THE DISTRIBUTION AND PARAGENESIS OF LOW TEMPERATURE NICKEL/IRON/COBALT SULPHIDES IN CENTRAL BRITAIN

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ABSTRACT

The previous literature on the nickel cobalt species and particularly bravoite is reviewed. The major associations of bravoite are 1) As an alteration product of pentlandite and 2) As a low temperature hydrothermal mineral commonly found within the Mississippi Valley Type deposits and a 'Red Bed Sandstone' type deposit.

An investigation of the occurrence and paragenesis of low temperature species of this type in the Central U.K. has been carried out. The areas covered were the lead-zinc mineralised deposits of Carboniferous Limestone in Derbyshire, North Pennines, the Mendips and additionally the mineralised Ordovician of the Shelve, Shropshire. The main minerals found were galena, sphalerite, chalcopyrite, pyrite, marcasite,bravoite, goethite, and very rarely nickeliferous marcasite. The non-metallic minerals, here referred to as 'gangue', were calcite, fluorite and barite. The bravoite was found mainly in the gangue as small inclusions.

Bravoite was found to occur throughout virtually all the low temperature lead, zinc, calcite, fluorite assemblages characteristically less than o.1% and rarely greater than 1% of it. Size, colour range and zoning characteristics are described but apart from vague similarities, no definate correlation between geographical location and appearance of the bravoites can be detected. The mineral paragenesis shows it to be the first mineral precipitated.

The optical properties of the bravoites are described and 13 quantitative electron probe analyses of bravoites from 6 localities are presented. Total nickel content ranges from 5.99 to 24.8 weight percent. The bravoites do not show any regional zoning, and are generally cobalt poor, not greater than 0.9%.

The optical properties of the nickeliferous marcasites are described and 8 quantitative electron probe analyses of the nickeliferous marcasites from 2 localities are given. No regional zoning is found, and the nickel content ranges from 0.1 to 28.8 weight percent. Maximum cobalt is 1.2 %.

An anisotropic arsenic-rich nickel/iron/cobalt mineral exhibiting a number of phases, from the Tynebottom Limestone of the Alston Block is described, and 6 electron probe analyses are presented. The chemical analyses are consistent with the phases being Nickel Iron Cobalt Arsenic Sulphides.

CHAPTER 1

INTRODUCTION

Hillebrand, (1907), whilst studying small isometric crystals associated with the vanadium ores of Minasragra, Peru, discovered a pyrite like mineral which contained 18.23% nickel. After a complete analysis he assigned the fomula $(FeNi)S_2$, and suggested the name Bravoite, after Senor Jose Bravo, a mining engineer, who had described the remarkable vanadium occurrence. Later Hewitt (1909), in a general description of the same ores showed a photo-micrograph of a polished surface in which the roughly square outlines of bravoite crystals (1-1.5mm) appeared to stand out in moderate to strong relief from a soft ground mass of patronite, VS_4.

Buddington (1924), identified a nickel iron sulphide from the vicinity of Chitina, Alaska, which corresponded to the bravoite of Hillebrand. The Alaskan material contained substantially more nickel than iron. (Table 1 No. 5.) Kalb and Meyer (1926), studied polished sections of a crushed ore from Mechernich, Germany, and observed small isometric crystals with a cross section which indicated a pyritohedral habit, and exhibited distinct zonal banding. Yellow-poor bands were nickelian pyrite, whilst steel-grey bands containing 3.28% cobalt, 24.73% nickel and 17% iron were classed as bravoite. (Table 1 No. 2.) This material was later X-ray diffracted by De Jong and Willems (1927) who determined the cell edge and the pattern to be of pyrite type. (Table 1. No 7.)

The first British report was by Bannister (1940) who described bravoite from Mill Close Mine, Derbyshire. Table 1. No. 1 shows the mineral contained 16.69% nickel. The specific gravity, 4.82, was higher than both the Peruvian and Alaskan material. Bannister also described a pinkish grey granular mixture of bravoite which surrounded pyrite and which had a 12% nickel content. This bravoite gave double lines on X ray powder photographs, and the same cell edge as the Mechernich material that contained 24.73% nickel. Bannister suggested that the double lines indicated that the material was a mixture of pyrite and bravoite and that if this bravoite contained the same proportion of nickel (24.73%,) as the Mechernich bravoite, a mixture of 43% bravoite and 57% pyrite was needed to yield the overall 12% nickel content.

By 1945 there were sufficient analyses for Kerr to propose a system of nomenclature for the iron nickel cobalt sulphides of the pyrite type.

