23.6	33.6	32.9	"

Table 3.1 (continued)

	Spec. No.	Composition (wt%)					(atomic%)				Comments
		Co	Fe	As	S	Total	Co	Fe	As	S	
18	BMKi.K.6.2	10.7	24.5	46.1	17.9	99.2	10.1	24.5	34.3	31.0	Glaucodot
19	"	12.8	22.4	46.7	17.2	99.1	12.1	22.5	35.3	30.1	"
20	78K.6.13	33.6	2.0	44.7	19.0	99.3	31.8	2.0	33.1	33.1	Cobaltite
21	78K.6.13	19.5	2.7	77.2	1.7	101.1	23.6	3.2	69.6	3.6	Skutterudite
22	K.6.4	26.6	8.9	46.7	18.9	101.1	24.7	8.7	34.7	32.0	Alloclase
23	"	24.5	10.3	47.4	19.2	101.4	22.8	10.1	34.6	32.6	"
24	"	29.9	5.6	45.5	18.9	99.9	28.1	5.6	33.8	32.5	"
25	"	29.8	5.5	46.4	18.9	100.6	28.0	5.3	34.3	32.3	"
26	"	30.8	4.9	45.8	19.4	100.9	28.7	4.7	33.3	33.3	"
27	K.6.5	28.3	6.8	47.5	17.7	100.3	26.9	6.6	35.5	30.9	"
28	"	30.7	5.2	46.9	18.1	100.9	28.7	5.3	34.7	31.4	"
29	"	27.5	8.0	46.0	19.0	100.5	25.6	8.0	33.9	32.6	"
30	K.6.6	29.7	6.2	47.0	18.6	101.5	27.8	6.0	34.4	31.8	"
31	78K.6.3i	31.5	4.9	45.7	18.8	100.9	29.3	4.9	33.6	32.2	"
32	"	30.6	6.0	45.9	18.6	101.1	28.5	5.9	33.8	31.8	"
33	"	30.7	5.5	45.2	18.6	100.0	28.9	5.6	33.4	32.1	"
34	"	30.2	5.4	44.0	18.7	98.3	28.9	5.3	32.9	32.9	"

Table 3.1 (continued)

	Spec. No.	Composition (wt%)					(atomic%)				Comments	
		Co	Fe	As	S	Total	Co	Fe	As	S		
35	78K.6.3i	32.0	4.8	46.6	18.0	101.5	30.0	4.9	34.2	30.9	Alloclase	(using Asp 200)
36	"	32.0	4.9	46.4	17.3	100.6	30.7	4.5	34.6	30.1	"	"
37	"	30.9	4.8	46.3	17.4	99.4	29.5	4.9	34.8	30.8	"	"
38	"	29.5	5.9	47.3	16.9	99.6	28.5	5.9	35.7	29.8	"	"
39	"	29.8	6.4	45.7	17.8	99.7	28.3	6.5	34.2	30.9	"	"
40	"	29.5	6.1	47.4	16.9	99.9	28.2	6.2	35.7	29.8	"	"
41	78K.6.3ii	29.4	6.8	45.9	18.9	101.0	27.4	6.6	33.7	32.3	"	"
42	"	30.1	5.6	47.3	18.4	101.5	28.1	5.6	34.8	31.5	"	"
43	"	30.4	5.6	47.5	17.7	101.2	28.6	5.6	35.2	30.6	"	"
44	"	28.2	6.7	48.1	16.9	99.9	27.1	6.9	36.3	29.7	"	"
45	"	27.1	8.0	48.3	16.8	100.2	26.1	7.9	36.3	29.7	"	"

TABLE 4.1 Electron microprobe data - Keswick copper mineralization

DALE HEAD NORTH VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments	
		Fe	As	S	Total	Fe	As	S		
1	78K.1.5	34.2	46.3	20.1	100.6	33.0	33.3	33.8	Arsenopyrite * (core)	ave. comp. 32.8 at% As
2	"	34.4	44.8	20.0	99.2	33.5	32.5	33.9	" "	
3	"	33.7	44.9	20.5	99.1	32.8	32.5	34.7	" "	
4	"	34.2	44.1	21.8	100.1	32.5	31.3	36.2	" (margin)	ave. comp. 31.6 at% As
5	"	34.1	43.9	21.8	99.8	32.6	31.2	36.2	" "	
6	"	34.3	44.3	21.2	100.2	32.7	31.4	35.9	" "	
7	"	34.0	45.0	21.2	100.2	32.5	32.1	35.3	" "	
8	"	34.5	44.2	20.4	99.1	33.5	32.0	34.5	" "	
9	"	33.9	44.2	21.2	99.3	32.7	31.8	35.6	" "	
		Fe	Zn	S	Total	Fe	Zn	S		
10	78K.1.5	7.7	58.0	33.6	99.3	6.7	42.8	50.6	Sphalerite	13.4 mole % FeS
11	78K.1.6	8.3	60.3	32.8	101.4	7.1	44.1	48.9	"	14.2 mole % FeS
12	"	7.8	60.4	32.1	100.3	6.7	44.7	48.5	"	13.4 mole % FeS
13	"	7.8	60.4	32.3	100.5	6.7	44.6	48.7	"	13.4 mole % FeS
14	78K.1.4	8.0	60.2	33.1	101.3	6.8	43.9	49.2	"	13.6 mole % FeS
15	"	7.9	58.7	32.7	99.3	6.8	43.6	49.5	"	13.6 mole % FeS

* using Asp 200 standard

Table 4.1 Dale Head North Vein (continued)

	Spec. No.	Composition	(wt%)					(atomic%)					Comments
				Fe	Zn	S	Total		Fe	Zn	S		
16	78K.1.4			7.9	58.6	33.5	100.0		6.8	42.9	50.2		Sphalerite 13.6 mole % FeS
					Fe	S	Total			Fe	S		
17	78K.1.6				60.1	39.2	99.3			46.8	53.2		Pyrrhotine N_{FeS} - 0.936
18	78K.1.5				58.5	40.0	98.5			45.6	54.4		" " 0.912
19	78K.1.4				59.7	39.3	99.0			46.6	53.4		" " 0.932
20	"				59.9	39.1	99.0			46.8	53.2		" " 0.934
21	78K.1.6				60.1	39.3	99.4			46.7	53.3		" " 0.935
22	"				60.7	40.0	100.7			46.6	53.4		" " 0.931
		Co	Fe	Ni	As	S	Total	Co	Fe	Ni	As	S	
23	77K.1.E	31.3	5.2	0.4	43.0	21.5	101.4	28.3	5.0	0.4	30.6	35.8	Cobaltite *
24	"	30.9	4.5	0.7	42.8	21.5	100.4	28.2	4.4	0.6	30.7	36.1	"
25	"	29.4	3.7	3.6	43.8	21.0	101.5	26.8	3.5	3.3	31.3	35.1	"
26	"	30.9	4.7	0.7	42.8	22.0	101.1	27.9	4.5	0.6	30.4	36.5	"
				Co	Fe	S	Total		Co	Fe	S		
27	78K.1.6			7.6	38.4	53.4	99.4		5.2	27.7	67.0		Cobaltiferous pyrite
28	"			7.9	38.3	53.7	99.9		5.4	27.4	67.1		"
29	"			7.0	38.8	53.6	99.4		4.8	27.9	67.3		"

* using Asp 200 standard

Table 4.1 Dale Head North Vein (continued)

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Co	Fe	S	Total	Co	Fe	S	
30	78K.1.6	7.4	38.1	53.4	98.9	5.1	27.6	67.4	Cobaltiferous pyrite
31	"	3.8	42.5	53.5	99.8	2.6	30.5	66.9	"
32	"	8.2	38.8	53.3	100.3	5.6	27.9	66.6	"
33	"	10.5	36.3	53.4	100.2	7.2	26.0	66.8	"

GOLDSCOPE COPPER VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	As	S	Total	Fe	As	S	
34	K.11.2	34.0	47.0	19.3	100.3	33.1	34.1	32.8	Arsenopyrite * (core) 34.1 at% As
35	"	33.6	44.0	20.8	98.4	32.8	31.9	35.3	" (margin) ave. comp. 31.9 at% As
36	"	33.5	45.4	20.2	99.1	32.7	33.0	34.3	" "
37	"	33.8	44.3	20.8	98.9	32.8	32.0	35.2	" "
		Fe	Zn	S	Total	Fe	Zn	S	
38	K.11.2	4.3	60.7	33.7	98.7	3.7	45.2	51.1	Sphalerite 7.4 mole % FeS
39	"	4.2	60.7	33.4	98.3	3.7	45.5	50.9	" "

* using Asp 200 standard

Table 4.1 (continued)

CASTLE NOOK COPPER VEIN

	Spec. No.	Composition	(wt%)		(atomic%)		Comments
		Fe	S	Total	Fe	S	
40	78K.17.3	60.6	38.8	99.4	47.3	52.7	Pyrrhotine incl. in arsenopyrite N_{FeS} = 0.946

WANTHWAITE VEIN

	Spec. No.	Composition		(wt%)			(atomic%)		Comments	
		Fe	As	S	Total	Fe	As	S		
41	78K.15.6	33.2	46.6	18.7	98.5	33.0	34.6	32.4	Arsenopyrite* (core)	ave. comp. 32.9 at% As
42	"	34.7	45.6	20.4	100.7	33.0	32.6	34.1	" "	
43	"	34.9	45.3	20.7	100.9	33.3	32.2	34.4	" "	
44	"	34.8	45.3	20.5	100.6	33.4	32.4	34.2	" "	
45	"	34.4	45.3	20.5	100.2	33.1	32.5	34.4	" "	
46	"	33.8	44.4	21.0	99.2	32.6	32.0	35.3	" (margin)	ave. comp. 31.9 at% As
47	"	34.0	44.1	20.7	98.8	33.0	31.9	35.0	" "	
48	"	34.4	43.6	21.3	99.3	33.1	31.3	35.7	" "	
49	"	33.8	44.9	19.5	98.2	33.4	33.1	33.6	" "	
50	"	34.9	44.2	20.9	100.0	33.5	31.6	34.9	" "	
51	"	34.7	45.3	20.5	100.5	33.3	32.4	34.2	" "	
52	"	34.7	43.3	21.0	99.0	33.5	31.2	35.3	" "	

* using Asp 200 standard

Table 4.1 Wanthwaite Vein (continued)

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	As	S	Total	Fe	As	S	
53	78K.15.6	35.2	44.0	21.0	100.2	33.7	31.4	35.0	Arsenopyrite* (margin)
54	"	34.9	45.0	20.5	100.5	33.5	32.2	34.3	" "
		Fe	Zn	S	Total	Fe	Zn	S	
55	78K.15.6	3.3	64.0	31.4	98.7	2.9	48.5	48.5	Sphalerite (+cpy exsoln.) 5.8 mole % FeS
56	"	4.6	60.0	33.4	98.0	4.0	45.0	51.0	" (no exsoln.) 8.0 mole % FeS
			Fe	S	Total		Fe	S	
57	78K.15.6		61.6	37.9	99.5		48.2	51.8	Pyrrhotine incl. in asp. N_{FeS} - 0.965

DALE HEAD SOUTH VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
58	K.01.2	1.3	66.2	32.4	99.9	1.1	49.4	49.4	Sphalerite 2.2 mole % FeS

* using Asp 200 standard

	Type of inclusion	No. of inclusions	Mean	S.D.	Range
Final melting point of ice.	Pseudo-secondary	17	-28.5℃	1.27	-32.4℃ to -27.7℃
Final solution point of hydrohalite.	"	17	-19.9℃	2.80	-23.4℃ to -15.2℃
Homogenization temperature.	"	33	120°C	3.90	108°C to 128°C

<u>TABLE 5.1</u> Summary of fluid inclusion results from Carrock East - West Vein fluorite.

	Type of inclusion	No. of inclusions	Mean	S.D.	Range
Final melting point of ice.	Primary	1	-27.0°C	-	-
	Pseudo-secondary	13	-28.3°C	1.15	-27.2°C to -30.4°C
	Secondary	10	-30.5°C	2.20	-27.1°C to -33.3°C
Final solution point of hydrohalite.	Primary	1	-13.3°C	-	-
	Pseudo-secondary	13	-15.3°C	2.00	-12.6°C to -18.4°C
	Secondary	10	-14.0°C	1.60	-11.2°C to -16.8°C
Homogenization temperature.	Primary	1	169.4°C	-	-
	Pseudo-secondary	13	115.0°C	6.60	105 °C to 133 °C
	Secondary	10	99.6°C	4.40	91 °C to 105 °C

TABLE 5.2 Summary of fluid inclusion results from Force Crag Vein sphalerite (specimens collected from No 0 and No 1 Levels).

	Type of inclusion	No. of inclusions	Mean	S.D.	Range
Final melting point of ice.	Primary or pseudosecondary.	8	-28.7°C	1.24	-26.3°C to -30.0°C
	Secondary	11	-30.1°C	1.54	-26.3°C to -31.5°C
Final solution point of hydrohalite.	Primary or pseudosecondary.	8	-18.3°C	6.53	-9.0 °C to -25.0°C
	Secondary	11	-3.8 °C*	1.17*	-5.2 °C* to -2.4 °C*
Homogenization temperatures.	Primary or pseudosecondary.	35	111.1°C	5.60	96.8°C to 118.0°C
	Secondary	11	93.7°C	5.30	81.0°C to 97.2°C

TABLE 5.3 Summary of fluid inclusion results for fluorite from Old Brandlehow Vein (* - excluding inclusions where hydrohalite was demonstrably metastable)

	Type of inclusion	No. of inclusions	Mean	S.D.	Range
Final melting point of ice	Primary and pseudosecondary	7	-24.6°C	0.68	-23.6°C to -25.3°C
	Secondary	3	-23.7°C	0.12	-23.6°C to -23.8°C
Final solution point of hydrohalite	Primary and pseudosecondary	7	-23.7°C	1.92	-21.2°C to -25.7°C
	Secondary	3	-21.6°C	0.45	-21.1°C to -22.0°C
Homogenization temperatures	Primary and pseudosecondary	7	111.3°C	3.51	106.5°C to 117.6°C
	Secondary	3	102.1°C	1.05	101.1°C to 103.2°C

TABLE 5.4 Summary of fluid inclusion results from Hartsop Hall fluorite.

	K - Ar isotopic ages (Ma)- Ineson & Mitchell (1974)	Pb isotopic ages (Ma) - Moorbath (1962)
KESWICK AREA		
Force Crag	349,365,367	-
Thornthwaite	311,314,332,339,365	-
Barrow	352,358	300 ± 80
Yewthwaite	345,362	-
Goldscope Lead	360,362	310 ± 80
Castlenook Lead	362,369	-
Threlkeld	316,329,331	-
Brundholme	272,284,332,340	-
CALDBECK FELLS AREA		
Potts Ghyll	229,249	-
Sandbeds	241,243,263,272	-
Roughtongill	178,189	220 ± 40
Driggith	236,239	260 ± 90
Carrock E - W	197,231,231,282	210 ± 70
HELVELLYN AREA		
Greenside	324,325,372	330 ± 90
Eagle Crag	-	170 ± 80
Myers Head	-	310 ± 80
Hartsop Hall	-	210 ± 70

TABLE 5.5 Summary of isotopic ages of the Lake District lead - zinc veins.

	Mean temperature (after applying a pressure correction - +10 °C)		Mean Salinity (equiv. wt% NaCl)
KESWICK AREA			
Force Crag sphalerite	Primary and pseudosecondary	125 °C	24.0
	Secondary	110 °C	24.3
Old Brandlehow fluorite	Primary and pseudosecondary	121 °C	23.5
	Secondary	104 °C	25.2
Keswick quartz (Shepherd, pers. comm.)	Primary and pseudosecondary	110 - 130 °C	
CALDBECK FELLS AREA			
Carrock Mine fluorite	Primary and pseudosecondary	130 °C	24.0
Sandbeds quartz (Smith,1973)	Primary and pseudosecondary	132 °C	-
Caldbeck Fells quartz (Shepherd, pers. comm.)	Primary and pseudosecondary	130 - 160 °C	-
HELVELLYN AREA			
Hartsop Hall	Primary and pseudosec. ondary	121 °C	23.3
	Secondary	112 °C	23.3
Helvellyn area quartz -(Shepherd, pers. comm.)	Primary and pseudosecondary	115 °C	

TABLE 5.6 Summary of fluid inclusion results for Lake District lead - zinc veins

	Ag (ppm)	Sb (ppm)
KESWICK AREA		
Threlkeld	200 - 250[1] 70[2]	500[2]
Thornthwaite	240 - 260[1] 100[2]	500[2]
Brandlehow	280[1]	-
Goldscope	170 - 190[1] 50[2]	300[2]
Force Crag	700 - 900[1]	
CALDBECK FELLS AREA		
Roughtongill	240[1]	-
Driggith	600 - 700[1]	-
HELVELLYN AREA		
Greenside	100 - 500[1] 150[2]	500 - 5000[1] 1500[2]
Eagle Crag	500[1]	5000[1]
Hartsop Hall	500 - 600[1]	10000[1]
Myers Head	350 - 500[1]	1500[1]

[1] Gough,1963

[2] El Shazly et al.,1957

TABLE 5.7 Silver and antimony trace element contents reported from Lake District galenas.

TABLE 5.8 Electron microprobe data - Lake District lead - zinc veins

DRIGGITH VEIN

	Spec. No.	Composition (wt%)					(atomic%)				Comments
		Cu	Pb	Sb	S	Total	Cu	Pb	Sb	S	
1	CF.15.2	13.4	43.2	24.7	18.1	99.4	17.8	17.5	17.1	47.6	Bournonite
2	"	13.5	43.0	24.8	18.3	99.6	17.7	17.4	17.1	47.8	"

		Cu	Ag	Fe	Zn	Sb	S	Total	Cu	Ag	Fe	Zn	Sb	S	
3	"	30.7	10.2	2.7	4.1	29.3	23.3	100.3	29.1	5.7	2.9	3.8	14.5	43.9	Argentian tetrahedrite
4	"	30.1	11.8	2.8	4.2	28.6	22.5	100.0	29.0	6.7	3.1	3.9	14.4	42.9	"

		Fe	Zn	S	Total	Fe	Zn	S	
5	"	1.7	64.7	32.2	98.6	1.5	49.0	49.5	Sphalerite 3.0 mole % FeS

ROUGHTONGILL SOUTH VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
6	CF.5.5	1.4	64.7	31.9	98.0	1.2	49.3	49.5	Sphalerite 2.5 mole % FeS
7	"	1.1	67.4	30.7	99.2	1.0	51.3	47.7	" 2.0 mole % FeS
8	"	1.2	65.2	31.8	98.2	1.0	49.6	49.4	" 2.0 mole % FeS

TABLE 5.8 (continued)

CARROCK EAST - WEST VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
9	CF.1.4	0.6	65.8	32.2	98.6	0.5	49.9	49.6	Sphalerite 1.0 mole % FeS

FORCE CRAG VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
10	K.7.16	2.2	63.9	31.4	98.0	1.9	48.6	49.5	Sphalerite 3.8 mole % FeS
11	"	2.8	63.8	32.1	98.7	2.5	48.2	49.4	" 4.9 mole % FeS
12	"	1.2	64.9	31.9	98.0	1.0	49.4	49.5	" 2.1 mole % FeS

SALT WELL VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
13	K.4.2	6.2	60.4	32.3	98.9	5.3	47.2	47.5	Sphalerite 10.5 mole % FeS
14	"	0.4	65.7	32.0	98.1	0.3	50.0	49.7	" 0.7 mole % FeS

TABLE 5.8 (continued)

OLD BRANDLEHOW VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
15	K.8.5	0.6	65.5	32.1	98.2	0.5	49.8	49.7	Sphalerite 1.1 mole % FeS
16	"	0.7	65.8	31.8	98.3	0.6	50.0	49.3	" 1.3 mole % FeS

GOLDSCOPE LEAD - ZINC VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
17	K.11.4	1.3	66.2	31.8	99.3	1.1	49.9	48.9	Sphalerite 2.3 mole % FeS
18	"	1.4	65.8	31.9	99.1	1.2	49.7	49.1	" 2.5 mole % FeS

BARROW VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Ni	Sb	S	Total	Ni	Sb	S	
19	K.12.1	26.2	58.2	14.1	98.5	32.7	35.0	32.3	Ullmannite

GREENSIDE VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
20	H.4.1	1.7	64.8	32.3	98.8	1.5	48.8	49.7	Sphalerite 3.0 mole % FeS
21	"	1.6	65.1	32.0	98.7	1.4	49.2	49.3	" 2.9 mole % FeS

TABLE 5.8 (continued)

HARTSOP HALL VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
22	H.3.6	0.4	66.0	32.3	98.7	0.3	50.1	49.6	Sphalerite 0.7 mole % FeS

EAGLE CRAG VEIN

	Spec. No.	Composition (wt%)								(atomic %)							
		Cu	Ag	Fe	Zn	Sb	As	S	Total	Cu	Ag	Fe	Zn	Sb	As	S	
23	77H.2.1	39.7	1.0	2.7	4.6	19.2	6.3	25.5	99.0	34.9	0.5	2.7	3.9	8.8	4.7	44.4	Tetrahedrite
24	"	38.0	1.2	1.7	5.7	27.6	0.6	24.7	99.5	34.5	0.6	1.7	5.0	13.1	0.5	44.5	"

TABLE 6.1 Electron microprobe data - Coniston - Greenburn - Tilberthwaite areas

BONSER VEIN

	Spec. No.	Composition	(wt%)				(atomic%)				Comments
				Fe	S	Total	Fe	S			
1	78Co.2.A			59.6	38.8	98.4	46.9	53.1			Pyrrhotine N_{FeS} - 0.937
2	"			59.5	38.8	98.3	46.8	53.2			" "
			Fe	Zn	S	Total	Fe	Zn	S		
3	"		7.9	58.5	32.8	99.2	6.8	43.5	49.7		Sphalerite 13.6 mole % FeS
4	"		8.3	57.8	32.5	98.6	7.2	43.2	49.5		" 14.4 mole % FeS
5	"		8.3	58.7	32.6	99.6	7.2	43.5	49.3		" 14.4 mole % FeS
			Fe	As	S	Total	Fe	As	S		
6	"		34.4	44.2	20.2	98.8	33.6	32.1	34.3		Arsenopyrite* (incl. in po)
7	"		34.8	43.7	21.4	99.9	33.3	31.3	35.7		" "
8	Co.2.5		34.9	44.9	19.6	99.4	34.1	32.6	33.3		" (core)
9	"		34.8	43.9	20.9	99.6	33.5	31.9	35.5		" (margin)
10	77Co.2.E		33.5	47.1	19.8	100.4	32.5	34.1	33.4		" (core)
11	"		33.8	46.3	20.2	100.4	32.6	33.4	34.0		" (margin)
		Bi	Te	Se	S	Total	Bi	Te	Se	S	
12	78Co.2.C	84.0	0.6	8.6	6.1	99.3	56.9	0.7	15.4	26.9	Laitakarite (A:X = 1.32)
13	"	81.8	1.2	13.2	3.6	99.8	57.6	1.3	24.6	16.5	" (A:X = 1.36)