Table 1. - Analyses of bravoite, after Bannister (1940)

	1	2	3	4	5	6	7
Fe	29.30	17.08	29.46	25.19	20.68	38.54	.
Ni	16.69	24.73	18.23	25.42	24.81	6.50	45.6
Co	trace	3.28	trace	0.35	--	--	
S	53.40	51.15	52.31	49.04	54.51	51.39	54.4
Totals	99.39%	95.24%	100.00%	100.00%	100.00%	96.43%	100.00%

1. Mill Close Mine, Derbyshire
2. Mechernich, Prussia
3. Minisragra, Peru
4. Main Creek, Tasmania.
5. Canyon Creek, Alaska.
6. Nickeliferous Pyrite, Denison Mine, Sudbury, Ontario.
7. Artificial nickel disulphide, de Jong and Willems (1927)

CHAPTER 2

BRAVOITE NOMENCLATURE

2.1 Nomenclature Presently Employed

RS_2 sulphides of pyritohedral symmetry with varying amounts of nickel, cobalt and iron forming an isomophous series have been described under the names of pyrite, nickelian pyrite and bravoite. Where minerals belong to isomorphous groups, the distinction between species of like structures is of course arbitrary and problems of nomenclature arise. Palache, Berman and Frondel (1944), in their review of the series NiS_2-FeS_2 proposed to apply the name bravoite only to members which contained more nickel than iron. Specimens which contained less nickel than iron would be termed nickeliferous pyrite. Under this system of nomenclature, the original bravoite of Hillebrand, (1907), as well as samples high in nickel described by Henglein (1914), referred to by Doelter and Leitmeier (1926), and mentioned by Bannister (1940), would no longer qualify as bravoite but would be known as nickeliferous pyrite. It is assumed a parallel system would apply in the case of cobalt, and any member of the group with less cobalt, than iron would be cobaltian pyrite.

The usage suggested is somewhat at variance with the literature. Bravoite has been recognised in at least twelve well established localities. The work of Hillebrand, (1907), de Jong and Willems, (1927) Buddington and Bannister had established bravoite as a mineral with definate properties, isostructural with pyrite, but which contained substantial amounts of nickel. Thomson and Allen (1939), and Peacock and Smith (1944), recognised nickelian pyrite with smaller amounts of nickel. The line between the two has not been definately established, but Bannister classed material that had 36.3% Ni to 63.7% Fe, a ratio of nickel to iron of about 3 to 5 as bravoite, and

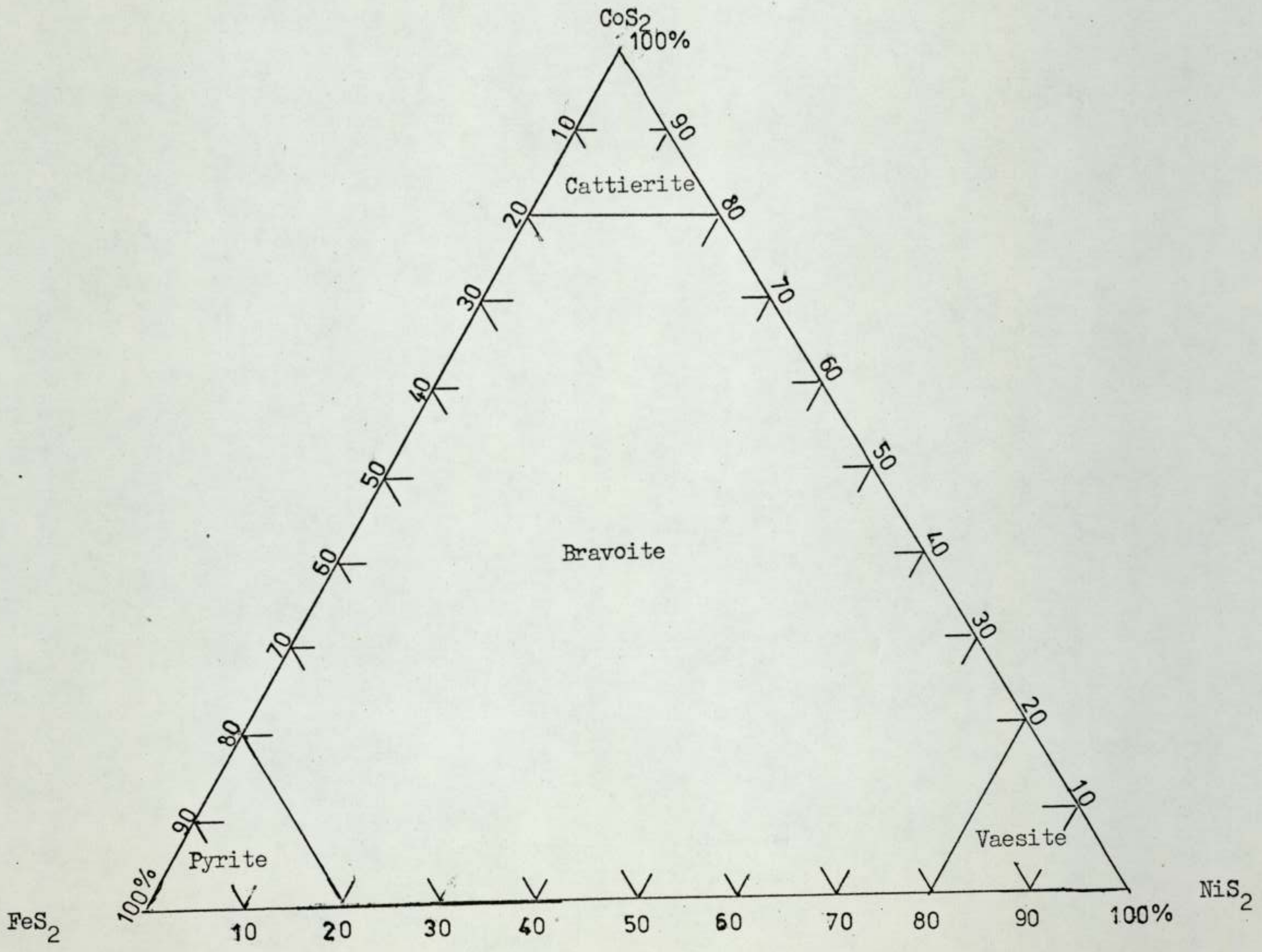


Fig. 1 FeS_2 NiS_2 CoS_2 triangular diagram. (After Kerr 1945) no objection has been expressed in considering material with a lower nickel content as bravoite. Even an excess above 20% Ni to 80%Fe would have a significance which would warrant more than adjectival description, particularly when accompanied by a definate change in lattice constant and physical properties.

The pure end members NiS_2 and CoS_2 are not known to occur in nature, but Kerr (1945) described minerals from the Belgian Congo, cattierite and vaesite, which had compositions close to the theoretical CoS_2 and NiS_2, Kerr proposed delineation of the end members at 80% Fe,Co or Ni, and left the composition of the centre of the triangular field as bravoite. See Fig. 1 . The nomenclature proposed by Kerr left no place for nickeliferous (or cobaltiferous) pyrite, yet as Bannister, Vaughan (1969) and other workers had shown, a mineral intermediate between bravoite and pure pyrite having less than the 20% nickel proposed by Kerr, existed with its own characteristics and deserved a name. A satisfactory solution to the problem has not, to the author's knowledge, yet been devised.

2.2 Bravoite nomenclature employed in this research

A nomenclature based upon a knowledge of the chemical composition of a mineral derived principally through the use of the electron probe is unsatisfactory because it does not permit immediate assignment of a name. A system employing as its basis the observable optical and physical properties of the mineral is more satisfactory.

The system of nomenclature used in this reseach is based entirely on the appearance of the iron/nickel/cobalt sulphide. If the sulphide is isotropic, of high reflectivity and obviously coloured mauve, lilac, purple or brown, or zoned with these colours, with or without yellow, it is called bravoite. If the crystal is yellow with just a hint of another shade, often pink, or exhibits a zoning whose colour is distinguished from the yellow only with the greatest difficulty, it is designated nickeliferous pyrite. In the absence of any of these features, it is called pyrite. Electron microprobe analyses were consistent with this system.

No problem has arisen over the identification of nickeliferous marcasite.

CHAPTER 3

PREVIOUS RESEARCH

3.1 Recorded Associations of Bravoite and Related Sulphides

Bravoites have been found to have two main associations.

1. Magmatic
2. Low Temperature hydrothermal

3.1.1 Magmatic Associations of Bravoite

Bravoite as an alteration product of pentlandite was commonly found associated with native nickel iron alloys, (awaruite, souseite, and josephenite), in serpentinised peridotites and dunites of alpine type. Krishnarao (1964), listed localities including Switzerland where it was found, and gave a paragenesis.

Ramdohr (1969) listed localities where bravoite had been reported as an alteration product of pentlandite as Horbach, Schwarzwald; Campello Monti, Italy; Lillehammer, Evje, Rana, all in Norway; Mouat Mine, Montana, U.S.A.; Farm Vlakfontein, Magnet Heights, Mooihock, S. Africa. He also stated that bravoites that had developed from pentlandite only rarely showed distinct zoning, and occasionally exhibited an apparent but variable anisotrophy.

Michener and Yates (1944), discussed the oxidation of the primary nickel/iron sulphides, pentlandite, pyrrhotite, pyrite, chalcopyrite, and cubanite found in the ore bodies of the Sudbury, Ontario, district using weathered old drill core material. They confirmed that violarite was formed rapidly from pentlandite, and subsequently leached by further oxidation to haematite. In addition pyrrhotite altered to pyrite and marcasite, and took up nickel from the violarite leachate, and formed nickeliferous pyrite containing up to 2% nickel.

They stated that violarite was found in the pyrite marcasite ores which had replaced pyrrhotite but that its origin there was obscure. Nickeliferous pyrites and bravoites often exhibited radiating structures and hence Michener and Yates suggested this indicated these two minerals were supergene.

Unlike the findings of Heyl (1956), that in the Mississippi Valley type assemblage violarite was an oxidation product of millerite, at Sudbury, Michener and Yates found millerite replaced violarite, and they stated special conditions of oxidation prevailed leading to formation of millerite rather than limonite.