* using Asp 200 standard

TABLE 6.1 (Bonser Vein - continued)

	Spec. No.	Composition	(wt%)				(atomic%)				Comments
		Bi	Te	Se	S	Total	Bi	Te	Se	S	
14	78Co.2.C	84.4	1.0	9.8	5.2	100.4	57.9	1.1	17.8	23.2	Laitakarite (A:X = 1.38)
15	"	77.8	13.0	2.2	5.9	98.9	54.2	14.9	4.1	26.8	Joseite (A:X = 1.18)
16	Co.2.11.iv	84.4	1.2	10.1	5.1	100.8	57.7	1.3	18.3	22.7	Laitakarite (A:X = 1.36)
17	"	82.2	1.1	9.0	5.7	98.0	56.6	1.3	16.4	25.6	" (A:X = 1.30)
			Pb	Bi	S	Total	Pb	Bi	S		
18	Co.2.21		41.0	42.4	16.3	99.7	21.8	22.3	55.9		Cosalite

PADDY END VEIN

	Spec. No.	Composition	(wt%)						(atomic%)						Comments
		Cu	Fe	Zn	Sb	As	S	Total	Cu	Fe	Zn	Sb	As	S	
19	Co.9.17	41.7	4.0	4.2	0.8	21.7	27.7	100.1	33.6	3.7	3.3	0.4	14.8	44.2	Tennantite
20	"	42.4	3.8	4.3	0.8	21.6	28.3	101.2	33.7	3.4	3.3	0.4	14.6	44.6	"
21	"	42.5	4.0	4.1	0.8	21.5	28.2	101.1	33.8	3.6	3.2	0.4	14.5	44.5	"

DRYGILL VEIN

	Spec. No.	Composition	(wt%)			(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
22	77Co.9.A	7.7	57.7	33.7	99.1	6.7	42.6	50.7	Sphalerite 13.4 mole % FeS
23	"	7.9	58.3	33.8	100.0	6.8	42.7	50.5	" 13.6 mole % FeS

TABLE 6.1 (Drygill Vein - continued)

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	As	S	Total	Fe	As	S	
24	77Co.19.A	34.3	45.2	20.8	100.3	32.9	32.3	34.8	Arsenopyrite *

SUMP VEIN, GREENBURN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	Zn	S	Total	Fe	Zn	S	
25	77Co.1.B	4.7	61.2	33.5	99.4	4.1	45.3	50.6	Sphalerite 8.2 mole % FeS
26	"	3.9	62.5	33.4	99.8	3.4	46.2	50.4	" 6.8 mole % FeS
		Fe	As	S	Total	Fe	As	S	
27	"	34.6	43.7	21.7	100.0	33.0	31.0	36.0	Arsenopyrite * (core)
28	"	34.7	42.1	23.2	100.0	32.6	29.5	38.0	" (margin)

PAVE YORK VEIN

	Spec. No.	Composition (wt%)							(atomic%)						Comments
		Cu	Fe	Zn	Sb	As	S	Total	Cu	Fe	Zn	Sb	As	S	
29	Co.8.4	41.9	3.2	4.8	0.8	21.2	27.1	99.0	34.2	3.0	3.8	0.4	14.7	43.9	Tennantite
			Fe	Zn			S	Total		Fe	Zn			S	
30	"		0.6	65.4			32.2	98.2		0.5	49.6			49.8	Sphalerite 1.0 mole % FeS

* using Asp 200 standard

TABLE 6.1 (continued)

BIRK FELL VEIN

	Spec. No.	Composition (wt%)							(atomic%)						Comments
		Cu	Fe	Zn	Sb	As	S	Total	Cu	Fe	Zn	Sb	As	S	
31	BMR.4145	42.7	3.6	4.3	0.1	21.0	27.4	99.1	34.7	3.3	3.4	0.1	14.4	44.1	Tennantite
			Fe			As	S	Total		Fe			As	S	
32	"		33.3			47.4	18.8	99.5		32.8			34.9	32.3	Arsenopyrite * (core)
33	"		33.7			46.9	19.7	100.3		32.7			34.0	33.3	" (margin)
34	"		33.7			47.4	19.6	100.7		32.6			34.3	33.1	" (core)
35	"		34.0			47.2	19.9	101.1		32.7			33.9	33.4	" (margin)

HELLENS VEIN

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Fe	As	S	Total	Fe	As	S	
36	77Co.4.B	34.2	44.5	21.7	100.4	32.5	31.5	36.0	Arsenopyrite * (core)
37	"	34.8	43.8	22.1	100.1	32.8	30.8	36.3	" (margin)
38	"	34.1	47.1	20.0	101.2	32.8	33.7	33.5	" (core)
39	"	34.5	44.2	21.8	100.5	32.7	31.3	36.0	" (margin)
		Fe	Zn	S	Total	Fe	Zn	S	
40	"	6.6	59.8	33.9	100.3	5.6	43.8	50.6	Sphalerite 11.2 mole % FeS
41	"	6.6	60.2	33.3	100.1	5.7	44.3	50.0	" 11.4 mole % FeS

* using Asp 200 standard

TABLE 6.1 (continued)

TILBERTHWAITE LEAD - ZINC VEIN

	Spec. No.	Composition (wt%)							(atomic%)						Comments
					Fe	Zn	S	Total	Fe	Zn	S				
42	77Co.16.2				6.2	59.3	33.5	99.0	5.4	44.0	50.6				Sphalerite 10.8 mole % FeS
					Fe	As	S	Total	Fe	As	S				
43	"				34.6	44.1	21.7	100.1	32.9	31.2	35.9				Arsenopyrite *
		Cu	Ag	Fe	Zn	Sb	S	Total	Cu	Ag	Fe	Zn	Sb	S	
44	"	27.2	13.6	3.2	4.7	27.5	24.7	100.9	25.5	7.5	3.4	4.3	13.5	45.9	Argentian tetrahedrite
45	"	24.8	16.7	5.3	1.7	27.6	24.4	100.5	23.7	9.4	5.8	0.9	13.8	46.3	"

* using Asp 200 standard

Parnamaa (1963)	VHN_{100}	161 - 195
Young and Millman (1964)	VHN_{100}	170 - 206
Nordrum (1972)	VHN_{100}	170 - 209
Seathwaite wittichenite (this work)	VHN_{100}	170 - 187
Wittichen wittichenite (this work)	VHN_{100}	178 - 197

TABLE 7.1 Vickers microhardness - wittichenite

Locality	Reference	a (Å)	b (Å)	c (Å)
Schapbachthal, Baden	Nuffield, 1947	7.66	10.31	6.69
Wittichen, Baden	Berry and Thompson, 1962	7.68	10.33	6.70
Grusen Mine, Fyresdal	Nordrum, 1972 (from 21 lines)	7.656 ±0.012	10.351 ± 0.019	6.705 ±0.010
Daniel Mine, Wittichen	Kocman and Nuffield, 1973	7.723	10.395	6.716
BM 1437 Wittichen, Baden	this work (from 28 lines)	7.677 ±0.010	10.349 ± 0.015	6.706 ±0.009
Seathwaite, Coniston	this work (from 28 lines)	7.657 ±0.015	10.308 ± 0.022	6.707 ±0.013

TABLE 7.2 Unit cell dimensions - wittichenite

TABLE 7.3 Electron microprobe data - Seathwaite Vein

SEATHWAITE VEIN

	Spec. No.	Composition (wt%)					(atomic%)				Comments	
		Co	Fe	As	S	Total	Co	Fe	As	S		
1	Co.6.1	32.4	2.5	46.9	19.3	101.1	30.3	2.4	34.3	33.0	Cobaltite	
2	"	30.2	3.4	48.1	19.4	101.1	28.1	3.4	35.3	33.2	"	
3	"	31.8	2.7	46.8	19.5	100.8	29.5	2.7	34.2	33.6	"	
4	"	31.3	2.6	48.0	19.6	101.5	29.1	2.7	34.8	33.4	"	
5	"	0.4	33.7	47.0	21.2	101.3	0.4	31.8	33.0	34.8	Arsenopyrite	
			Cu	Bi	S	Total	Cu	Bi	S			
6	"		37.8	43.2	18.5	99.5	43.1	15.0	41.9		Wittichenite	
7	"		38.1	42.9	18.4	99.4	43.5	14.9	41.6		"	
8	"		37.4	43.2	18.5	99.1	42.9	15.1	42.0		"	ave. comp. Cu - 38.0 wt% Bi - 43.4 wt% S - 18.3 wt%
9	"		38.3	42.0	18.1	98.4	44.0	14.7	41.3		"	
10	"		38.2	42.7	18.0	98.9	44.0	14.9	41.1		"	
11	"		38.3	42.9	18.0	99.2	44.0	15.0	41.0		"	

WITTICHEN, BADEN, WEST GERMANY

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Cu	Bi	S	Total	Cu	Bi	S	
12	BM 1437	37.8	43.1	19.1	100.0	42.6	14.7	42.7	Wittichenite
13	"	37.6	43.8	19.1	100.5	42.3	15.0	42.7	"

TABLE 7.3 (Wittichen, Baden, West Germany - continued)

	Spec. No.	Composition (wt%)				(atomic%)			Comments
		Cu	Bi	S	Total	Cu	Bi	S	
14	BM 1437	37.8	43.5	19.0	100.3	42.6	14.9	42.5	Wittichenite
15	"	37.4	43.5	18.2	99.1	43.2	15.2	41.6	"
16	"	37.5	43.4	18.2	99.1	43.2	15.2	41.6	"
17	"	37.7	43.2	18.5	99.4	43.1	15.0	41.9	"
18	"	37.9	43.9	19.1	100.7	42.5	14.9	42.5	"

ave. comp.
Cu - 37.7 wt%
Bi - 43.4 wt%
S - 18.7 wt%

TABLE 8.1 Electron microprobe data - Russell and Kingsbury Collection specimens from Coniston

RUSSELL COLLECTION SPECIMENS

	Spec. No.	Composition (wt%)						(atomic%)					Comments
		Ni	Co	Fe	As	S	Total	Ni	Co	Fe	As	S	
1	BMR.2	28.6	0.5	0.1	71.0	0.4	100.6	33.4	0.5	0.1	65.1	0.8	Rammelsbergite
2	"	33.2	0.1	0.1	49.9	17.9	101.1	31.5	0.1	0.1	37.1	31.1	Gersdorffite
3	"	1.1	21.4	8.0	62.8	7.2	100.5	1.2	22.9	9.0	52.8	14.1	Safflorite
4	"	14.5	11.7	3.2	66.6	4.5	100.5	16.1	13.0	3.7	58.0	9.1	"
5	"	3.7	19.7	6.1	67.4	3.8	100.7	4.1	21.9	7.1	59.0	7.8	"
6	"	9.6	15.5	4.7	64.4	7.4	101.6	10.2	16.4	5.2	53.7	14.4	"
7	"	4.4	18.7	7.0	66.4	5.3	101.8	4.8	20.2	8.0	56.5	10.5	"
8	"	4.0	18.8	6.7	67.6	4.1	101.2	4.4	20.8	7.8	58.7	8.3	"
9	"	1.4	19.7	8.0	68.2	4.0	101.3	1.6	21.7	9.3	59.2	8.1	"
10	"	8.2	16.3	5.2	65.5	5.3	100.5	9.0	17.9	6.0	56.4	10.7	"
11	856.BMR.13	39.2	4.7	0.1	55.6	0.4	100.0	43.9	5.3	0.1	48.7	2.0	Nickeline
12	"	25.5	4.0	0.2	68.2	1.8	99.7	29.5	4.6	0.3	61.8	3.8	Rammelsbergite (adjacent to nickeline)
13	"	24.8	3.6	0.1	67.6	2.2	98.3	29.0	4.2	0.1	62.0	4.7	" "
14	"	25.6	2.9	0.1	70.1	0.4	99.1	30.4	3.4	0.1	65.2	0.8	Rammelsbergite

TABLE 8.1 (Russell Collection specimens - continued)

	Spec. No.	Composition (wt%)						(atomic%)					Comments
		Ni	Co	Fe	As	S	Total	Ni	Co	Fe	As	S	
15	856.BMR.13	22.2	5.5	0.1	69.7	0.7	98.2	28.4	7.0	0.2	69.8	1.7	Rammelsbergite
16	"	22.9	4.7	0.1	70.6	0.2	98.5	27.5	5.6	0.1	66.3	0.4	"
17	"	3.4	22.8	4.3	67.8	2.3	100.6	3.9	25.8	5.1	60.4	4.8	Safflorite
18	"	2.9	22.4	3.0	70.1	1.2	99.6	3.4	26.1	3.7	64.3	2.5	"
19	BMR.11	13.4	17.7	1.1	49.7	17.3	99.2	13.0	17.1	1.1	37.8	30.8	Cobaltite
20	"	14.6	15.9	1.1	52.7	15.3	99.6	14.5	15.7	1.2	40.9	27.7	"
21	"	20.7	7.3	1.0	69.6	2.4	101.0	23.5	8.3	1.2	62.0	5.0	Rammelsbergite
22	"	0.5	21.7	3.4	72.7	0.6	98.9	0.6	25.8	4.3	68.0	1.3	Safflorite

KINGSBURY COLLECTION SPECIMENS

	Spec. No.	Composition (wt%)						(atomic%)					Comments
		Ni	Co	Fe	As	S	Total	Ni	Co	Fe	As	S	
23	BMK.1	7.9	19.9	6.9	47.8	18.2	100.7	7.5	18.7	6.9	35.4	31.5	Cobaltite
24	"	6.4	23.8	6.1	45.4	19.4	101.1	5.9	22.0	5.9	33.1	33.0	"
25	"	0.3	2.9	30.9	47.0	19.7	100.8	0.3	2.6	29.9	33.9	33.2	Cobaltian arsenopyrite *
26	"	0.2	3.9	30.0	45.3	19.9	99.3	0.2	3.6	29.3	33.0	33.9	"

* using Asp 200 standard

TABLE 8.1 (Kingsbury Collection specimens - continued)

	Spec. No.	Composition (wt%)						(atomic%)					Comments
		Ni	Co	Fe	As	S	Total	Ni	Co	Fe	As	S	
27	BMK.1	1.1	14.9	19.3	46.9	19.3	101.5	1.0	13.7	18.7	33.9	32.6	Glaucodot
28	"	0.2	7.1	26.9	46.3	19.4	100.9	0.2	6.6	26.4	33.8	33.1	Cobaltian arsenopyrite
29	"	0.2	3.6	30.6	45.8	19.3	99.6	0.2	3.3	30.0	33.5	33.0	"
				Fe		S	Total		Fe	S			
30	"			59.7		39.1	98.8		46.7	53.3			Pyrrhotine $N_{FeS} \simeq 0.934$
				Au		Ag	Total		Au	Ag			
31	"			82.1		17.4	99.5		72.1	27.9			Gold
32	"			81.7		18.0	99.7		71.3	28.7			"
33	"			83.5		16.6	100.1		73.5	26.5			"
				Bi		Te	Total		Bi	Te			
34	"			69.9		29.8	99.7		58.8	41.2			Wehrlite (Bi:Te - 1.43)
35	"			70.3		30.3	100.6		58.6	41.4			" (Bi:Te - 1.42)
36	"			70.2		29.7	99.9		59.1	40.9			" (Bi:Te - 1.44)

TABLE 9.1 Classification of Lake District mineralization

AGE	REFERENCE	CHARACTERISTIC MINERALS	EXAMPLES
Uncertain	Strens (1962,1965) Ineson & Mitchell (1975)	GRAPHITE - pyrite - chalcopyrite	Borrowdale
Lower to Middle Devonian c.390 - 370 Ma (occupying normal faults or less commonly thrust and tear faults associated with the Caledonian Orogeny)	Hitchen (1934) Shepherd et al. (1976)	QUARTZ - MUSCOVITE - APATITE - WOLFRAMITE SCHEELITE - ARSENOPYRITE - PYRITE - PYRRHOTINE - chalcopyrite - bismuthinite native bismuth - bismuth sulphotellurides molybdenite - sphalerite - fluorite (purple	Carrock (associated with the Skiddaw Granite)
	Russell (1924) Firman (1957)	QUARTZ - FLUORITE (purple) - PYRITE - MOLYBDENITE - BISMUTHINITE - native bismuth - chalcopyrite - pyrrhotine - magnetite	Shap (associated with the Shap Granite)
	This work (Ch.3)	QUARTZ - APATITE - CHLORITE - ARSENOPYRITE - Co - Fe SULPHARSENIDES - pyrite - native bismuth - bismuthinite	Scar Crag

TABLE 9.1 continued.

AGE	REFERENCE	CHARACTERISTIC MINERALS	EXAMPLES
Lower to Middle Devonian (cont.)	This work (Ch.4, Ch.6 & Ch.8)	QUARTZ - CHLORITE - DOLOMITE - ARSENOPYRITE - PYRITE - CHALCOPYRITE ± magnetite pyrrhotine ± native bismuth ± bismuthinite ± bismuth sulphoselenides and sulphotellurides ± sphalerite ± galena ± Co/Ni minerals	Ulpha, Bonser Vein, Paddy End Vein, South Vein, Drygill (Coniston) Vein, Long Crag, Greenburn Veins, Tilberthwaite Copper Veins, Dale Head North, Goldscope, Castle Nook, Manesty, Copper Plate, Thirlspot, Birkside Gill, Wanthwaite, Haweswater Veins, Potts Ghyll Copper, Carrock End and others.
Uncertain	This work (Ch.4, Ch.6 & Ch.7)	(oxidation assemblages of the above primary mineralization) BORNITE - COPPER SULPHIDES - MALACHITE - chalcopyrite ± tennantite ± haematite ± wittichenite ± sphalerite	Pave York, Birk Fell, Seathwaite Veins, Dale Head South
Uncertain	Postlethwaite (1913) Davidson and Thompson (1948)	QUARTZ - STIBNITE	Robin Hood Bassenthwaite, St Sunday Crag

TABLE 9.1 continued.

AGE	REFERENCE	CHARACTERISTIC MINERALS	EXAMPLES
Upper Devonian to Lower Carboniferous (Dinantian) c.360 - 330 Ma (mostly along normal faults with N - S, NW - SE and NE - SW directions)	This work (Ch.5)	QUARTZ - CHALCEDONY - BARYTES - GALENA - SPHALERITE ± chalcopyrite ± native antimony ± tetrahedrite ± antimony sulphosalts ± calcite ± dolomite ± fluorite (amber or pale green)	Greenside, Hartsop Hall, Myers Head, Eagle Crag, Ruthwaite Lodge, Wythburn, Brown Cove, Tilberthwaite Pb-Zn, Barrow, Force Crag, Goldscope Pb, Castle Nook Pb, Yewthwaite, Brandlehow, Old Brandlehow, Thornthwaite, Threlkeld, Brundholme, Driggith, Roughtongill, Red Gill, Carrock E-W, and others
Upper Carboniferous (Stephanian) to Permian c.290 - 260 Ma (mostly along E - W normal faults, and in joints in the Carboniferous Lst.)	This work (Ch.5) also Gough(1963) Strens(1962)	BARYTES ± quartz ± carbonates ± galena	Potts Ghyll, Sandbeds, Ruthwaite, Force Crag?, Brundholme?, and others

TABLE 9.1 continued.

AGE	REFERENCE	CHARACTERISTIC MINERALS	EXAMPLES
Permo - Triassic ?	Shepherd (1973) Rose & Dunham (1977)	HAEMATITE ± quartz ± calcite ± dolomite ± barytes ± fluorite	West Cumbria haematite deposits
Jurassic c.190 - 180 Ma	Davidson and Thompson (1948) Rastall (1942)	(alteration in the Caldbeck Fells area) PYROMORPHITE - COPPER SULPHIDES - MALACHITE ± mimetite ± linarite ± anglesite ± cerussite ± psilomelane ± smithsonite ± numerous other species	Roughtongill, Driggith, Drygill (Caldbeck Fells), Red Gill, Poddy Gill

AIR

	R$_1$			R$_2$		
λ nm	mean	range	s.d.	mean	range	s.d.
400	52.8	51.7 - 54.3	0.98	48.2	47.3 - 50.8	1.15
420	50.7	49.1 - 51.8	0.89	47.1	45.9 - 47.9	0.74
440	49.2	48.6 - 49.7	0.37	46.6	45.8 - 47.1	0.37
460	48.3	48.1 - 48.8	0.20	46.3	46.1 - 46.5	0.12
480	48.1	47.8 - 48.4	0.20	46.3	46.1 - 46.4	0.14
500	48.3	48.1 - 48.5	0.13	46.4	46.2 - 46.6	0.13
520	48.5	48.3 - 48.7	0.13	46.6	46.4 - 46.8	0.12
540	48.7	48.6 - 49.0	0.10	46.8	46.6 - 47.0	0.11
560	49.1	48.9 - 49.4	0.15	47.1	47.0 - 47.3	0.09
580	49.4	49.2 - 49.5	0.08	47.4	47.2 - 47.5	0.07
600	49.6	49.4 - 49.9	0.15	47.6	47.4 - 47.9	0.11
620	49.8	49.6 - 49.9	0.12	47.8	47.6 - 48.0	0.14
640	49.8	49.7 - 50.1	0.11	47.9	47.6 - 48.3	0.19
660	49.9	49.7 - 50.1	0.18	48.0	47.6 - 48.3	0.20
680	49.9	49.7 - 50.3	0.18	48.0	47.8 - 48.1	0.13
700	49.9	49.7 - 50.3	0.16	48.0	47.7 - 48.2	0.15

OIL

	R$_1$			R$_2$		
λ nm	mean	range	s.d.	mean	range	s.d.
400	38.6	35.9 - 41.9	2.43	40.3	37.2 - 44.9	2.94
420	36.8	36.0 - 37.7	0.64	37.4	36.7 - 38.2	0.48
440	35.6	35.3 - 36.2	0.32	34.9	34.3 - 35.5	0.35
460	34.9	34.7 - 35.2	0.15	33.2	33.1 - 33.5	0.15
480	34.9	34.5 - 35.1	0.18	32.7	32.4 - 32.9	0.14
500	35.2	34.8 - 35.5	0.19	32.8	32.5 - 33.2	0.19
520	35.5	35.3 - 35.7	0.12	32.9	32.6 - 33.1	0.13
540	36.0	35.9 - 36.2	0.10	33.2	33.1 - 33.5	0.10
560	36.1	36.0 - 36.3	0.09	33.3	33.1 - 33.4	0.21
580	36.3	36.1 - 36.4	0.08	33.6	33.5 - 33.8	0.09
600	36.1	36.0 - 36.3	0.10	33.7	33.5 - 33.9	0.13
620	36.0	35.7 - 36.3	0.17	33.8	33.6 - 34.4	0.22
640	35.6	35.4 - 35.8	0.12	33.8	33.6 - 34.0	0.15
660	35.4	35.3 - 35.7	0.16	33.8	33.7 - 34.1	0.15
680	35.2	35.1 - 35.4	0.11	33.9	33.7 - 34.1	0.14
700	34.9	34.7 - 35.3	0.19	33.8	33.6 - 34.0	0.17

TABLE A II. 1 Reflectance data for alloclase

	Mean	Range	Standard error
Arsenopyrite	1011	960 - 1040	7.06
Glaucodot	956	920 - 1011	9.68
Alloclase	881	818 - 940	15.52

TABLE AII.2 Vickers microhardness (100 g load) for Scar Crag arsenopyrite, alloclase and glaucodot.