Lochhead (1955) described nickel bearing pyrite, marcasite, and bravoite, occurring in alteration haloes which extended up to 3 m either side of fractures in pentlandite $(FeNi)_9S_8$ and pyrrhotite $FeS_{1.14}$ in the Falconbridge ore deposit, Sudbury, Ontario. Because these occurrences extended to great depths, he regarded them as of hypogene rather than supergene origin. These fractures were generally filled with sphalerite, galena, marcasite, and carbonates, and he suggested they were apparantly the final phases of ore making solutions.

Andrews (1962) stated that small amounts of cobalt/nickel pyrites were found disseminated throughout the major pentlandite ore body of the Lynn Lake area, Manitoba, and Scott (1973), reported bravoite, violarite, smythite Fe_3S_4, pyrrhotite, and sphalerite, from Bird River, Manitoba, associated with argentian pentlandite, in massive sulphide deposits emplaced under the influence of regional metamorphism accompanying the main orogeny of the area.

From the same area, Thomson and Allen (1939), reported that the nickel sulphide "beyrichite", in a regionally metamorphosed norite, variously altered to a quartz diorite or a chlorite schist, from the Denison Mine, Sudbury, Ontario, was in reality a pyrite of varying nickel content, some with true pyrite colours, and either nickel free or nickel poor, other parts with a slightly violet tinge, and containing nickel in varying amounts upto 6.5wt.%. (Table 1, No. 6.) This nickeliferous pyrite is mixed very intimately with normal pyrite, and sometimes occurs as outer or inner zones in the pyrite crystals. The mixture, which is associated with quartz occurs chiefly as small aggregates or crystals in somewhat concentric arrangement with ore-free bodies of gangue, bands of ore alternating with bands of gangue. The authors stated that judging by the etch reactions it was possible there may be portions intermediate in nickel content between the two extremes. They suggest it may be a mixture of pyrite and bravoite. Their intermediate nickel content had 6½% nickel.

Krutov (1970), reviewed the special conditions which surrounded the formation of high cobalt and nickel concentrations in high temperature hydrothermal processes. He found that depending on temperature conditions, a characteristic ratio of cobalt to nickel was established, up to 1 in 4 under high temperatures, this appeared as widespread cobalt bearing pyrite. Where a high cobalt and nickel content co-existed together he believed the metals to be extracted from the host rock, for example the large copper pyrite deposit Outukumpu, Eastern Finland. He discussed the behaviour of cobalt and nickel during metamophism of previously formed pyrite deposits, from the least metamorphosed deposits (Northern Caucasus, Urals) to the most metamorphosed deposits (Rammelsberg), the cobalt content of the pyrite increased from 0.001% or 0.01% to 1% or more. Simultaneously there was an increase in cobalt/nickel ratios from 1:4 to 12:1.

Ewers and Hudson (1972) described an ortho-magmatic nickel iron sulphide mineralisation at Kambalda, Western Australia and produced data which indicated that immiscible sulphide/oxide liquids solidified at 1140°C from which pyrite was the first sub-solidus mineral to crystallise at about 400°C and grew to give bands and subhedra near the top of the massive ore, (with rejected nickel and iron diffused away) cobalt was preferentially concentrated in this pyrite and depleted from the surrounding sulphide. Pentlandite exsolving at lower temperature, however, competed favourably with late forming pyrite for available cobalt. Nickel was low in the early pyrite, but concentrated in pyrite formed at lower temperature. Thirtyone electron probe analyses revealed 0.5% to 3% cobalt but low nickel in the early formed pyrite, whereas late pyrite grains showed 0 to 1.5% cobalt and upto 3% nickel. A tendency for zonation in nickel rich pyrites was pointed out by Woodall et al (1966), grains having relatively cobalt poor and nickel rich rims. The authors found pyrrhotite contained 0.5% nickel throughout the ore zone and that some pentlandite was altered to violarite.

Blockley (1972), stated that minerals found in the Gurkha ore body, Northampton mineral field, Western Australia, were galena, pyrite, and marcasite. A specimen of marcasite and pyrite assayed 0.45% nickel and suggested the presence of pentlandite; but possibly the presence of bravoite.

3.1.2 Low Temperature Hydrothermal Associations

Ramdohr gave a selection of localities where bravoites precipitated from low temperature hydrothermal solutions are found, Mechernich, Eifel; Wissen and Grunau, Siegerland; Fredericktown Missouri; Cape Thinnes, Lancaster Co, Pa, U.S.A.; Mina Ragra, Peru; and several occurrences in the Bushveld Igneous Complex, Transvaal, S. Affica.