Wittichen, Baden Berry and Thompson (1962)		Seathwaite, Coniston This work	
d (A)	I	d (A)	I
5.68	1	5.71	2
5.22	1	5.23	2
4.55	4	4.55	4
3.83	3	3.85	4
3.62	1	3.60	2
3.34	1	3.33	2
3.19	3	3.18	4
3.08	8	3.08	10
2.96	1	2.93	1
2.85	10	2.85	10
2.81	½	2.77	½
2.66	4	2.66	4
2.58	2	2.57	1
2.49	½	2.47	½
2.39	3	2.40	3
2.34	½	2.33	½
2.28	½	2.26	½
2.17	2	2.18	2
2.10	½	2.11	½
2.05	2	2.05	1
1.989	2	1.994	2
1.910	½	1.914	1
1.895	3	1.893	2
1.821	3	1.819	3
1.762	3	1.763	2
1.734	2	1.730	2
1.681	3	1.680	3
1.600	1	1.601	1
		+ 23 lines	

TABLE AII.3 X - ray data for wittichenite

Petruk et al.(1971)		Scar Crag - this work	
d (A)	I	d (A)	I
3.584	5	3.56	3
2.904	2	2.89	1
2.811	2	2.79	1
2.744	10	2.73	8
2.461	10	2.46	10
2.410	9	2.39	9
2.329	1	2.32	½
-	-	2.21	½
2.155	3	2.15	2
1.965	4	1.958	4
1.818	8	1.813	10
1.797	1	1.790	1
1.739	2	1.733	2
1.696	2	1.700	2
1.639	4	1.638	6
1.587	3	1.585	4
1.548	1	1.544	4
-	-	1.489	2
-	-	1.457	1
-	-	1.407	½
-	-	1.385	4
-	-	1.372	1
-	-	1.332	½
-	-	1.259	½
-	-	1.232	1
-	-	1.215	2
-	-	1.201	3
-	-	1.123	4
		+ 14 lines	

TABLE AII.4 X - ray data for alloclase

STANDARDS	RADIATIONS
FeS_2	FeKα, S Kα
Co	CoKα
Ni	NiKα
As	AsKα
FeAsS*	FeKα, AsKα, S Kα
Bi_2S_3	BiLα, BiMα, S Kα
Cu	CuKα
Ag	AgLα
Au	AuLα
PbS	PbMα, S Kα
$AgBiSe_2$	AgLα, BiMα, SeKα
Te	TeLα
Sb	SbLα
Zn	ZnKα
Ca	CaKα
Bi	BiMα

* Kretschmar's Asp 200 standard
Fe - 34.51 wt%, As - 44.44 wt%, S - 21.03 wt%

TABLE AII.5 Standards and radiations used in electron probe microanalysis.

PLATES

PLATE 1

SCAR CRAG VEIN

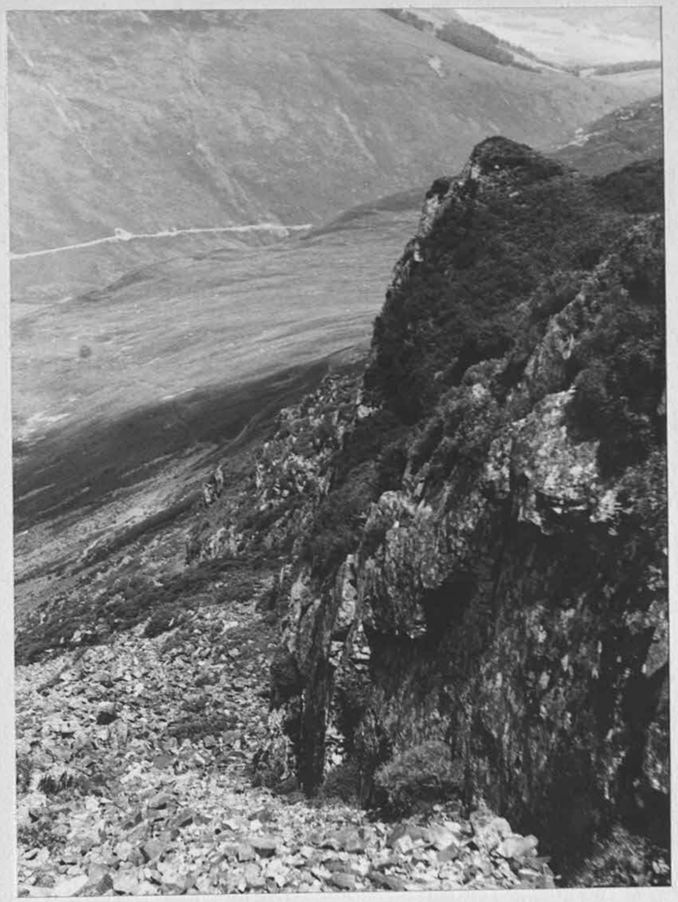
View northeast towards Coledale along the outcrop of the vein. Much of the debris in the foreground is mineralized float.

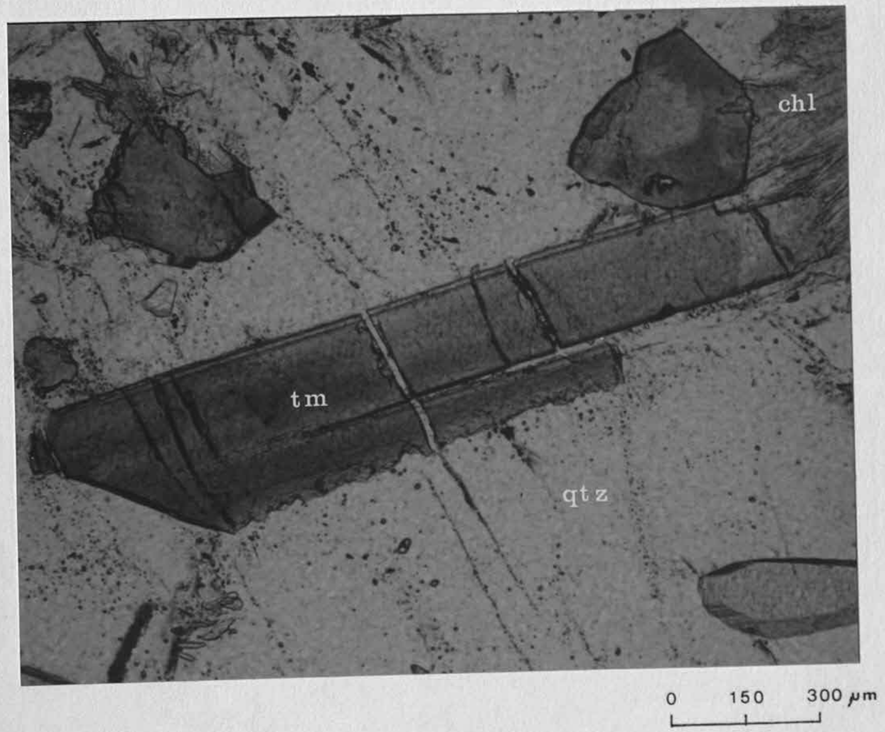
SCAR CRAG VEIN

Euhedral tourmaline with chlorite in quartz.

(T-K.6.6)

(plane polarized light)





DALE HEAD NORTH VEIN

View westwards along the vein, which has been stoped out to the surface for part of its length. Specimens were collected from the mouth of the small cross - cut adit on the west side of the beck, and also from a level driven on the vein and visible in the far distance.

GOLDSCOPE COPPER VEIN

View westwards to the vein which can be seen dipping south. Much of the dump material was derived from the north - south Goldscope Lead Vein (not seen).

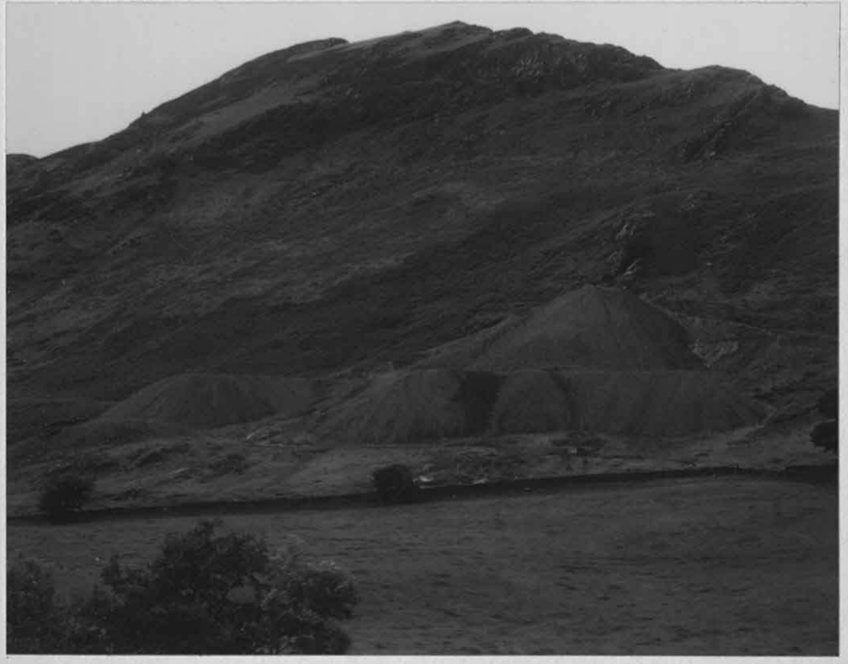
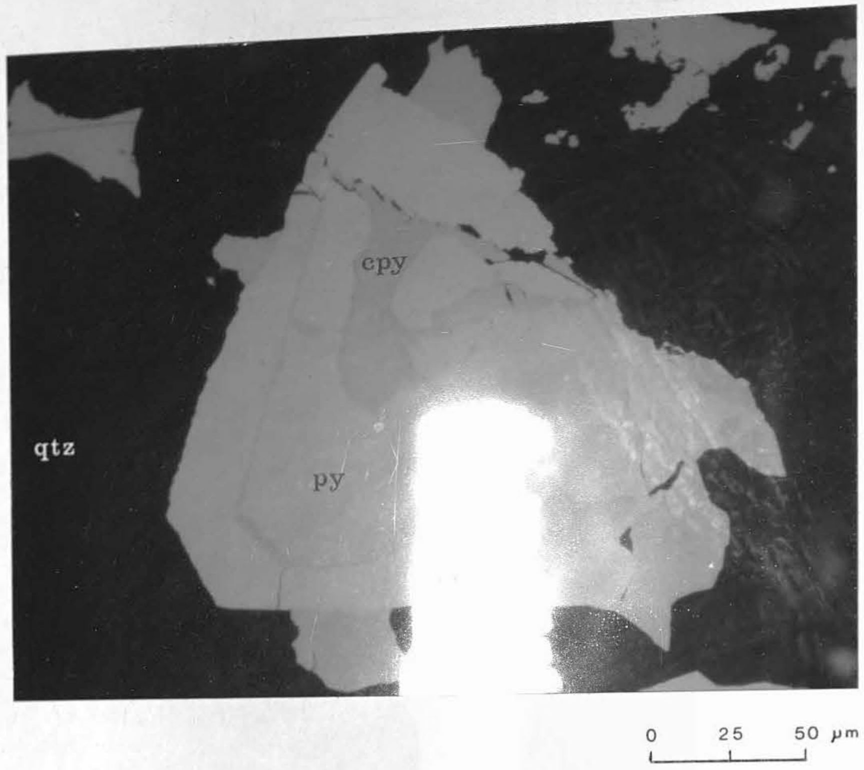


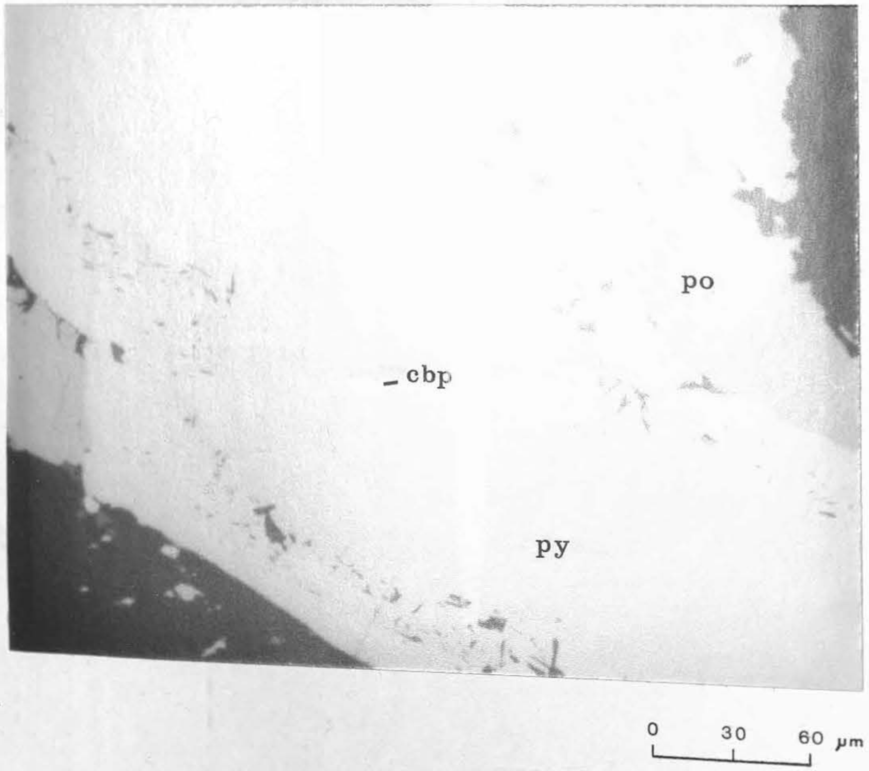
PLATE 3



DALE HEAD NORTH VEIN

Pyrite, subsequently overgrown by cobaltite, has been preferentially replaced by chalcopyrite.

(P-77K.1.E) (reflected light - oil)



DALE HEAD NORTH VEIN

A pyrite cube overgrown by a zone of cobaltiferous pyrite, and subsequently enclosed by later pyrite which has been partially replaced by pyrrhotine.

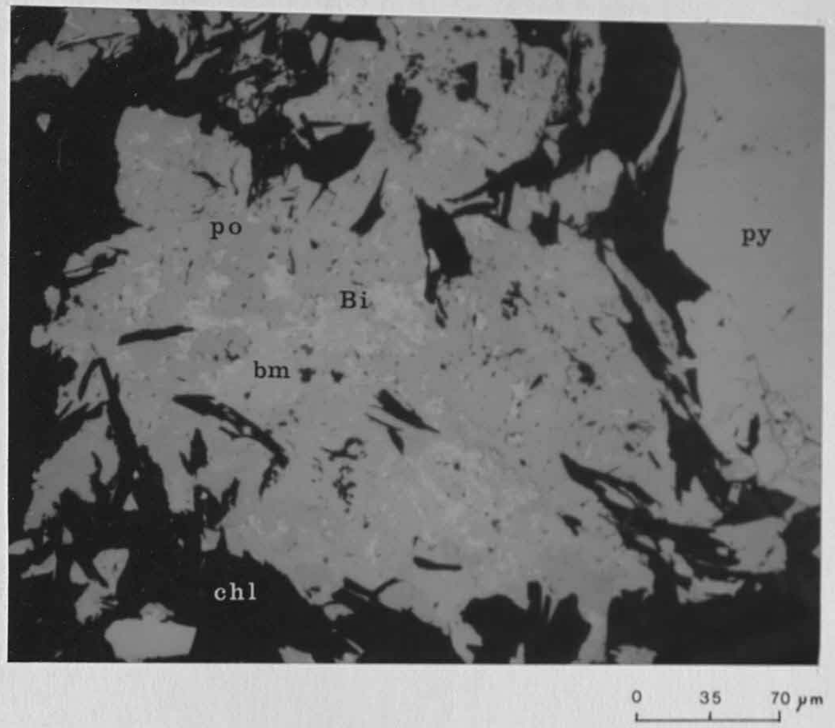
(P-78K.1.6) (reflected light - oil)

PLATE 4

DALE HEAD NORTH VEIN

Native bismuth (white) and bismuthinite (grey) enclosed in pyrrhotine. The gangue mineral is mainly chlorite.

(P-78K.1.6) (reflected light - oil)



DALE HEAD NORTH VEIN

Pyrite is subhedral and replaced by pyrrhotine. Aggregates of euhedral cobaltite may originally have overgrown pyrite.

(P-78K.1.6) (reflected light - oil)

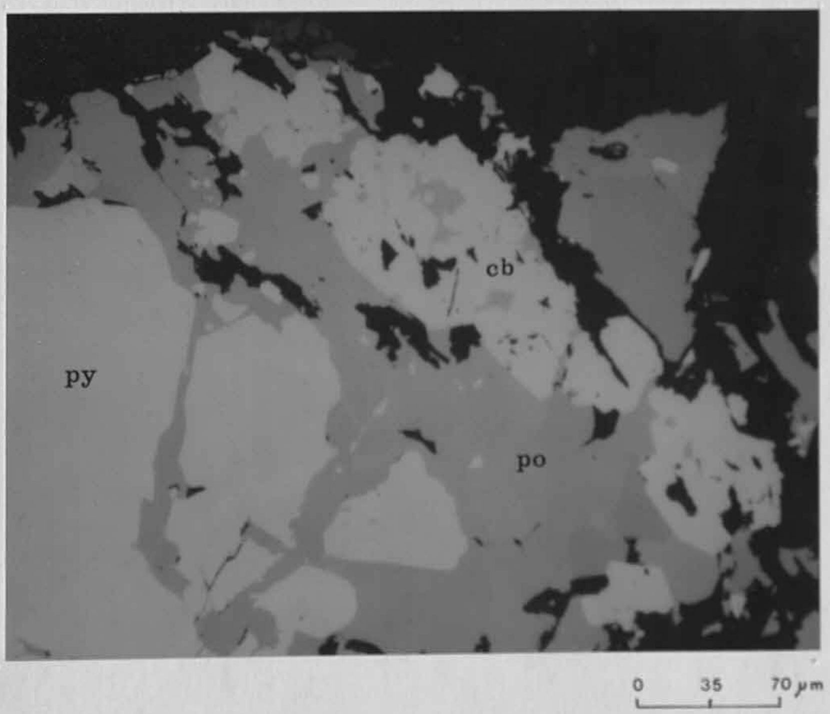
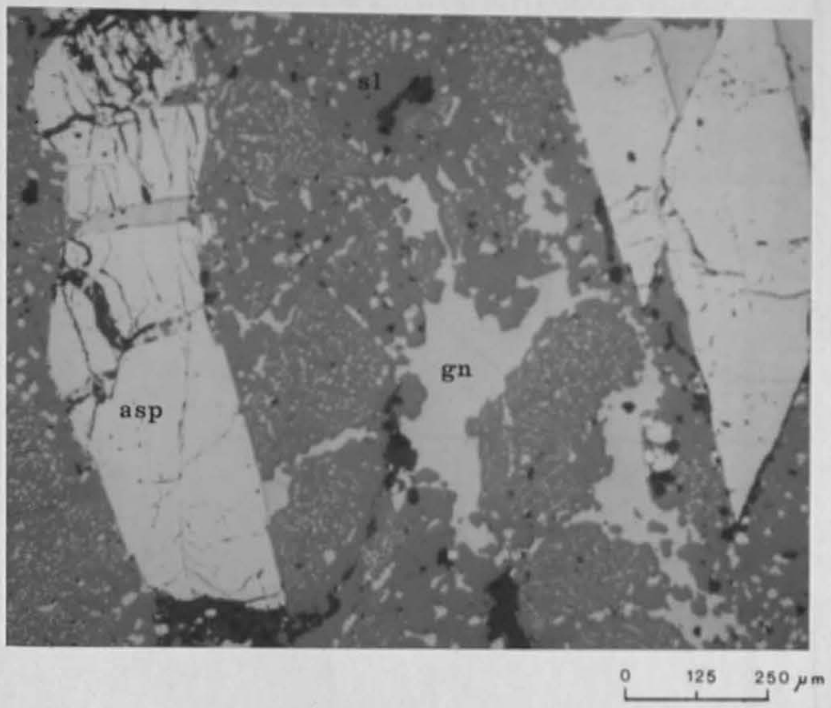


PLATE 5

WANTHWAITE VEIN

Early euhedral arsenopyrite with fractures subsequently infilled by sphalerite, chalcopyrite and galena. Sphalerite contains finely exsolved chalcopyrite.

(P-77K.15.3) (reflected light)



WANTHWAITE VEIN

Pyrrhotine in the centre of euhedral arsenopyrite, surrounded by sphalerite with exsolved chalcopyrite.