For the purposes of this research, low temperature hydrothermal occurrences of bravoite have been subdivided into two:

1. Mississippi Valley Type.
2. Red Bed Sandstone Type

3.1.2.1 Mississippi Valley Type

The main features of Mississippi Valley deposits were summarised by White (1968). The mineralogy of the deposits is generally simple. Galena and sphalerite are the commonest sulphides; pyrite, chalcopyrite marcasite and wurtzite are widespread but in smaller amounts, and other sulphides containing Cu, Co, Ni, Ag, and Hg occur locally (Heyl and others, 1959; Hagni and Graw 1964). Dolomite, calcite, barite, fluorite, chalcedony and quartz are the commonest gangue minerals. The ores contain J-type lead which is enriched in the radiogenic isotopes relative to nonradiogenic Pb^{204}. Gold content is very low, and silver is generally low. Many of the ore deposits are strata-bound, occurring largely in carbonate rocks of Palaeozoic age but may occur in large fissure veins. Commonly only slight structural deformation of the host rocks has occured, either before or after ore deposition; however, faults, fractures, and open folds control most of the ore deposits in detail. The ores are generally considered to have been formed at depths in the order of 300 metres to 1000 metres, and temperatures of homogenisation of fluid inclusions are systematically low - from about 70° to 180°C.

Occurrences of bravoite in Mississippi Valley type ore deposits are now described.

Bravoite occurred in a mixed Fe-Pb-Cu-Ni-Co-Zn-Sulphide ore which occurred at Fredericktown, Missouri, in the shaly and glauconitic zone between the Lamotte sandstone and the Bonneterre dolomite of the Upper Cambrian. The sulphides occurred in layers, layered disseminations and displayed several geopetal structures, and these features and certain geochemical considerations suggest a diagenetic age for the sulphides. (Amstutz, et al., 1961, Amstutz, 1959; Amstutz and El Baz, 1962).

Here bravoite was associated with marcasite, siegenite $(NiCo)_3S_4$, pyrite, chalcopyrite, galena and a little fluorite. Euhedral bravoite crystals ranged in grain size from 1 to 30 microns and contained thin violet or lavender zonal bands from 0.5u to 5u in width. Rasor (1943) suggested that the bravoite was later than the siegenite, replacing it, or more commonly, replaced the pyrite.

Heyl (1956) was the first to realise that nickel minerals occurred in comparative abundance as accessories in the Upper Mississippi Valley zinc-lead district in south west Wisconsin, north west Illinois, as well as other localities in Wisconsin, Illinois, Missouri and Indiana. In south west Wisconsin millerite was the commonest nickel mineral and it was generally associated with violarite and bravoite. Because of its normal occurrence inside vugs in the central parts of veins, Heyl suggested millerite was deposited near the end of the main period of the primary sulphides. Violarite (Ni_2FeS_4) occurred as an alteration product of millerite, pseudmorphing it; and replaced chalcopyrite with which it was intimately associated. Bravoite was also intimately associated with violarite and with 'honnesite', ($NiSO_4$) a secondary oxidation product of primary millerite. Millerite was often peripherally altered to violarite and honnesite accompanied by bravoite, and Heyl believed all the nickel minerals were probably products of oxidation and secondary enrichment of millerite.

Ramsbottom (1962) mentioned the occurrence in two veins struck at depth in the Tansley, Ashover, Derbyshire borehole, of bravoite pyrite, millerite, pyrrhotite, chalcopyrite and sphalerite, the bravoite and marcasite was associated with pyrite, the bravoite occurred in sheath-like aggregates in a thin vein. The country rocks were limestones of low D_2 or high D_1 age, Visean and were associated with the Matlock lavas.

Following Bannister's identification of bravoite at Mill Close Mine (1940), Ramsbottom's discovery in the Fallgate borehole, and Vaughan's (1969) work, Ixer (1972), found Bravoite as the earliest hydrothermal sulphide occurring in all non-sulphide phases, at Clitheroe and in a fluorspar flat at Masson, Derbyshire. He described texture, zoning, reflectivity, and modal proportions and presented 4 micro-probe analyses showing nickel content from 12% to 18% and cobalt from 0.8% to 1.2%. The crystals were 10 to 30u across, zoned and exhibited a pentagonal dodecahedral habit. From the field evidence in Derbyshire and later Clitheroe, he suggested it was a characteristic primary accessory sulphide of the low temperature lead-zinc-barite-fluorite mineralisation.

A deposit designated as probably Mississippi Valley Type is described by Ashley and Creelman (1975), from Cooleman Plains, Southern New South Wales. The orebody occurred in weakly metamorphosed Silurian limestone or dolomite as bedded replacements or veins in a collapse breccia which contained a simple mineral assemblage of dominant quartz with sphalerite, galena, carbonates, barite, fluorite, and minor chalcopyrite, nickeliferous pyrite and cobaltiferous pyrite, marcasite and tetrahedrite. The pyrite formed about 1% of the total sulphides and occurred as fine grained to medium grained anhedra which contained, from micro-probe analysis, up to 1% nickel and 3.2% cobalt, with arsenic up to 0.8% showing an inverse relationship to cobalt.

This deposit bore certain similarities to that of the Shelve, Shropshire, except that there the mineralised rock was a brecciated, slightly metamorphosed flag and shale.

3.1.2.2. 'Red Bed Sandstone' Type

A further association of bravoite is within the mineralised 'Red Bed Sandstone' type deposits.

'Red Bed Sandstone' type deposits differ from 'Red Bed Copper' deposits in being enriched in lead, barium and nickel, and depleted in selenium, vanadium and uranium.