(P-78K.15.4) (reflected light - oil)

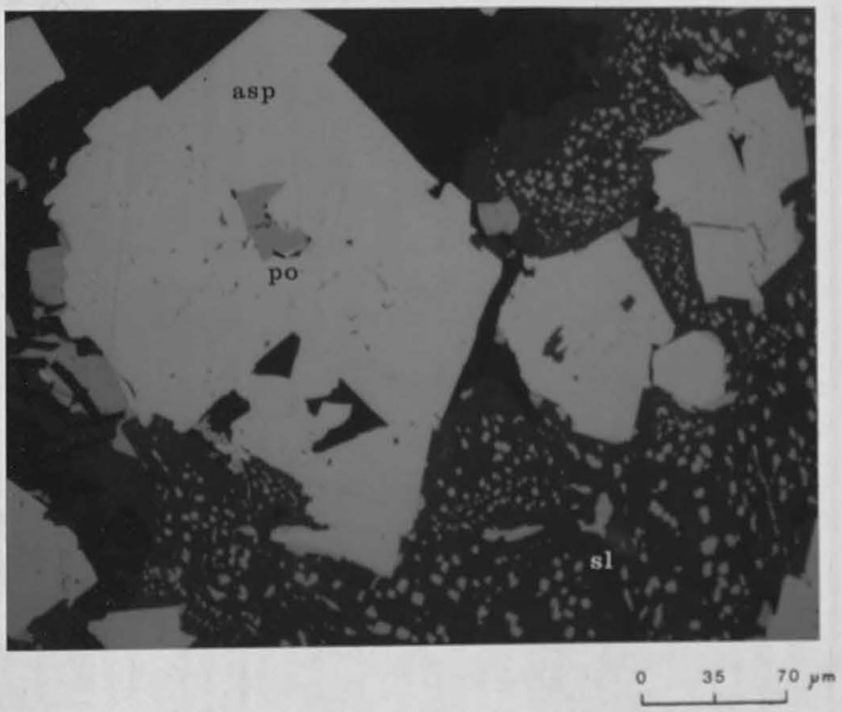


PLATE 6

WANTHWAITE VEIN

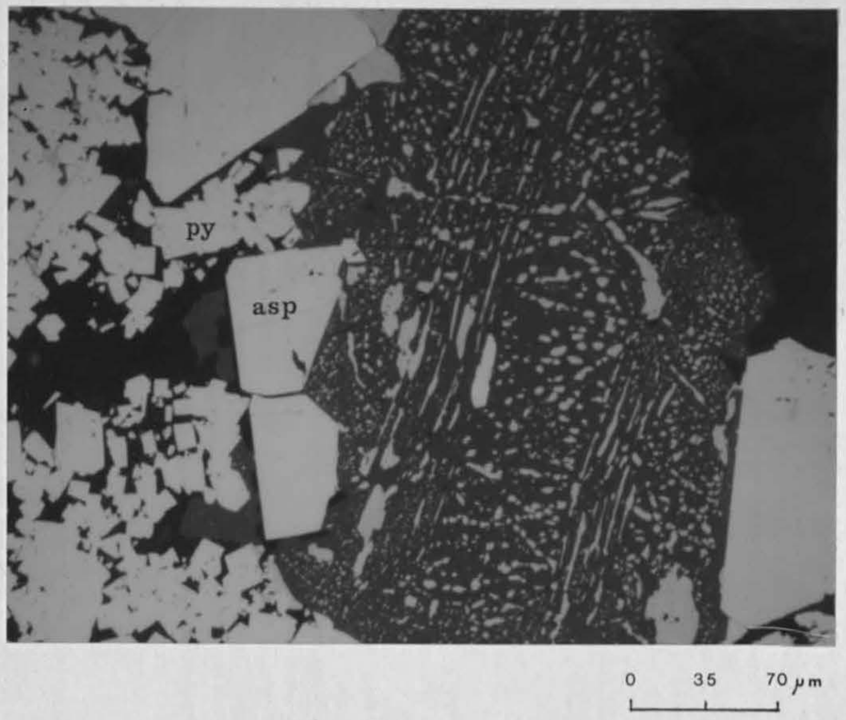
Aggregates of euhedral pyrite with arsenopyrite, and sphalerite with chalcopyrite exsolution.

(P-78K.15.1) (reflected light - oil)

WANTHWAITE VEIN

Euhedral arsenopyrite with cores of a different composition to the outer arsenopyrite.

(P-78K.15.6) (reflected light - oil
- partially crossed nicols)



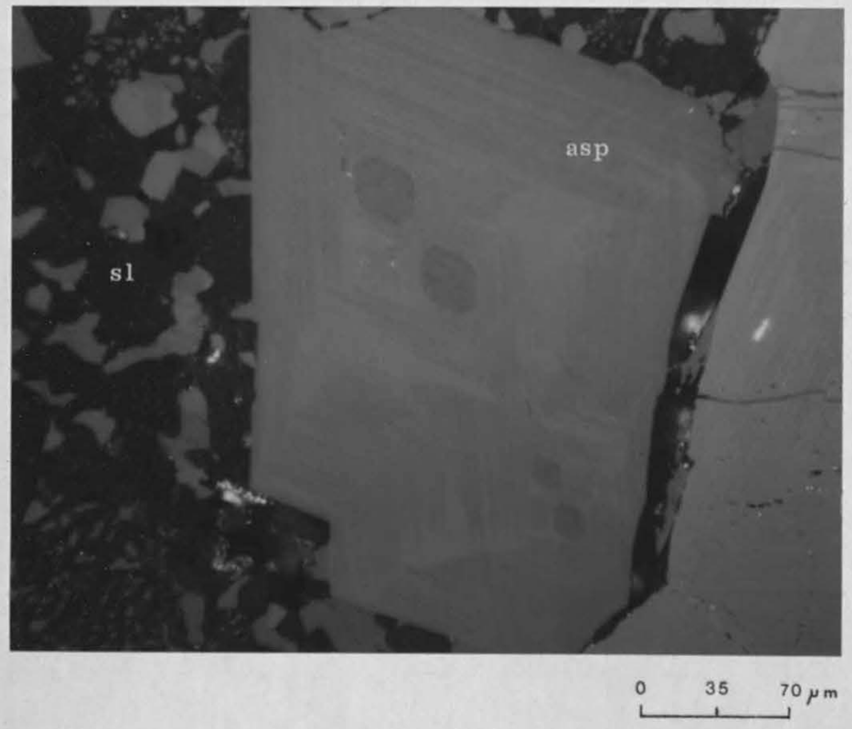


PLATE 7

WANTHWAITE VEIN

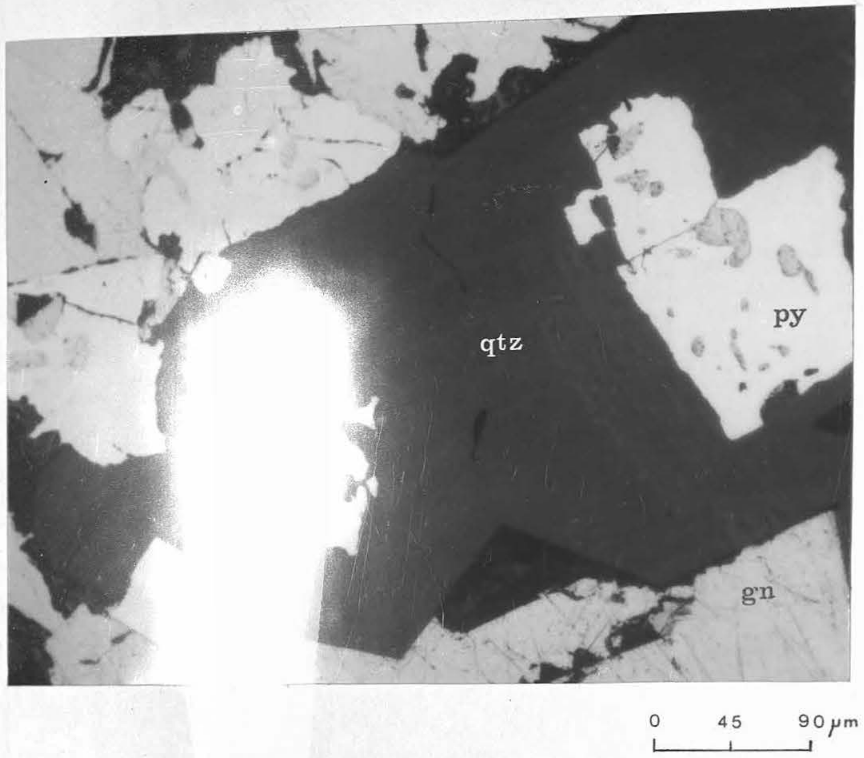
Euhedral pyrite, partially replaced by galena and subsequently enclosed in late quartz.

(P-77K.15.3) (reflected light - oil)

DALE HEAD SOUTH VEIN

Sphalerite replaced by bornite and chalcopyrite. Covelline infills late fractures.

(P-K.01.2) (reflected light)



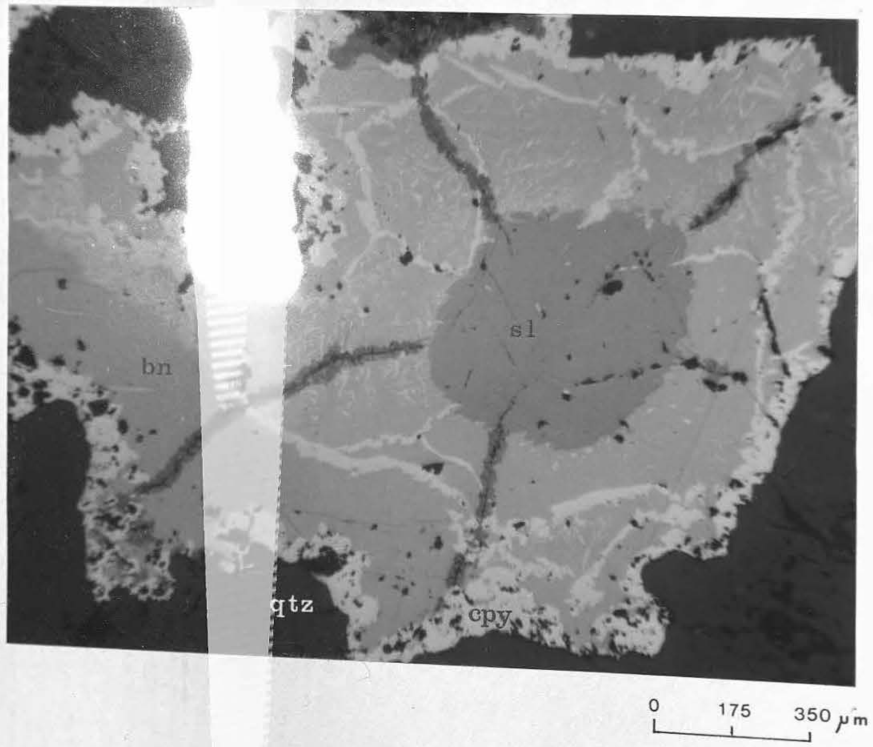


PLATE 8

ROUGHTONGILL MINE

View south towards the dumps of Roughtongill Mine, once one of the most important mines in the Lake District. The two Roughtongill Veins cut across the stream in the middle and far distance respectively.

DRIGGITH VEIN

Galena replaced along cleavages by an intimate mixture of djurleite and anglesite. Covelline has subsequently replaced the djurleite.

(P-CF.15.20) (reflected light - oil)

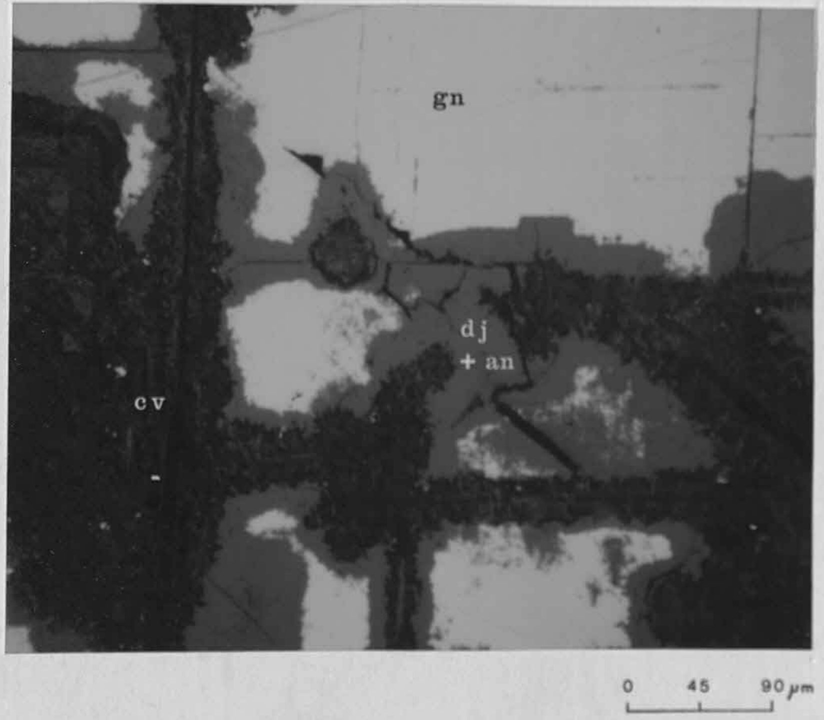


PLATE 9

FORCE CRAG MINE

View northwest towards Force Crag Mine, which can be seen in the bottom of the valley. The vein (dashed line) can be traced from surface workings on the hillside in the west, through the screes behind the mine buildings, to the No O Level cross - cut adit in the east.

FORCE CRAG VEIN

Early mineralization of quartz and minor pyrite was brecciated, along with the Skiddaw Slate country rock, and recemented by quartz. Further brecciation occurred prior to deposition of sphalerite, galena, dolomite and barytes.
(H-K.70.1.1)

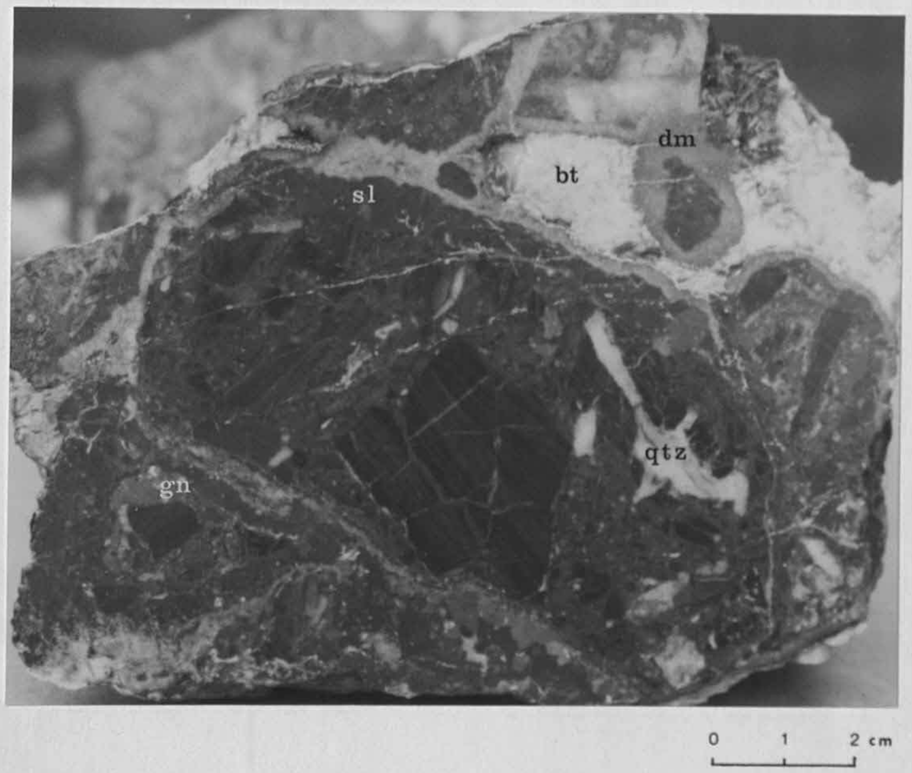


PLATE 10

CONISTON MINES

View northwest towards the huge spoil heap of the Coniston Mines, which predominantly worked the Paddy End and Bonser Veins. The cleft where the Paddy End Vein has been mined ('Simon's Nick') is in the far distance.

BONSER VEIN

Laths of magnetite possibly pseudomorphing early haematite, with later anhedral pyrite and calcite.

(P-78Co.2.A) (reflected light)

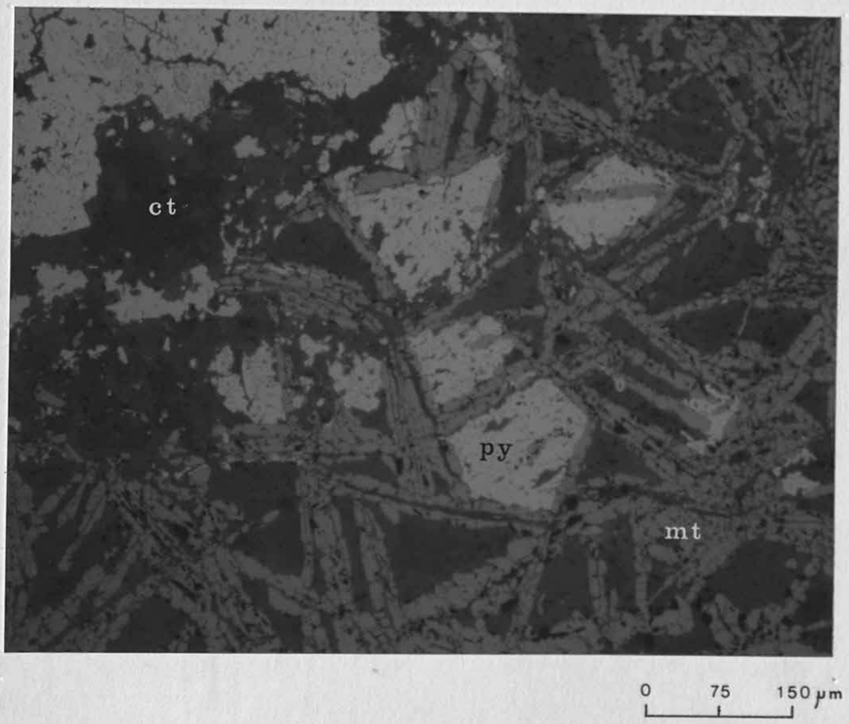
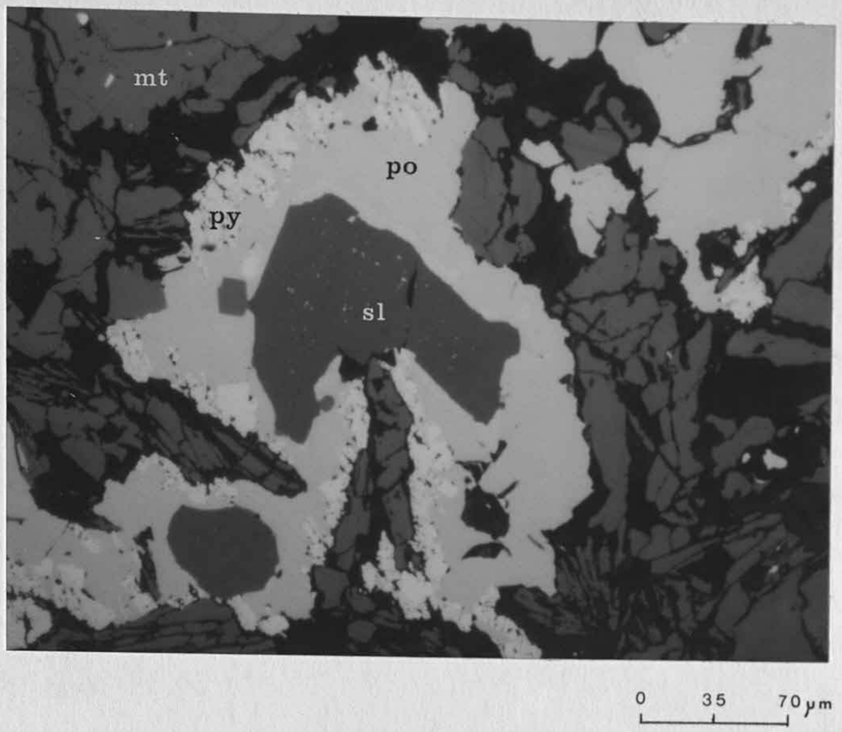


PLATE 11

BONSER VEIN

Pyrrhotine, later than magnetite, contains irregular grains of sphalerite with marginal chalcopyrite. Late pyrite and marcasite partially replace pyrrhotine.

(P-78Co.2.A) (reflected light - oil)



BONSER VEIN

Chlorite, showing fine botryoidal development, overgrown and partially replaced by matted aggregates of stilpnomelane. Dolomite is later than these two minerals.

(T-Co.2.11) (plane polarized light)

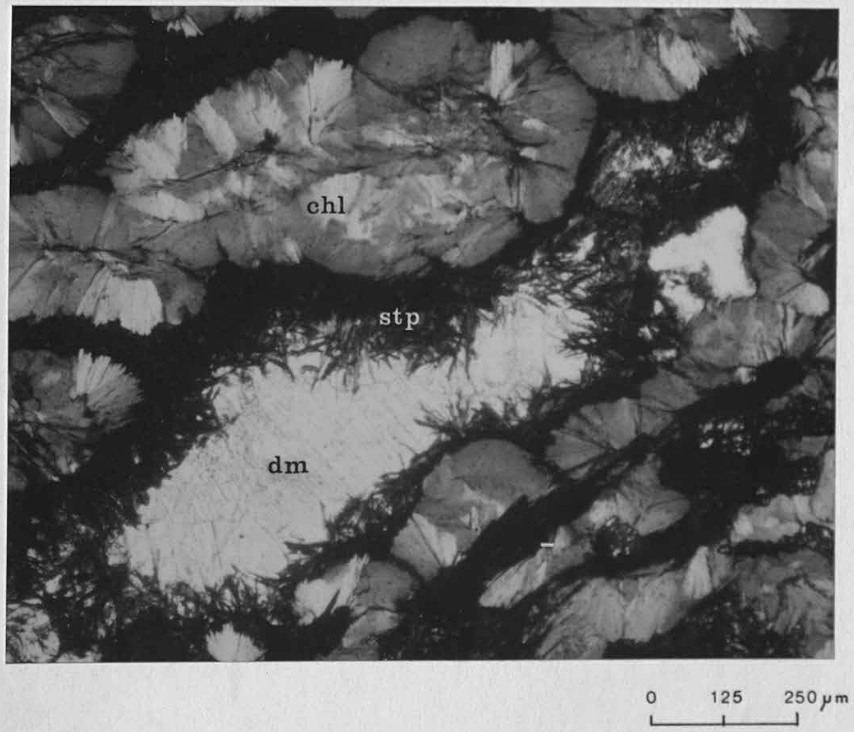


PLATE 12

BONSER VEIN

Native bismuth closely associated with bismuthinite.

(P-Co.2.11.x) (reflected light - oil)

PAVE YORK VEIN

Tennantite, bornite and chalcopyrite extensively replaced by covelline and various hydrated carbonates.