Boyle (1971), cited the occurrence of bravoite in pyrite in the 'Red 'Bed Magnet Cove of the lead-zinc-silver-copper deposits of the Walton Cheverie area, Nova Scotia. He gave a paragenetic sequence of pyrite chalcopyrite, sphalerite and galena, associated with barite and dog-tooth spar which filled later fractures.

The textures of the bravoite and associated marcasite in this deposit were divided into five varieties.

1. Small (50 to 100μ) zoned, nickel and cobalt-rich pyrite crystals replacing sandstone.
2. Large colloform masses, apparently representing a coelescence of type 1. These appeared as interbedded layers of pyrite and marcasite, some pyrite layers being nickel/cobalt-rich, others not. The marcasite contained little or no nickel. Associated with these colloform masses were subordinate galena, sphalerite, and covellite and later infilling and cross-cutting chalcopyrite.
3. Concretionary, tubercular, and zoned masses of continguous nickel cobalt rich spheres (buckshot pyrite). The spheres averaged 2 to 5 microns in diameter. The spheres replaced siderite, and had in turn been extensively replaced by galena and chalcopyrite.
4. Very fine botryoidal masses of pyrite with nickel cobalt rich colloform zones shown by electron probe analysis to be bravoite.
5. Individual spheres ranging from 10 to 20μ in diameter. They possessed a varied outline and generally had a nickel-rich core or zone.

He suggested the globular forms of nickel cobalt pyrite found amongst plant beds in this Series might be organic framboids of bacterial origin.

He postulated the nature of mineralisation as hypogene. Connate brines ascended from the Windsor evaporites at depth and stimulated by Triassic Volcanic activity, had leached out various elements from the sandstones above, and deposited them in chemically replaceable rocks and dilatant zones along faults.

Ageykin et al (1969), described an occurrence of bravoite in the Voronezh region, 55 Km south west of Moscow. A Permian cupriferous sandstone series overlies the Precambrian crystalline basement which contained numerous basic and ultra-basic nickel bearing intrusives. The mineralised sandstone was a coarse grained inequigranular rock of a quartz/feldspar composition of which 80% was angular or half rounded quartz, 8% was feldspar and a little mica, cemented by carbonate and sulphide. The sulphides accounted for 30 to 35% by volume of the rock and were composed of bravoite and pyrite, 55 to 60%, and arsenopyrite 10 to 12%. Euhedral to subhedral bravoite crystals (50µ to 1mm), showed distinct poly-zonal texture which becomes particularly clear on etching. The chalcopyrite, in allotriomorphic aggregates (0.1 to 3mm), or thin (10µ to 10mm) veinlets, frequently replaced the pyrite and bravoite.

Ageykin maintained the distinct stratification of the mineralisation and its confinement to the basal horizon of the sandy kaolin series was evidence of a sedimentary or sedimentary infiltrational origin of the copper and nickel. He further suggested that deposits of this nature could serve as prospecting indications of deposits of the Precambrian copper-nickel sulphide ores.

Warrington (1965,)described the mineralisation of the sandstones of Alderley Edge, Cheshire. He stated that cobalt and nickel occurred in association with manganese in the form of wad, as large segregations; vein-like masses, and spots in both the Bunter and lower Keuper host rocks. Galena occurred as disseminations in the sandstone, often following current bedding and within fault breccias. The galena contained a cobalt/nickel ratio of 50:1, which is important since it is a feature of the geochemistry of ore bodies whose source was an acid igneous mass (Davidson, 1962). Such a source body could account for the abundance of arsenic present and supply the combination of ores noted at Alderley. It is concluded from the fact that since cobalt never predominates over nickel in sedimentary ore deposits (Davidson, 1962), the ratio of cobalt to nickel in galena from Alderley Edge indicated an epigenetic origin. (Mohr, 1964).

The bulk of the minerals were secondary, the primary sulphide ores being restricted to the faults. Nickel/cobalt rich pyrites have been subsequently discovered in this assemblage. (Ixer, 1974, personal communication).

3.1.3. Miscellaneous

Another mode of occurrence of bravoite was as an accessory mineral in a chalcopyrite ore body in the Palabora Carbonatite complex, Transvaal, S.A. Heinrich (1970) quoted Foster (1958) and Lombard et al (1964), who reported pentlandite, millerite, bravoite, linnaeite, violarite, covellite, tetrahedrite, sphalerite galena, pyrite, marcasite, gold, silver, uranium and baddelyite.

The occurrence of bravoite in the North Caucasus is discussed by Bocharova (1970). The ore bodies have the form of veins, lenses and stockworks, closely associated with zones of tectonic crushing in granites, metamorphosed schists, and rarely, in ultrabasic rocks transformed into highly altered carbonatised serpentinites. The mineralisation was galena and sphalerite, with subsiduary pyrites, and minor chalcopyrite, tetrahedrite, arsenopyrite, marcasite, native silver and rarely, native gold. Quartz, barite and carbonates were widespread vein materials.

At Chochukulak, nickel minerals (Chloanthite, $(CoNiFe)As_3$, breithauptite, NiSb and particularly bravoite) were widespread, and occurred with the pyrite and marcasite. Bocharova suggested the source of the nickel was a large serpentinite mass 10Km away, the nickel being removed in solution by hydrothermal fluids passing through the serpentinites. He postulated a case of the contamination of post magmatic hydrothermal solutions of granitic magmas with the elements of basic magmas.

An arsenic rich bravoite was described by Petruk (1971), in a cross-vein of the Keewatin lava flows, Cobalt Gowganda regions, Canada. Sulphide assemblages of the galena, pyrite, sphalerite, marcasite type occurred in cross veins between the main veins which yielded a composition equivalent to $Co_{0.62}Ni_{0.19}As_{0.15}S_{1.84}$.

Colour zoning in iron pyrites is apparently not of itself sufficient to enable a positive identification of bravoite to be made. Burkart-Bauman and Otteman (1971), reported arsenic up to 7% in pyrite in Peru, and in Tunisia which produced zoning similar to bravoite, whilst Lazar and Otteman (1973), described a Roumanian hydrothermal vein deposit which yielded a cupriferous pyrite, distinguished optically from common pyrite by brownish yellow colour and lower reflectance and was shown by electron probe analysis to contain upto 1.2% copper.

Millerite is recorded from at least four localities in the United Kingdom. Howarth (1930), reported it as tufts or radiated groups of very slender or even capillary rhombohedral crystals which occurred in cracks or concretions in clay ironstones associated with the coal measures of South Wales and reported one occurrence actually in the coal. Associated minerals were quartz, calcite, barites, dolomite, or ankerite, chalcopyrite, pyrite, galena and blende.

An unprovenanced specimen of millerite is in the British Museum, from Weardale. It is stated to be still found in the Tynebottom Limestone, but the present author has been unable to locate any. Ramsbottom, (1962), reported it from the Fallgate borehole with bravoite, and Wilson (1921,) reported it with other nickel compounds as a metasomatic replacement mineral at certain localities in Scotland.

Linnaeite, Co_3S_4 was reported by Howarth (1930), from five localities in the South Wales coal field.

La Neve Foster (1887), described a remarkable occurrence of a nickel cobalt wad at Foel Hiraddug mine, near Rhyl. The wad occurred as black lumps with haematite and limestone fragments in a red clay matrix filling a very irregular perpendicular vein. The wad contained around 30% Co_2O_3, 10% Ni_2O_3, 35% MnO_2, 15% Fe_2O_3, 10% H_2O and just under 3 tons of cobalt and 2 tons of nickel were recovered from the ore between 1878 and 1880. Iron pyrites, found as the core of a piece of haematite, on analysis yielded traces of cobalt and copper, and he presented the view that the present vein is the gossan of a lode of cobaltiferous iron pyrites.

There are many reports of cobalt and nickel from Cornwall. Dewey (1923), reports cobalt and nickel from Dolcoath Copper mine associated with uranium, bismuth and silver and from Fowey, associated with iron pyrites, nickel, antimony, tin, cadium and silver ores.

Andrews (1962), reports cobalt bloom, (erythrite $Co_3As_2O_8.8H_2O$) from near Barmouth, and nickel and cobalt oxides from Motrram St. Andrews, Cheshire, near Alderly edge, and Gunshill Copper mines, Shrewsbury.

3.2 Descriptions of Bravoite

Springer, Schachner-Korn and Long (1964), analysed natural bravoites from Mechernich, Germany, using the electron probe and from the analyses obtained showed that complete metastable solid solution between all three disulphides was highly probable. They reviewed previous experimental work on bravoites and their experimental production of artificially zoned bravoites precipitated from aqueous solution was described. H_2S and sulphur were introduced into $FeSO_4$, $CoSO_4$ and $NiSO_4$ solutions of 0.1 moles/litre concentration, the solutions sealed in glass tubes and heated to up to 300°C for four days. The precipitated products were examined optically and in the electron probe as polished sections and found to be identical to naturally occurring zoned bravoites. From thermodynamic considerations they showed that under certain concentrations and pH levels, a very small change in a solute concentration can lead to a much more pronounced change in the composition of the crystal, leading to a zonal strucutre. They found both zoned and unzoned crystals in the precipitation products of one experiment, and suggested that the concentration changes in a solution which led to zoning seem to have occurred around certain crystals only, and were probably caused by very localised convections of liquid. They suggested that natural bravoite was formed under conditions similar to those in the experiment.

Zoned bravoites from Maubach, Germany, and Mill Close, Derbyshire, were examined by Vaughan (1969), to determine variations in colour, reflectivity and micro-hardness in relation to compositional variations. In both localities nickel and cobalt showed a sympathetic relationship in the zones, which was antipathetic to iron. Iron rich memebers were found to be harder and have a higher reflectivity than those rich in cobalt and nickel. The analyses suggested variable amounts of non-stoichiometry, and reflectivity also decreased with increase in total metals. Variations in the geometry of the zones were considered, and in some cases were considered to have been probably related to properties of the crystal surfaces. The zoning was probably the result of very local variations in conditions.