(P-Co.8.4) (reflected light - oil)

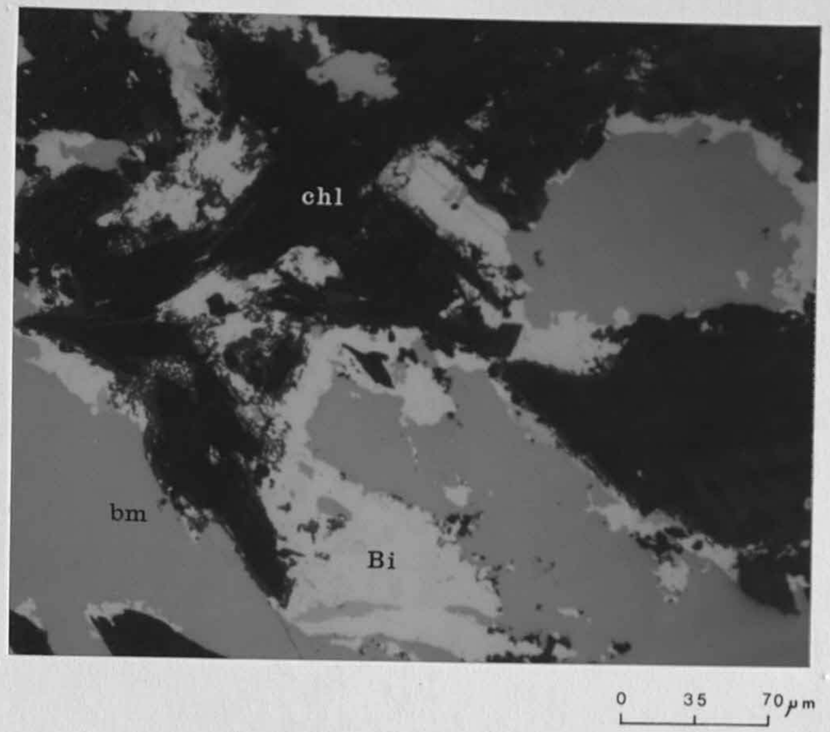
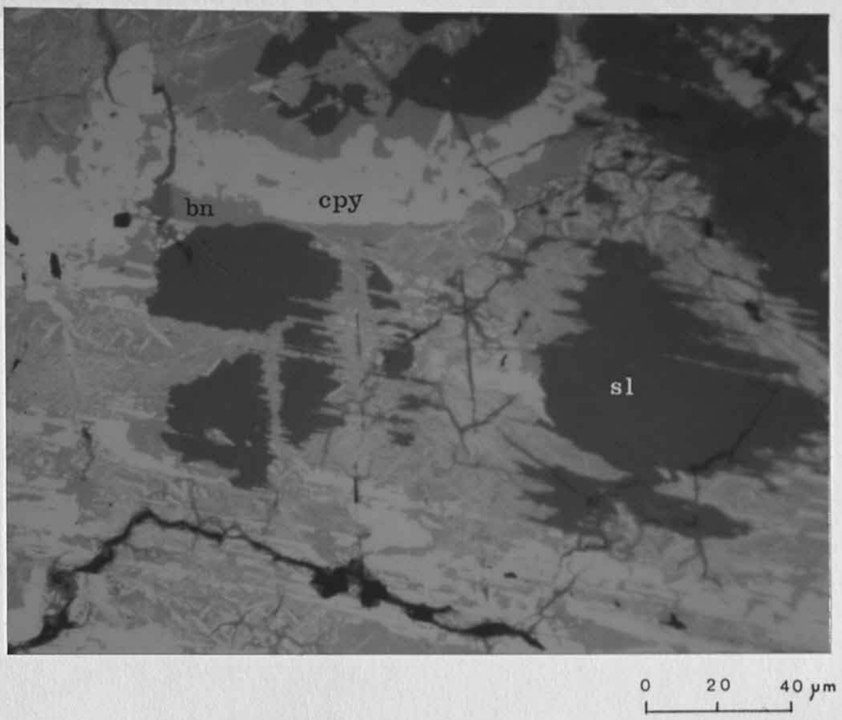


PLATE 13

PAVE YORK VEIN

Sphalerite replaced by bornite and chalcopyrite.

(P-Co.8.4) (reflected light - oil)



PAVE YORK VEIN

Tennantite replaced by copper sulphides ('chalcocite' and covelline) with later carbonates.

(P-Co.8.4) (reflected light - oil)

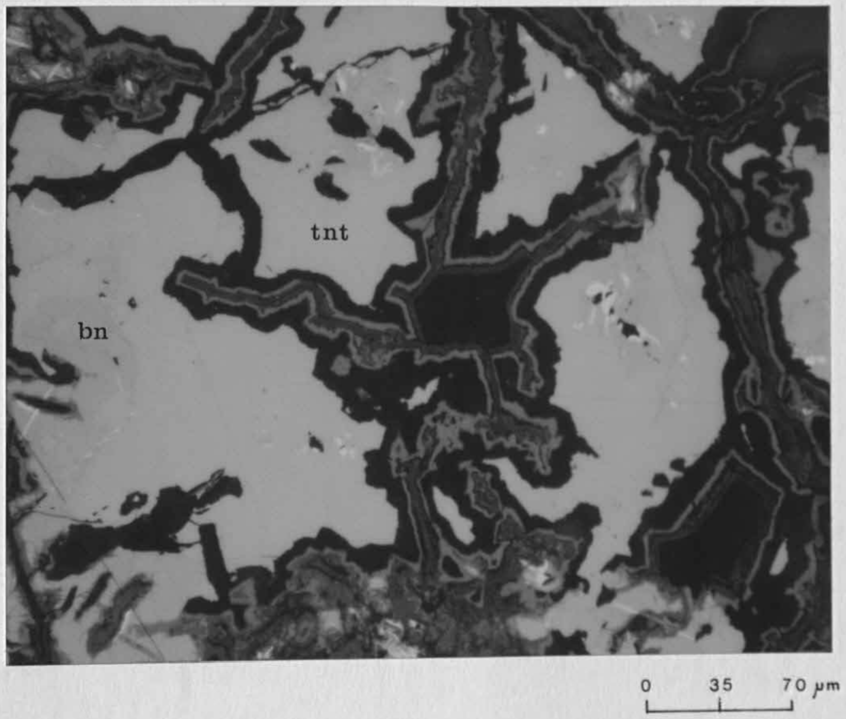


PLATE 14

PAVE YORK VEIN

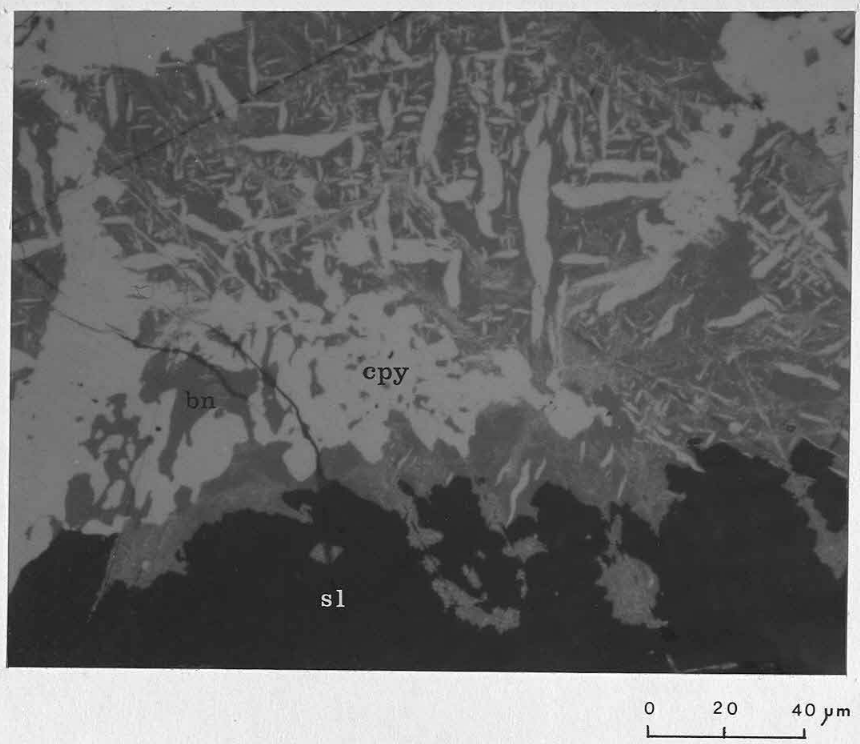
Sphalerite replaced by bornite and chalcopyrite intergrowths showing partial development of 'basket - weave' texture.

(P-Co.8.4) (reflected light - oil)

LONG CRAG VEIN

Haematite and magnetite with small grains of interstitial bismuthinite.

(P-77Co.11.A) (reflected light - oil)



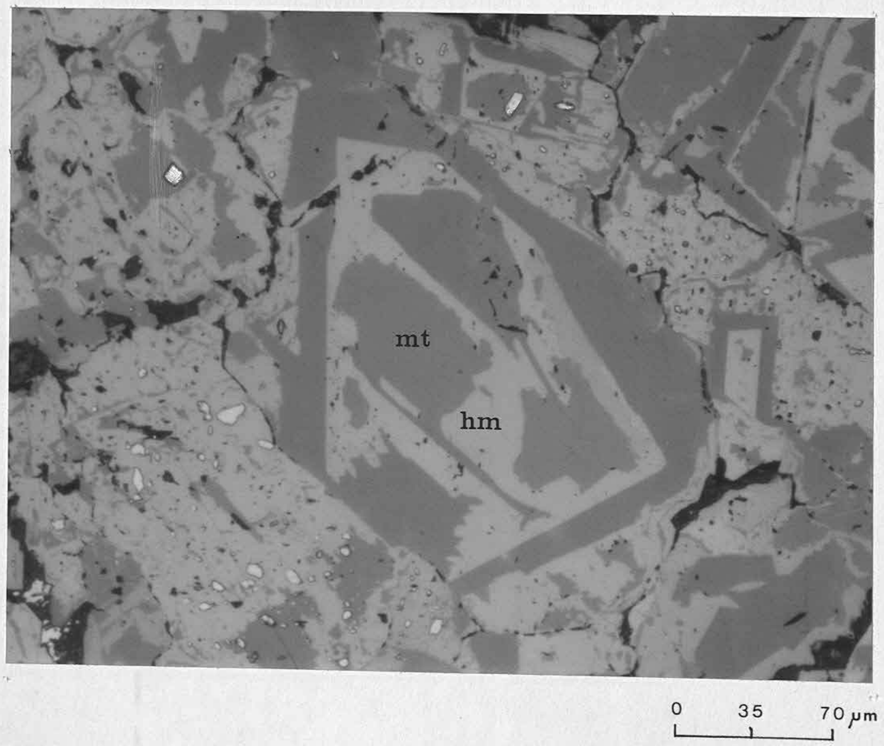
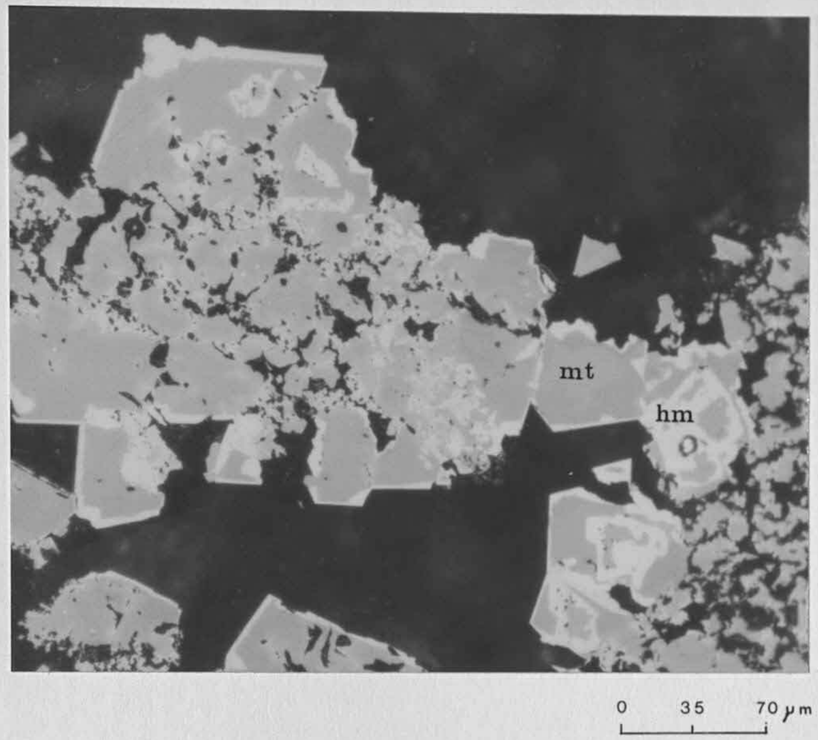


PLATE 15

LONG CRAG VEIN

Euhedral magnetite with partial replacement by haematite.

(P-77Co.11.A) (reflected light - oil)



SEATHWAITE VEIN

Bornite replacing digenite and intergrown with wittichenite.

(P-Co.6.1) (reflected light - oil)

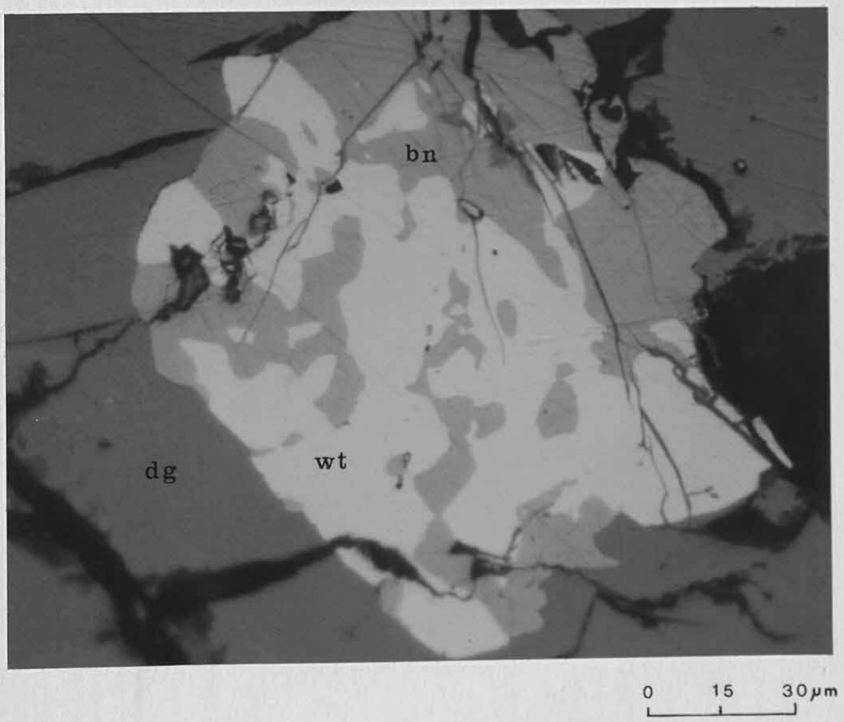


PLATE 16

SEATHWAITE VEIN

Wittichenite and haematite with minor bornite replace digenite. Covelline also replaces digenite along fractures and cleavages.

(P-Co.6.1) (reflected light - oil)

SEATHWAITE VEIN

Bornite and chalcopyrite replacing digenite which has altered to blaubleibender covelline. Relict digenite cleavages are clearly visible.

(P-Co.6.4) (reflected light - oil)

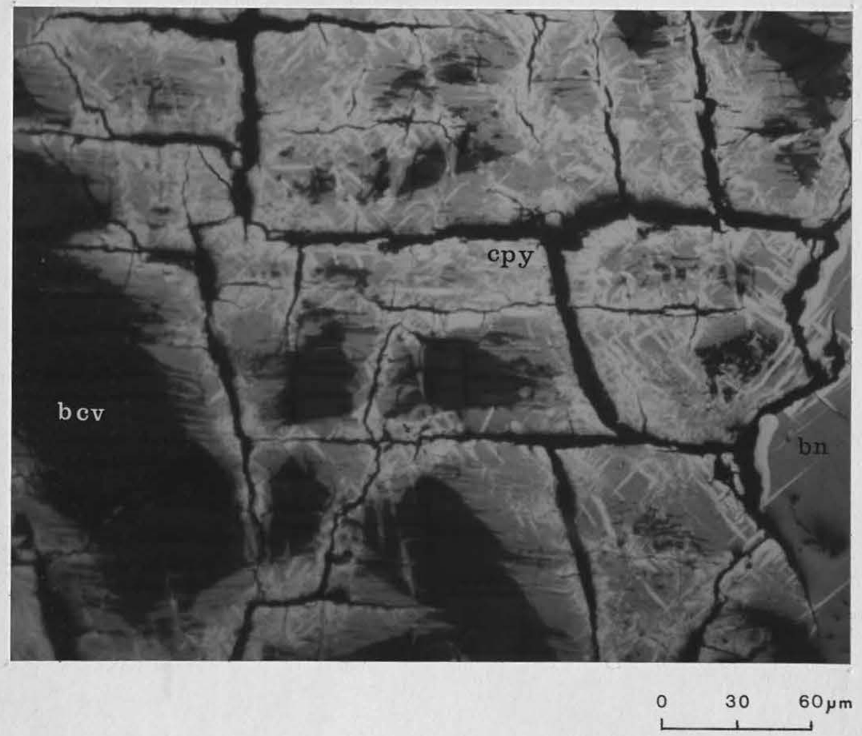


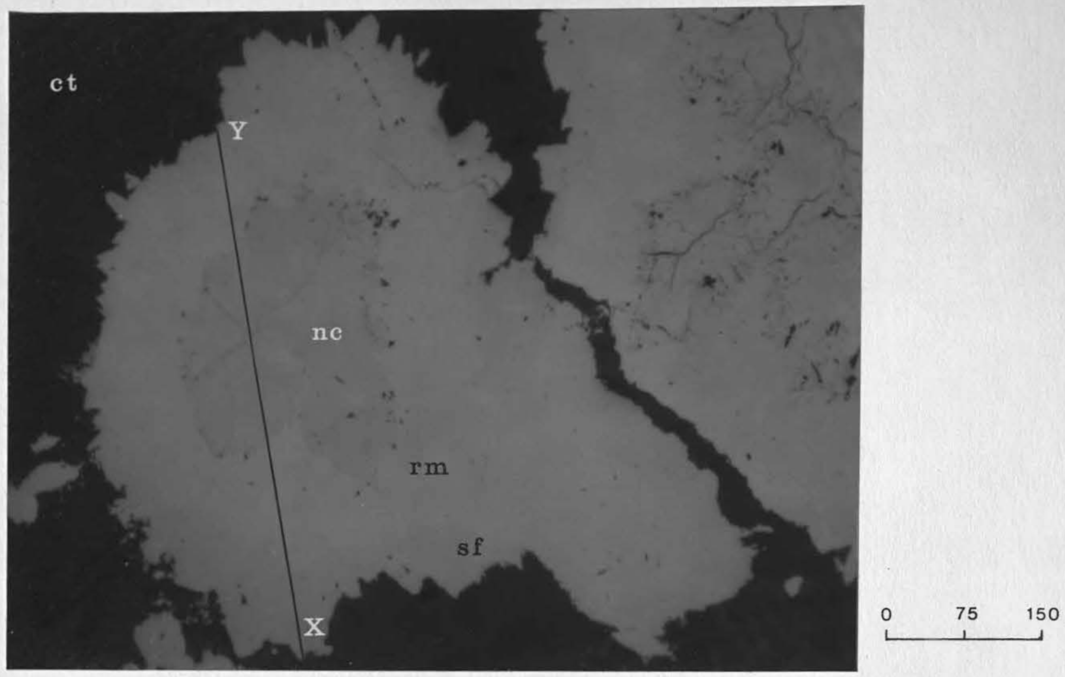
PLATE 17

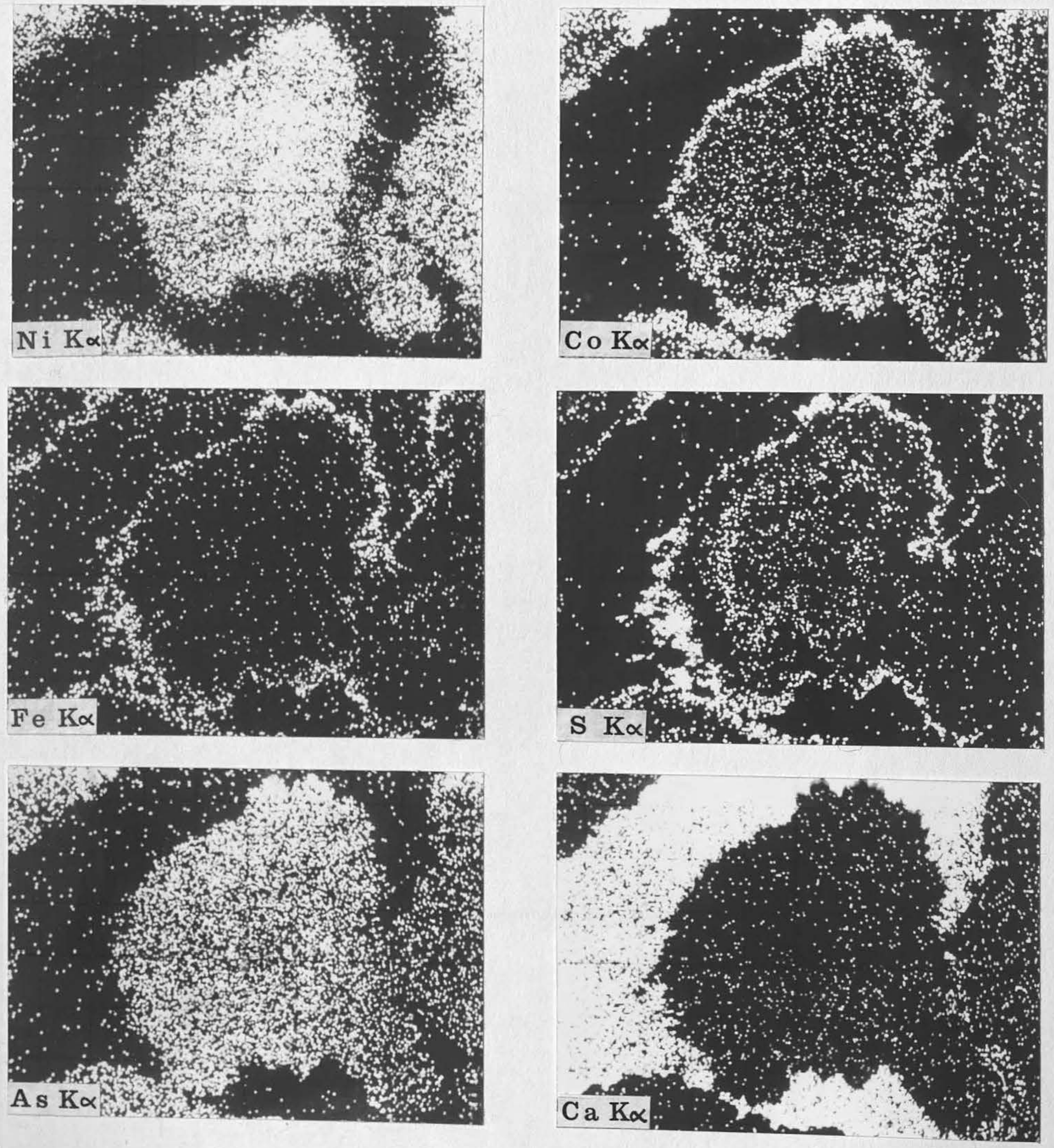
RUSSELL COLLECTION

Rosette with nickeline in the core, overgrown by rammelsbergite and safflorite. The gangue mineral is calcite. Line X - Y indicates the electron microprobe line profile of Fig.8.4.

(P-856BMR.13) (reflected light - oil - partially crossed nicols)

Electron microprobe X - ray scanning micrographs illustrate the distribution of the respective elements.

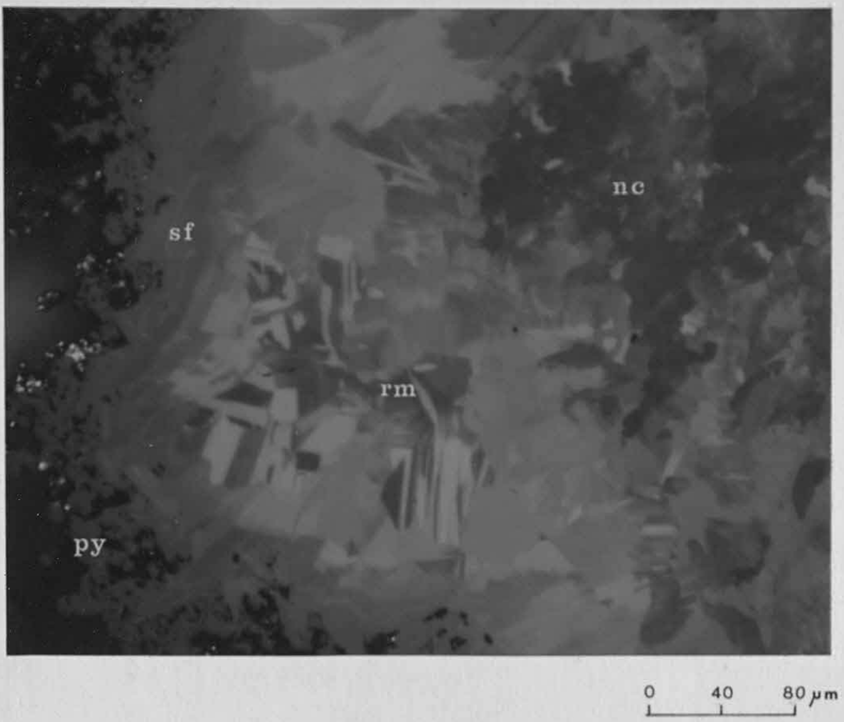




RUSSELL COLLECTION

Nickeline in the core of a rosette overgrown by rammelsbergite, safflorite and finally pyrite.

(P-856BMR.13) (reflected light - oil - partially crossed nicols)



RUSSELL COLLECTION

Detail of rammelsbergite and safflorite overgrowths on nickeline.

(P-856BMR.13) (reflected light - oil - partially crossed nicols)

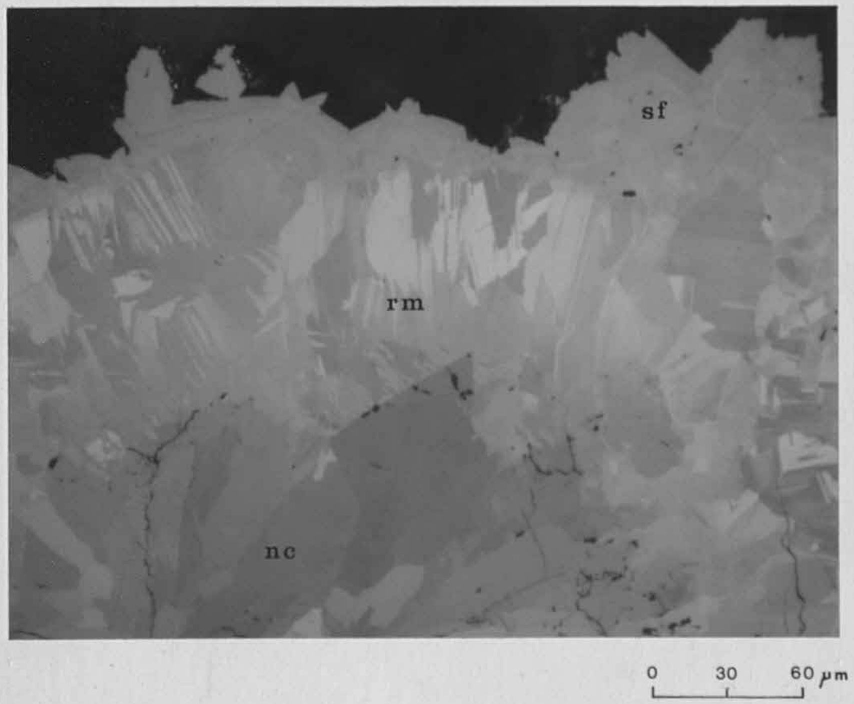


PLATE 19

SCAR CRAG VEIN

A - Compositional zoning in glaucodot. X - Y represents an electron microprobe line profile (see Fig.3.1).
(P-BMKi.K.6.2) (horiz. field - 400μm) (reflected light - oil - partially crossed nicols)

B - Euhedral cobaltite with partially altered alloclase. Gangue is mostly chlorite.
(P-K.6.4) (horiz. field - 400μm) (reflected light - oil)

C - Zoned grain. Cobalt - poor zones have been preferentially replaced by scorodite to those of glaucodot composition.
(P-K.6.5) (horiz. field - 800μm) (reflected light)

D - Alloclase intergrown with quartz.
(P-78K.6.3) (horiz. field - 400μm) (reflected light - oil)

E - Twinning in alloclase.
(P-78K.6.3) (horiz. field - 350μm) (reflected light - oil - partially crossed nicols)

F - Cobaltite euhedra growing along a small fracture in alloclase which overgrows arsenopyrite.
(P-78K.6.3) (horiz. field - 400μm) (reflected light - oil)

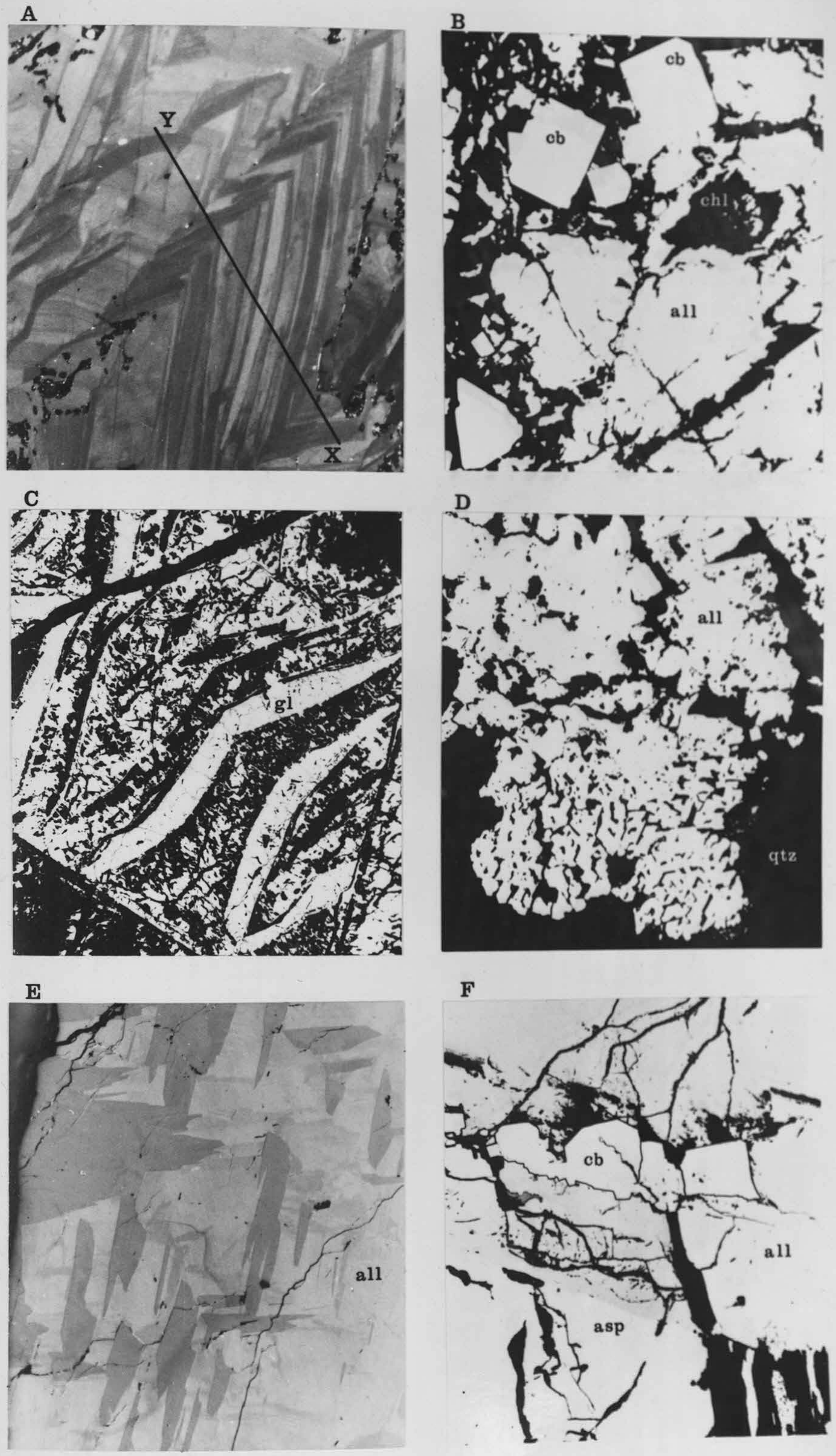


PLATE 20

DALE HEAD NORTH VEIN

A - Euhedral pyrite with an internal cobaltiferous zone.
(P-78K.1.6) (horiz. field - 200 µm) (reflected light - oil)

B - Pyrite with lamellar marcasite and interstitial galena.
(P-77K.1.G) (horiz. field - 500µm) (reflected light)

C - Marcasite replacing pyrrhotine with chalcopyrite and euhedral arsenopyrite.
(P-77K.1.E) (horiz. field - 350µm) (reflected light - oil- partially crossed nicols)

D - A small grain of gold enclosed in chalcopyrite, which also contains a few rounded grains of pyrrhotine.
(P-BMKi.K.1) (horiz. field - 350µm) (reflected light - oil)

E - Sphalerite 'stars' in chalcopyrite.
(P-BMKi.K.1) (horiz. field - 100µm) (reflected light - oil)

F - Small euhedra and subhedra of arsenopyrite in fragmental country rock, with later sphalerite and chalcopyrite.
(P-78K.1.2) (horiz. field - 500µm) (reflected light)

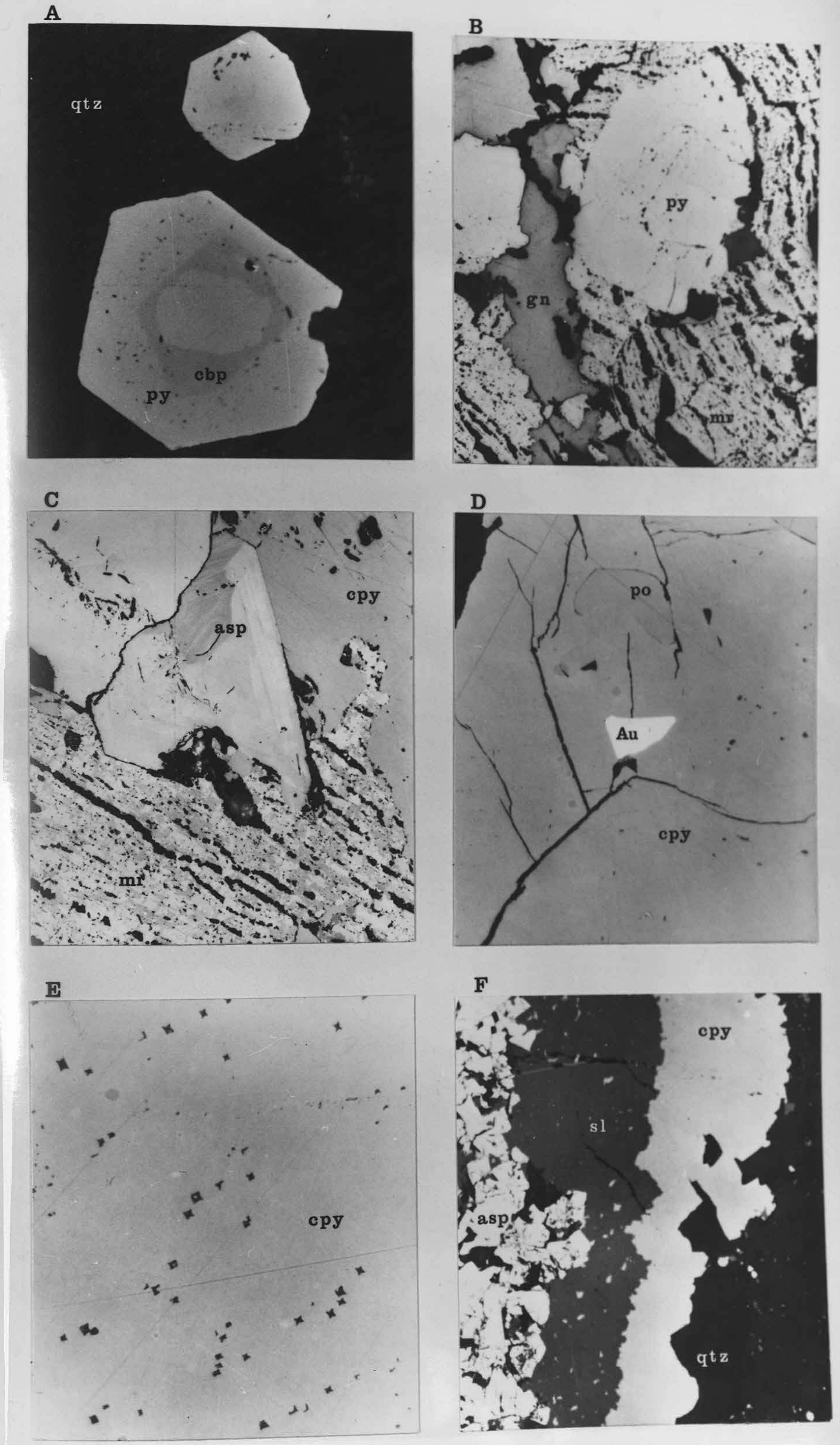


PLATE 21

WANTHWAITE VEIN

A - Early arsenopyrite with later sphalerite, chalcopyrite and galena.
(P-77K.15.3) (horiz. field - 1.25mm) (reflected light)

B - Detail of chalcopyrite exsolution in sphalerite.
(P-77K.15.3) (horiz. field - 300 µm) (reflected light - oil)

C - Arsenopyrite, euhedral where unaltered by later sphalerite with chalcopyrite exsolution.
(P-78K.15.4) (horiz. field - 300 µm) (reflected light - oil)

D - Sphalerite with chalcopyrite (in exsolution) and galena.
(P-78K.15.4) (horiz. field - 400 µm) (reflected light - oil)

E - Galena, partly intergrown with chlorite, replacing sphalerite.
(P-77K.15.3) (horiz. field - 400 µm) (reflected light - oil)

F - Detail of chalcopyrite exsolution in sphalerite, with blebs alligned along structural planes.
(P-78K.15.4) (horiz. field - 300 µm) (reflected light - oil)

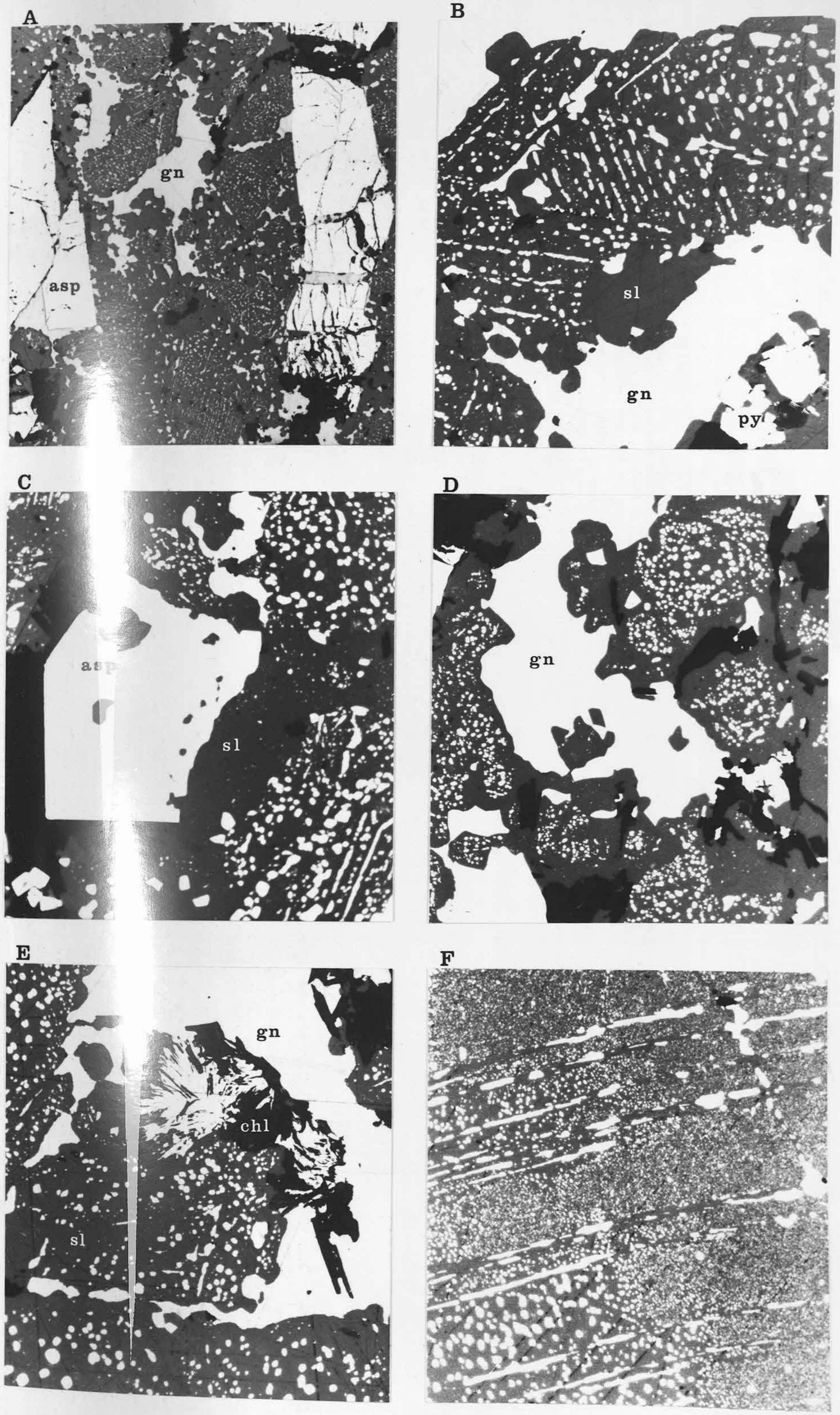


PLATE 22

DRIGGITH VEIN

A - Bournonite inclusion in argentian tetrahedrite.
(P-CF.15.2) (horiz. field - 250µm) (reflected light - oil)

B - As above, to illustrate twinning in bournonite.
(P-CF.15.2) (horiz. field - 250µm) (reflected light - oil - partially crossed nicols)

C - Galena replaced by djurleite and anglesite. Covelline appears to have subsequently replaced djurleite.
(P-CF.17.18) (horiz. field - 500µm) (reflected light)

D - Galena replaced by djurleite with a botryoidal development of covelline and anglesite inclusions.
(P-CF.17.20) (horiz. field - 300µm) (reflected light - oil)

E - Galena with replacement by cerussite and minor quartz along cleavages.
(P-77CF.16.A) (horiz. field - 750µm) (reflected light)

F - Total replacement of djurleite by covelline. Djurleite and anglesite originally replaced galena.
(P-CF.15.20) (horiz. field - 300µm) (reflected light - oil)

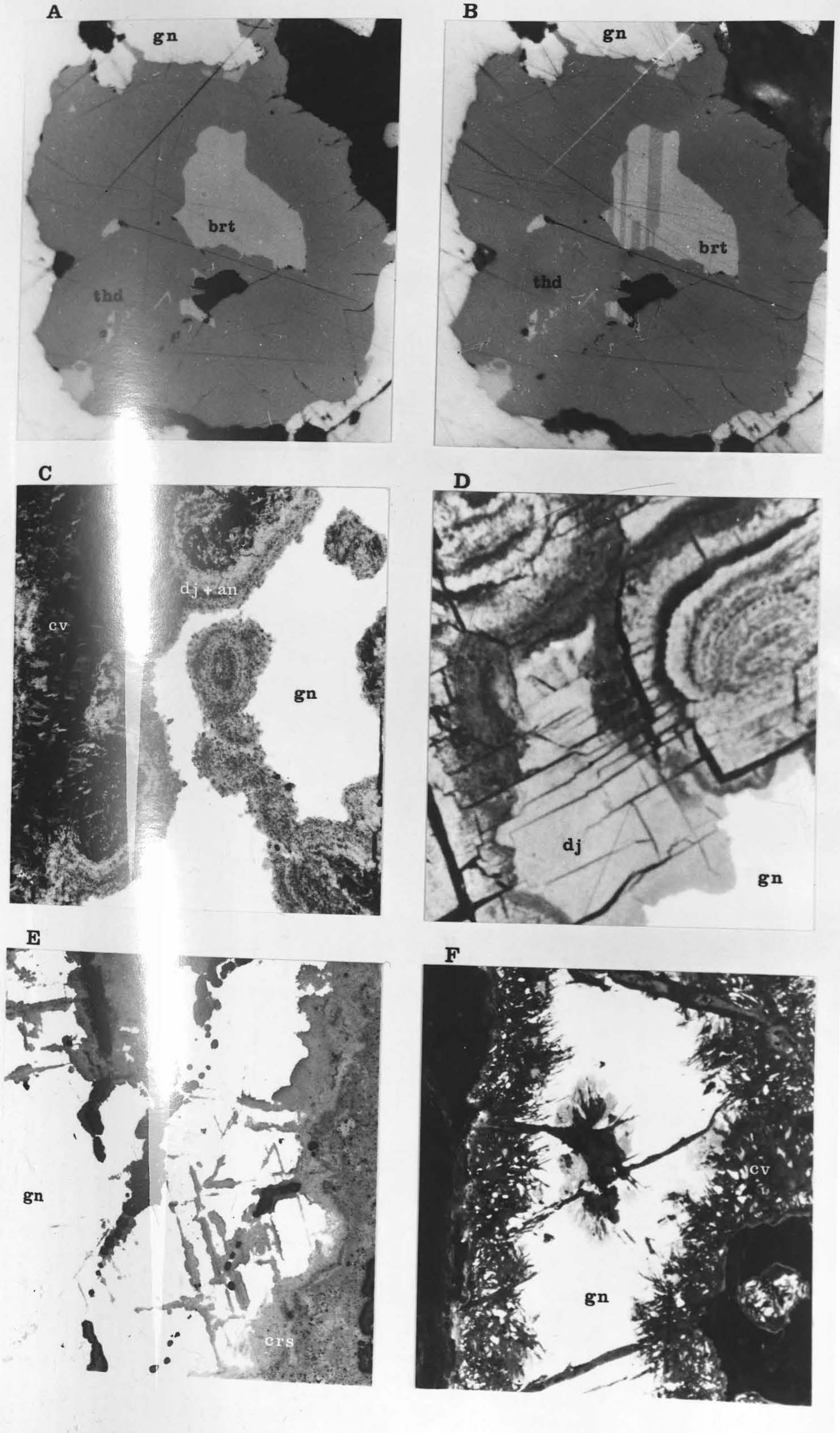


PLATE 23

EAGLE CRAG VEIN

A - Bournonite inclusion (twinned) in galena.
(P-H.2.1) (horiz. field - 150 µm) (reflected light - oil - partially crossed nicols)

DRIGGITH VEIN

B - Native antimony and bournonite inclusions in galena.
(P-CF.17.20) (horiz. field - 30 µm) (reflected light - oil)

C - Native antimony, partly replaced by bournonite in galena.
(P-CF.17.20) (horiz. field - 30 µm) (reflected light - oil)

D - As for C above.
(P-CF.15.20) (horiz. field - 50 µm) (reflected light - oil)

E - Bournonite and native antimony (bright white) orientated exsolution in galena.
(P-CF.15.20) (horiz. field - 70 µm) (reflected light - oil)

F - Djurleite and anglesite replacing galena but not bournonite which is present as inclusions.
(P-CF.17.18) (horiz. field - 300 µm) (reflected light - oil)

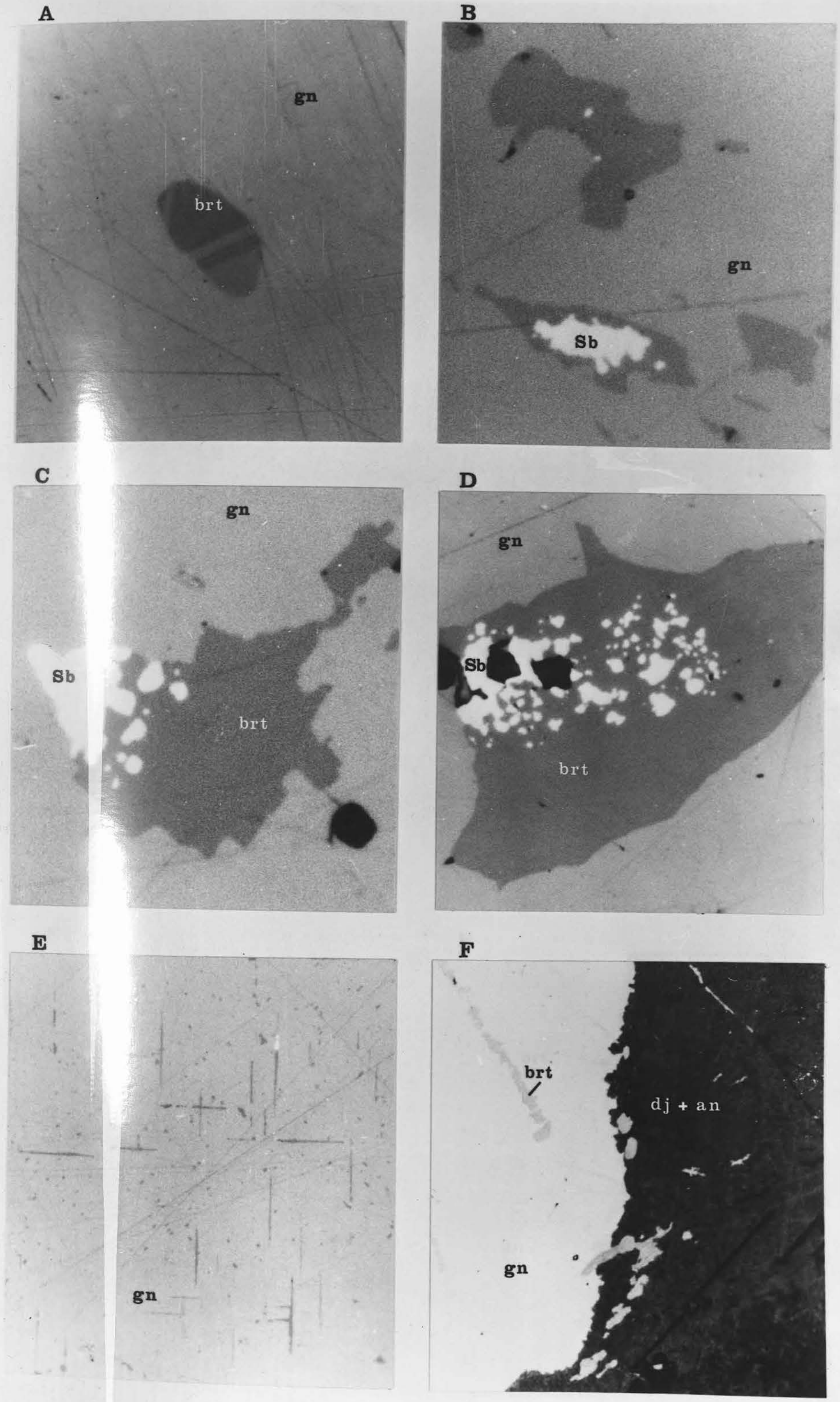


PLATE 24

FORCE CRAG VEIN

A - Laths of pyrite with minor marginal marcasite, overgrown by arsenopyrite euhedra.
(P-K.70.2.2) (horiz. field - 300μm) (reflected light - oil)

B - As above.
(P-K.70.2.2) (horiz. field - 350μm) (reflected light - oil)

C - Anhedral (possibly recrystallized -?) pyrite.
(P-K.70.2.2) (horiz. field - 300μm) (reflected light -oil)

GREENSIDE VEIN

D - Barytes pseudomorphed by chalcedony and quartz. Lamellae, formerly of barytes are defined by dusky inclusions.
(T-H.4.3) (horiz. field - 500μm) (plane polarized light)

E - Euhedral calcite rhomb enclosed in quartz.
(T-H.4.3) (horiz. field - 500μm) (plane polarized light)

F - Veinlet with calcite at the margin, and quartz and sphalerite in the centre.
(T-H.4.3) (horiz. field - 300μm) (plane polarized light)

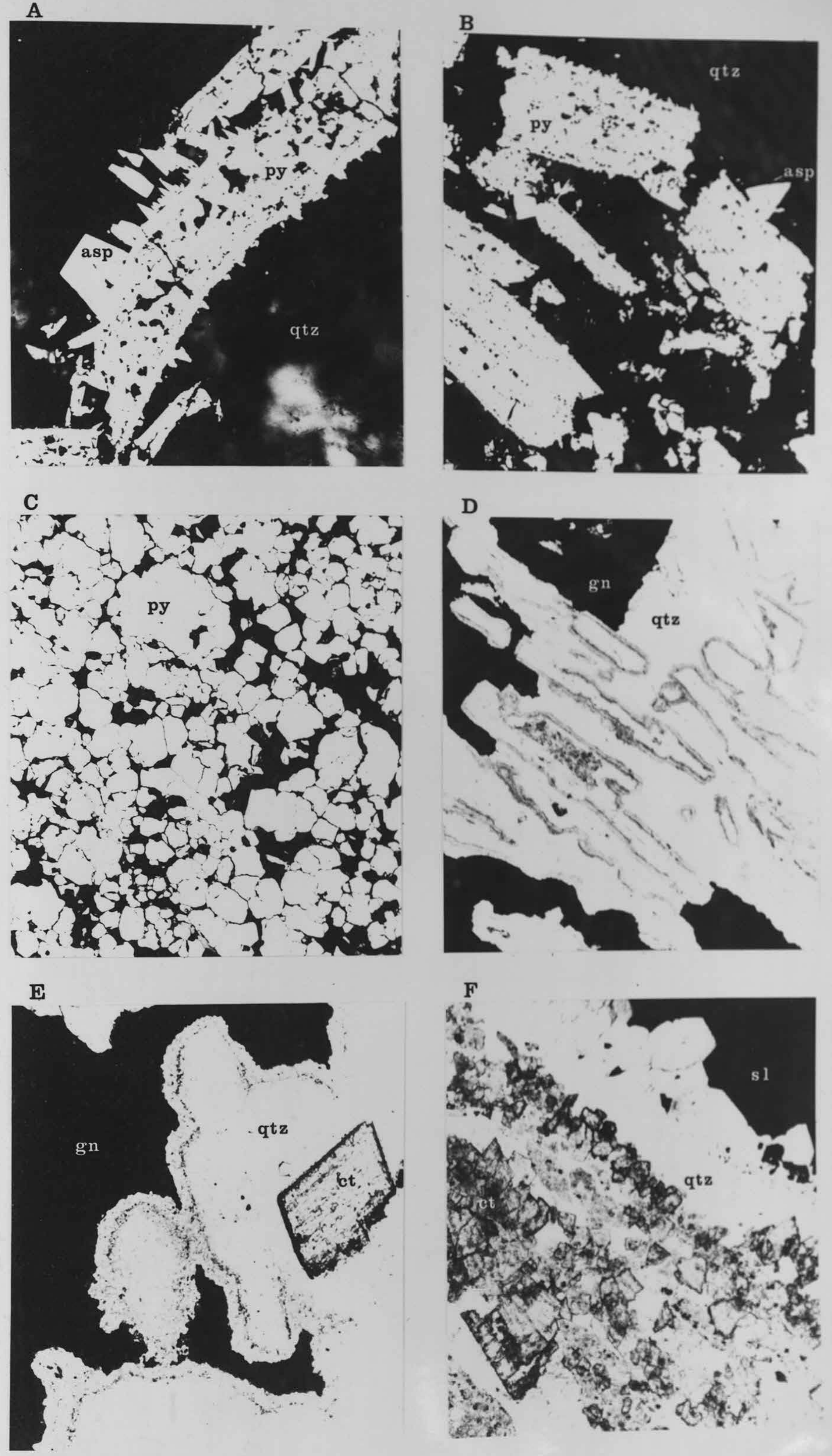


PLATE 25

OLD BRANDLEHOW VEIN

A - Daughter minerals in a pseudosecondary fluid inclusion in fluorite. The cubic phase is not halite (or other readily soluble salt) as it did not dissolve on heating.
(horiz. field - 300 µm) (plane polarized light)

B - As above, with vapour bubble in focus.
(horiz. field - 300 µm) (plane polarized light)

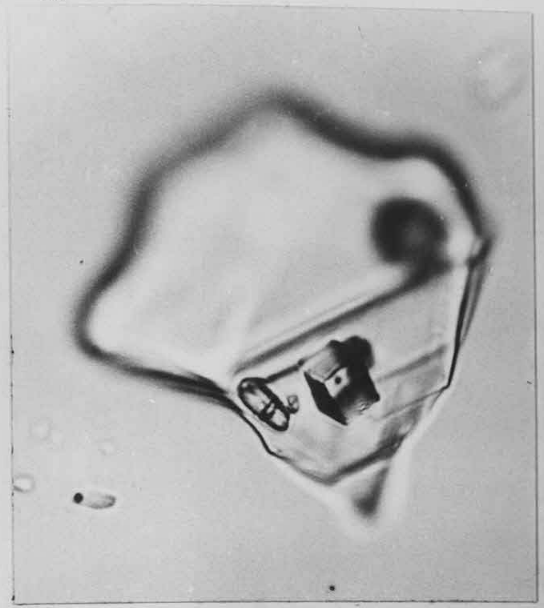
C - Necked pseudosecondary inclusion in fluorite (unsuitable for fluid inclusion analysis) with several unidentified daughter phases.
(horiz. field - 450 µm) (plane polarized light)

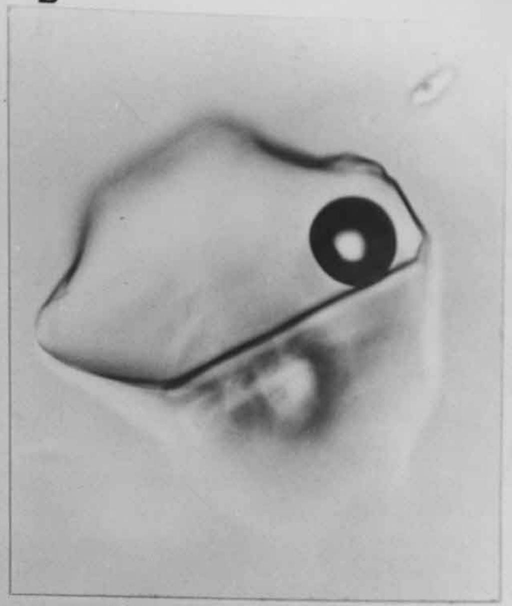
D - Euhedral primary or pseudosecondary inclusion in fluorite with daughter phases near the vapour bubble.
(horiz. field - 750 µm) (plane polarized light)

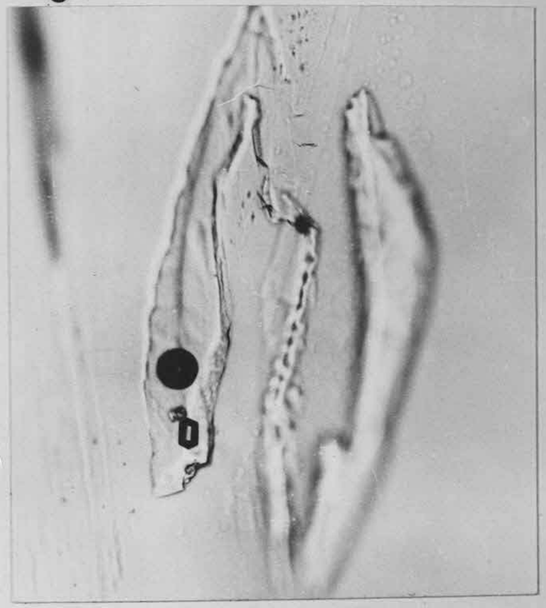
E - Halite daughter phase in pseudosecondary inclusion in fluorite. Unfortunately this inclusion leaked before measurements were possible.
(horiz. field - 300 µm) (plane polarized light)

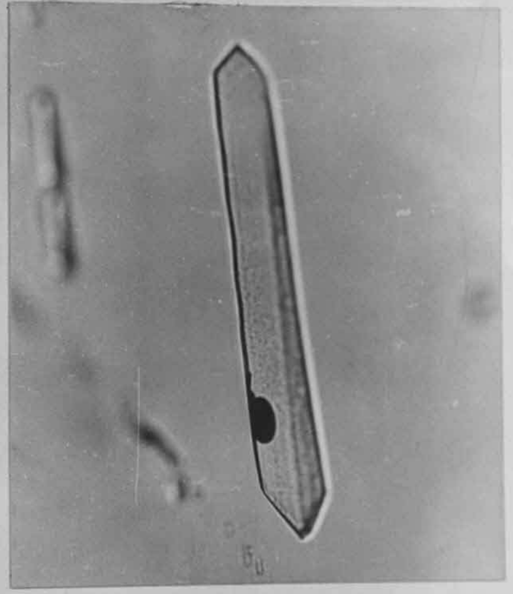
FORCE CRAG VEIN

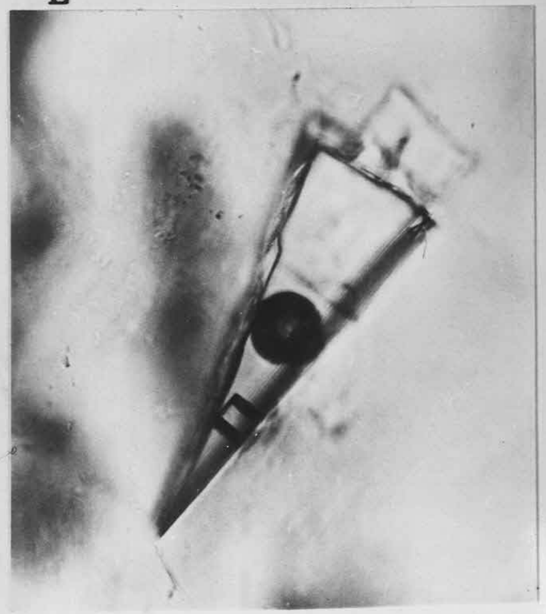
F - Secondary inclusions in sphalerite arranged along a fracture or cleavage plane.
(horiz. field - 300 µm) (plane polarized light)

A


B


C


D


E


F


PLATE 26

FORCE CRAG VEIN

A euhedral primary fluid inclusion in sphalerite is used to illustrate the phase changes observed during heating and freezing. The high homogenization temperature of this inclusion compared to those from inclusions identified as pseudosecondaries (see Table 5.2), may be evidence of leakage at some time in the past.
(horiz. field - 600μm) (plane polarized light)

A -	-98°C	Ice + vapour.
B -	-59°C	Ice + solution + vapour.
C -	-32°C	Hydrohalite + ice + solution + vapour.
D -	-27.6°C	As for C; hydrohalite is in small euhedral grains with higher relief than ice, which is close to its final melting point.
E -	-27.0°C	Final melting point of ice. Hydrohalite + solution + vapour.
F -	+20°C	Hydrohalite dissolved at 13.3°C. Solution + vapour.
G -	+150°C	Vapour bubble about to homogenize.
H -	+169°C	Homogenization

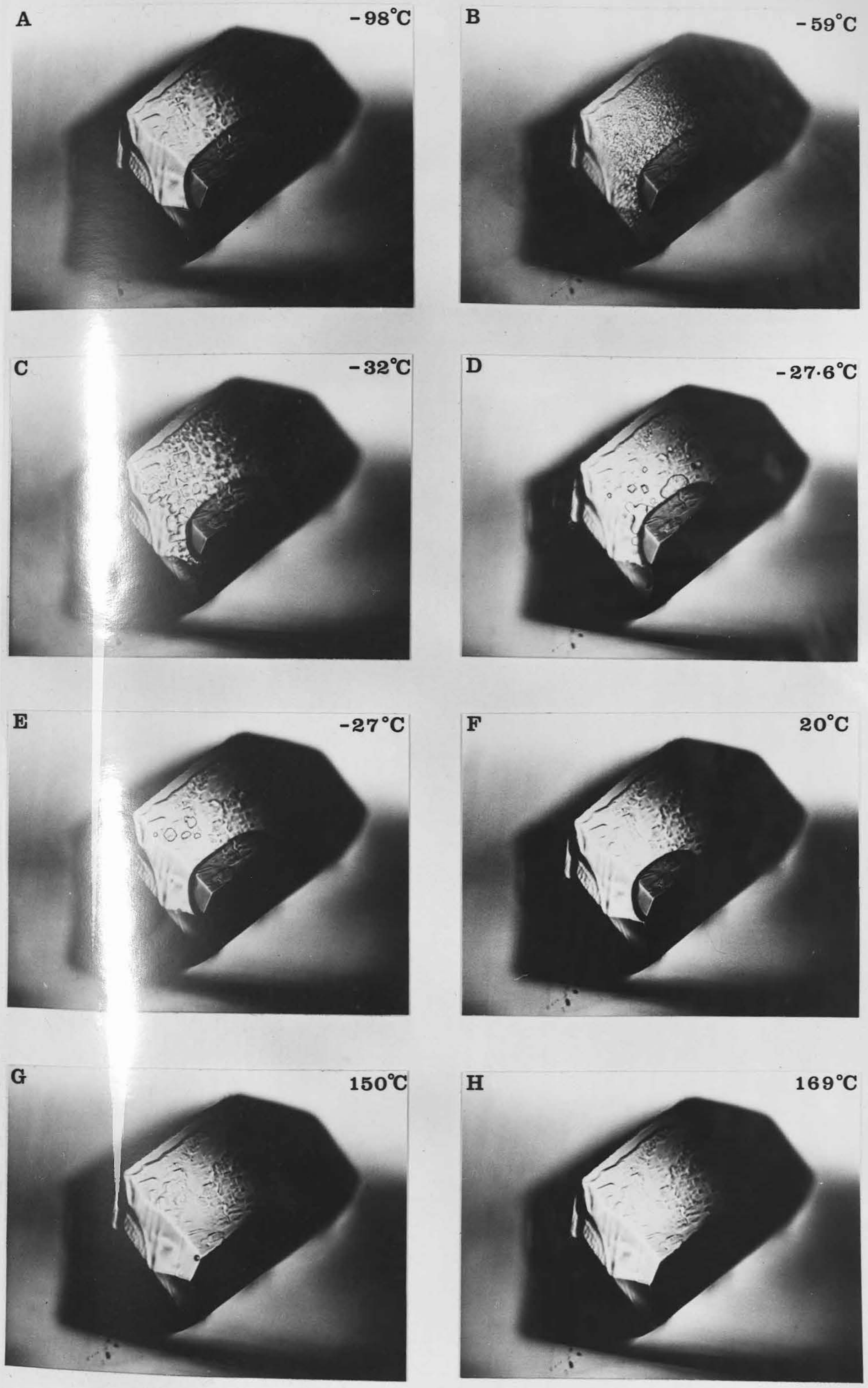


PLATE 27

BONSER VEIN

A - Botryoidal chlorite with stilpnomelane, dolomite and euhedral quartz.
(T-Co.2.11) (horiz. field - 1.5mm) (plane polarized light)

B - Zoned quartz overgrows laths of magnetite.
(T-Co.2.11) (horiz. field - 1.5mm) (plane polarized light)

C - Magnetite laths possibly pseudomorphing haematite, with interstitial calcite.
(P-77Co.2.2) (horiz. field - 1.0mm) (reflected light)

D - Pyrite along cleavages in calcite.
(P-78Co.2.A) (horiz. field - 500 µm) (reflected light)

E - Bismuthinite, with fine chlorite along cleavages, replaced by laitakarite and small grains of native bismuth (bright white).
(P-78Co.2.C) (horiz. field - 300 µm) (reflected light - oil)

F - Laitakarite and native bismuth inclusions in bismuthinite.
(P-78Co.2.C) (horiz. field - 300 µm) (reflected light - oil)

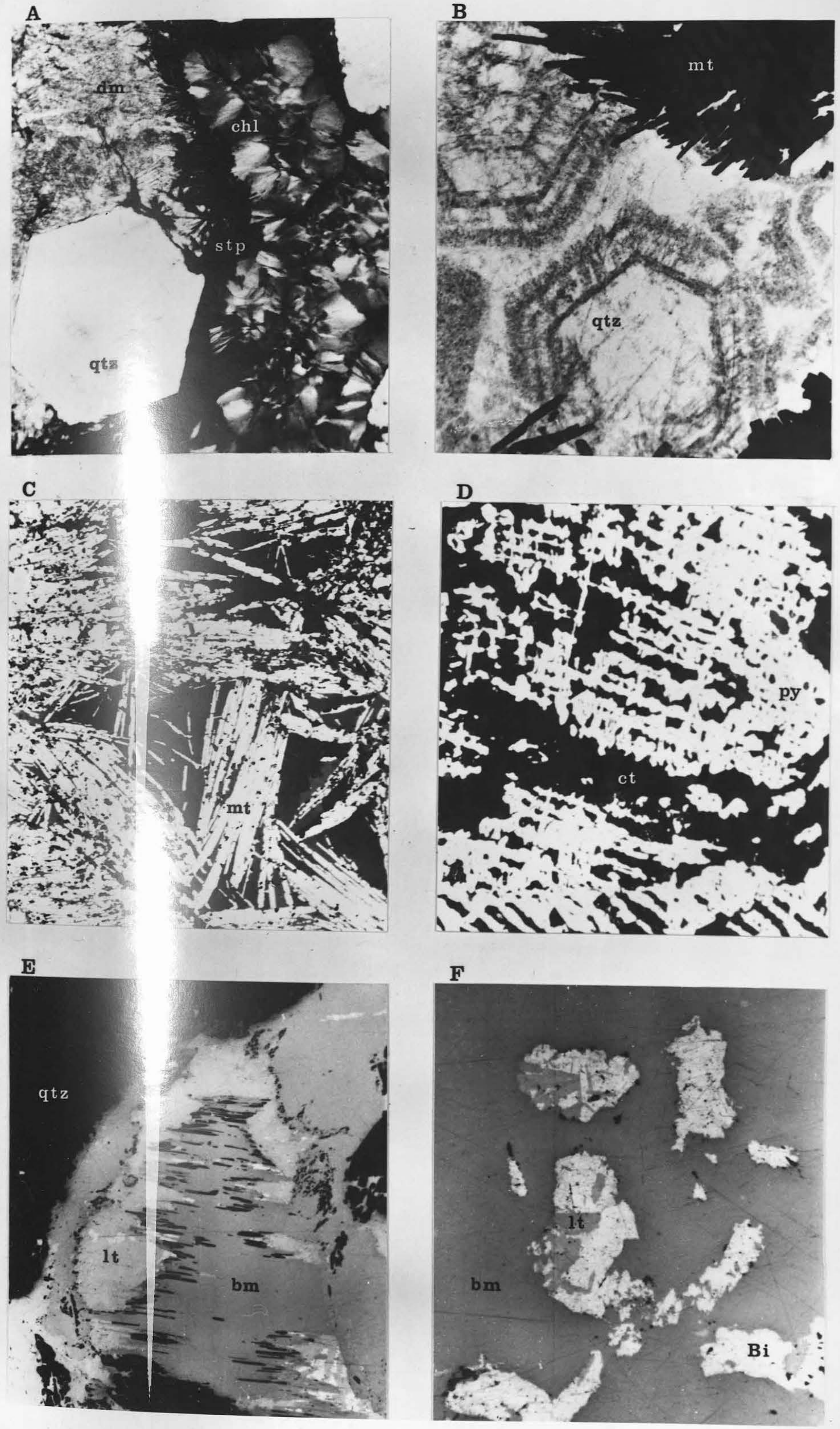


PLATE 28

BONSER VEIN

A - Pyrite replaced by galena.
(P-77Co.2.F) (horiz. field - 500µm) (reflected light)

LONG CRAG VEIN

B - Magnetite with haematite.
(P-77Co.11.A) (horiz. field - 370µm) (reflected light - oil)

C - Magnetite with haematite and interstitial bismuthinite.
(P-77Co.11.A) (horiz. field - 370µm) (reflected light - oil)

D - As for C above.
(P-77Co.11.A) (horiz.field - 300µm) (reflected light - oil)

GOSSAN VEIN, GREENBURN

E - Native bismuth and galena replaced by chalcopyrite.
(P-Co.1.1) (horiz. field - 100µm) (reflected light - oil)

BIRK FELL VEIN

F - Arsenopyrite replaced by chalcocite (along fractures) and bornite.
(P-Co.14.4) (horiz. field - 370µm) (reflected light - oil)

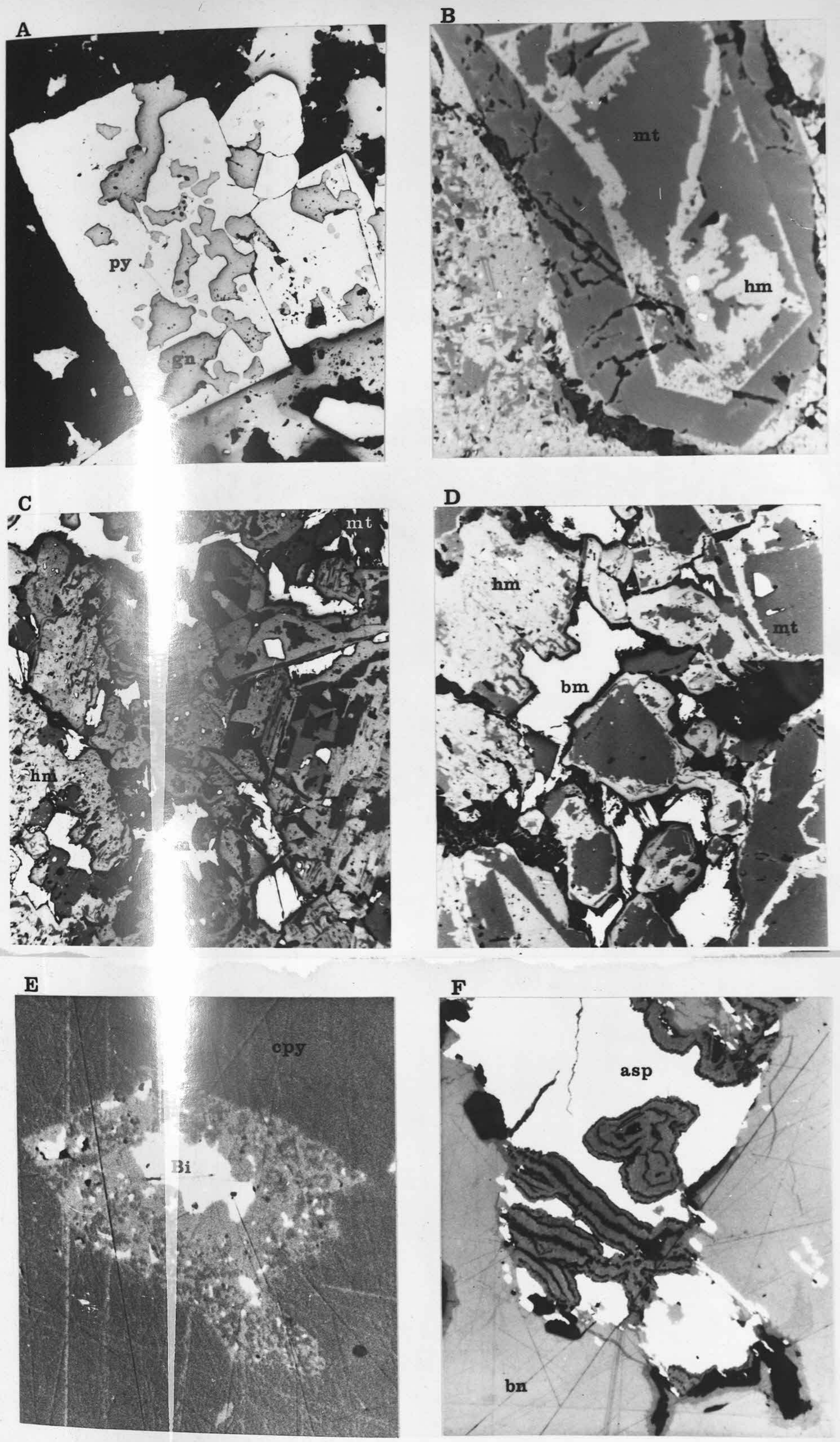


PLATE 29

SEATHWAITE VEIN

A - Wittichenite replacing digenite (which shows alteration to covelline along cleavages) at its grain boundary with quartz.
(P-Co.6.1) (horiz. field - 400 μm) (reflected light)

B - Wittichenite associated with haematite replacing digenite at grain boundaries and along cleavages.
(P-Co.6.1) (horiz. field - 300 μm) (reflected light - oil)

C - As for B above.
(P-Co.6.1) (horiz. field - 300 μm) (reflected light - oil)

D - Digenite has altered to blaubleibender covelline. Wittichenite and haematite are closely associated.
(P-Co.6.1) (horiz. field - 120 μm) (reflected light - oil)

E - Graphic intergrowth of wittichenite and digenite.
(P-Co.6.1) (horiz. field - 120 μm) (reflected light - oil)

F - Early haematite grain, also graphic intergrowth of wittichenite and digenite. Covelline replaces digenite along cleavages.
(P-Co.6.1) (horiz. field - 120 μm) (reflected light - oil)

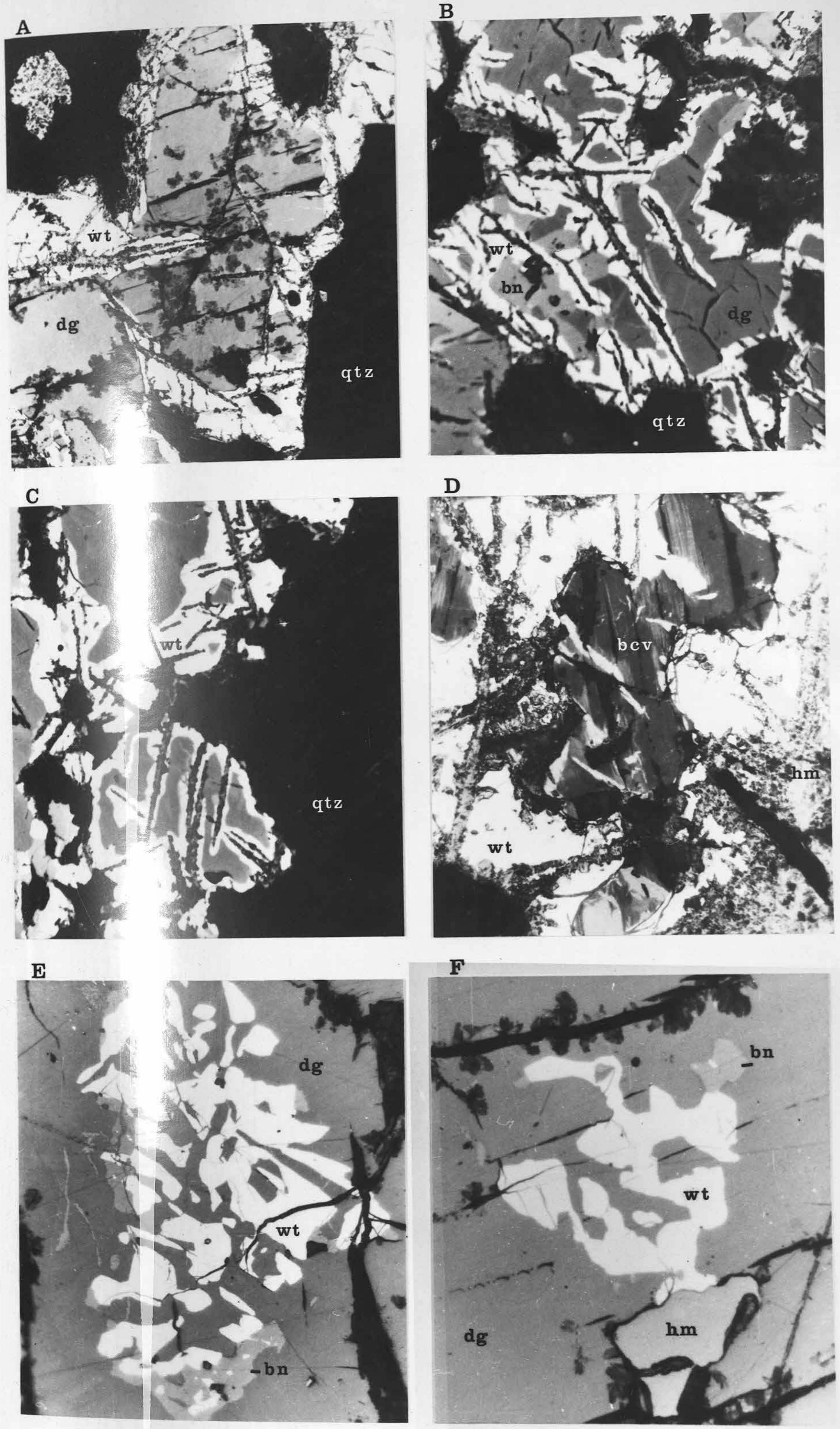


PLATE 30

SEATHWAITE VEIN

A - Intergrowth of wittichenite, associated with minor bornite in digenite.
(P-Co.6.1) (horiz. field - 200μm) (reflected light - oil)

B - Intergrowth of wittichenite in bornite, the latter with haematite inclusions.
(P-Co.6.1) (horiz. field - 200μm) (reflected light - oil)

C - Bornite replacing digenite (of which little remains). Haematite shows a relict texture where it once grew along digenite cleavages.
(P-Co.6.1) (horiz. field - 300μm) (reflected light - oil)

D - Bornite and wittichenite replacing djurleite. Wittichenite is separated from djurleite by a thin margin of chalcopyrite (white) and bornite. Haematite and wittichenite are closely related.
(P-Co.6.5) (horiz. field - 300μm) (reflected light - oil)

E - Euhedral cobaltite inclusions in digenite (the latter replaced by minor bornite).
(P-Co.6.1) (horiz. field - 300μm) (reflected light - oil)

F - Euhedral pyrite in bornite. Covelline and haematite replace bornite and pyrite at grain boundaries.
(P-Co.6.5) (horiz. field - 300μm) (reflected light - oil)

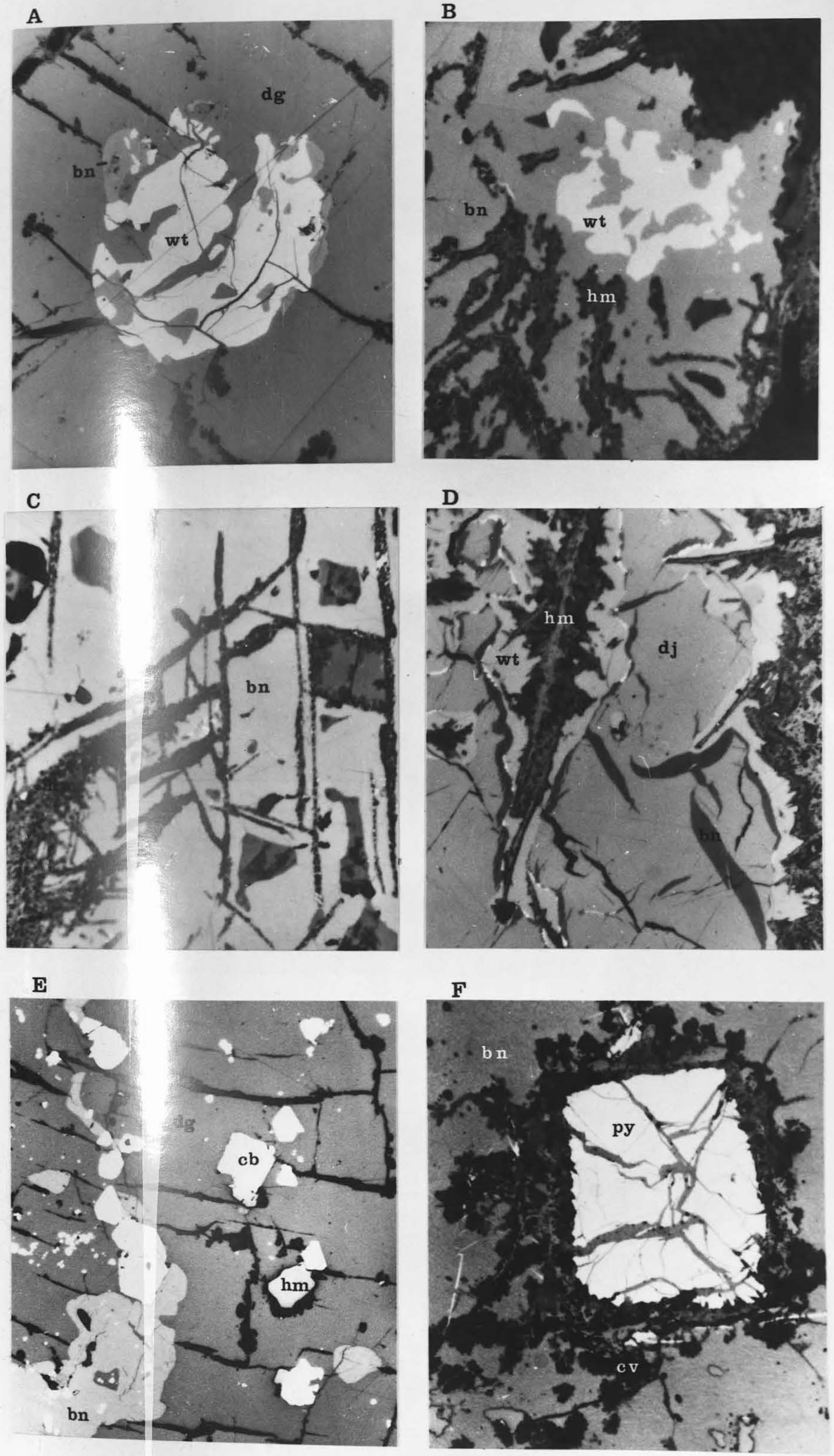


PLATE 31

RUSSELL COLLECTION

A - Cobaltite (compositionally zoned) in the centre (grey), overgrown by rammelsbergite and safflorite (light grey). X - Y indicates an electron microprobe line profile (see Fig.8.2).
(P-BMR.11) (horiz. field - 150μm) (reflected light - oil - partially crossed nicols)

B - Central euhedral zoned cobaltite, overgrown by rammelsbergite (twinned) and safflorite.
(P-BMR.11) (horiz. field - 150μm) (reflected light - oil - partially crossed nicols)

C - Rammelsbergite has been altered preferentially. Cobaltite (centre) and safflorite remain unaltered.
(P-BMR.11) (horiz. field - 250μm) (reflected light - oil)

D - Safflorite replaces and overgrows rammelsbergite.
(P-856.BMR.13) (horiz. field - 300μm) (reflected light - oil - partially crossed nicols)

E - Native bismuth with early euhedral gersdorffite enclosed in rammelsbergite.
(P-BMR.2) (horiz. field - 150μm) (reflected light - oil)

F - Interpenetrating lamellar twins in rammelsbergite.
(P-BMR.2) (horiz. field - 300μm) (reflected light - oil)

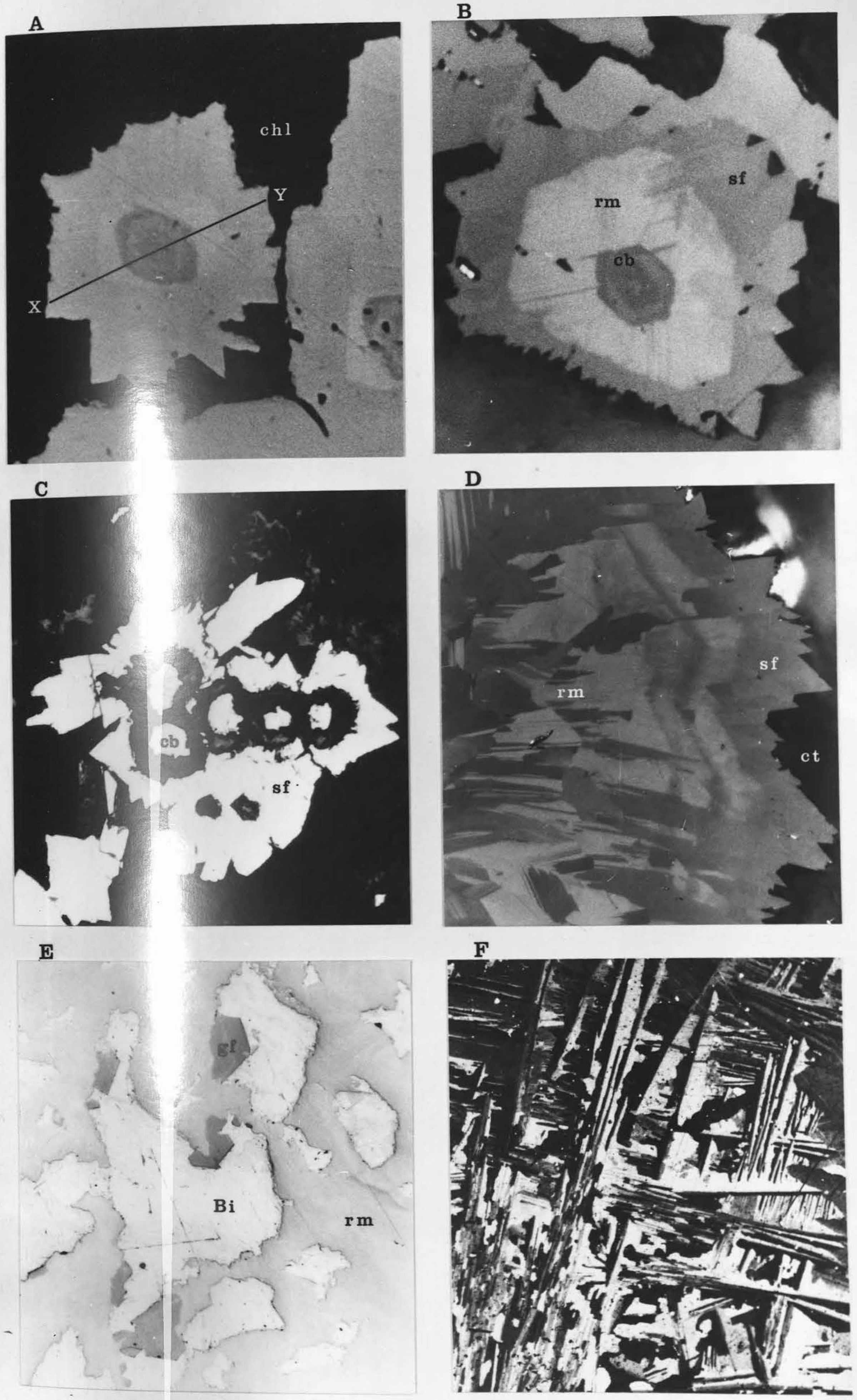


PLATE 32

KINGSBURY COLLECTION

A - Early arsenopyrite partially replaced by pyrrhotine. Pyrrhotine contains euhedral cobaltite.
(P-BMK.1) (horiz. field - 350µm) (reflected light - oil)

B - Cobaltian arsenopyrite has a fine 'herringbone' zonation. Cobalt - rich zones have been preferentially replaced by pyrrhotine.
(P-BMK.1) (horiz. field - 350µm) (reflected light - oil)

C - Pyrite along grain boundaries and cleavages in dolomite.
(P-BMK.9) (horiz. field - 300µm) (reflected light - oil)

D - Wehrlite and gold, with galena, chalcopyrite and arsenopyrite.
(P-BMK.1) (horiz. field - 200µm) (reflected light - oil)

E - Cobaltite, gold and wehrlite, the latter intergrown with pyrrhotine.
(P-BMK.1) (horiz. field - 200µm) (reflected light - oil)

F - Wehrlite, intergrown with pyrrhotine in chalcopyrite.
(P-BMK.1) (horiz. field - 150µm) (reflected light - oil)