El Baz and Amstutz (1963) conducted a statistical study of bravoite zoning exhibited by bravoite crystals from Fredrickstown, Missouri. They classified them into eight zoning types, and discussed the internal regularities of the grains as well as their relationship to the surroundings, and concluded that factors other then temperature and pressure controlled such crystallisation phenomenon as zoning.

Zimmerman and Amstutz (1973), offered a condensed atlas of possible section shapes of cubes, octahedra, and pyritohedra for use in habit determinations of pyrite, bravoite, and other cubic minerals in thin and polished sections. They presented references to previous attempts to solve shape changes mathematically and stated that mathematicians have confirmed a theoretical treatment was not feasible.

Cobaltiferous pyrite in magnetite skarns from Kazakhstan was investigated by Velkiboretz and Lukyanchenko (1970). Parallel sections of pyrite crystals cut in different orientations were examined in the electron probe and the data indicated two modes of occurrence of cobalt, nickel, and arsenic in pyrite.

1. As isomorphous substitution for iron
2. As discrete inclusions of cobaltite.

The cobalt substitution was greater along 100 planes than along 111 planes, and they attributed its greater capacity for absorbing cobalt to the lesser reticular density of the 100 planes composed of regularly alternating iron and sulphur atoms as compared with the monatomic 111 planes. A rhythmic variation was detected along a normal to these planes, concentrations on 111 planes varied about a definate level, whilst on the 100 planes, traversing from the periphery to the centre, it varied about a slightly ascending straight line.

CHAPTER 4

FIELD STUDIES

4.1 Introduction

The major quantity of material collected for examination came from four regions. These were in order of abundance of material collected, Derbyshire; Alston Block and Askrigg Block, (North Pennines); and West Shropshire, (Shelve area).

Active 'metalliferous' mining in every locality with the exception of the Youlgrave Mine, Derbyshire, ceased prior to 1950. In many areas the industry had ceased before the close of the 19th century. As a consequence of this, material was collected extensively from old workings, rakes, hushes, and mine dumps. With few exceptions, material was not collected in-situ, because it was either unavailable or did not fulfil the collection criteria, namely showing signs of visible mineralisation. The use of mine dumps and other waste material introduces an element of uncertainty as to the exact source of the material, both geographically in a horizontal plane, and stratigraphically in the vertical plane. However, material collected from dumps in particular was probably quite representative of the immediate vicinity as a whole. Unfortunately it is impossible in most cases to assign a definate stratigraphic horizon to collected material because the depth of origin is unknown, and also any orientation of material with respect to the sides of a vein, or top and bottom of a flat, or the nature of the adjacent sidewalls is information which is completely unobtainable.

As the research progressed however it became apparant that lack of this information was not going to be in any way crucial to the success of the investigation. The research was directed towards determining whether there was a regional variation of bravoite so detailed location was not so important, and in the few places where it was possible to obtain data of this nature, there was no correlation between it and mode of occurrence, appearance, texture, or associated mineralogy of the bravoite crystals being found.

Many areas visited, although both from maps, published accounts and the obvious disturbed nature of the ground had been localities worked for minerals in the past, yielded no material. This accounts for the great disparity in abundances of material collected from different localities. The Mendips was the most difficult in this respect.

A brief description of each region will be given emphasising its structural and mineralogical aspects. After each description there will be a table listing the grid reference of the find spot and giving a statement of the nickel minerals found, and in the remarks column a brief description of the polished section.

The minerals listed in the remarks column as present in the section do not include galena although it is to be understood that it is present in almost every section. The oxidation products of lead, iron zinc or copper are not listed, although it is to be understood that wherever galena, pyrite, marcasite, sphalerite or chalcopyrite occur, the oxidation products, cerrusite, geothite, smithsonite, covelline and chalcocene nearly always occur. Due to much of the material collected having lain on the surface and weathered for many years, oxidation in many specimens is far advanced.

The geographical order of description of the specimens is from north to south and where applicable from west to east along the rakes and veins.

4.2 Description of the Peak District orefield, Derbyshire.

The orefield of the Southern Pennines extends from Castleton in the north down the eastern half of the North Derbyshire Carboniferous Limestone massif through Bakewell, Darley and Matlock as far south as Wirksworth. The broad geological picture is one of a series of massive well-bedded Avonian limestones of the Dibunophylum zone approaching 1000m maximum and exhibiting a bewildering variety of litho- and biofacies, deposited on a 'Derbyshire Massif' with a suggested Llanvirnian 'basement' found at the bottom of the Eyam borehole. (Dunham, 1974). Some beds are darker and shaly, e.g. the Davisiella beds at the base of the exposed sequence, some are dolomitic, some cherty, and some are locally silicified. (Bemrose 1898). Unpublished work by Thach (1965) has demonstrated a wide zone of reef knolls, separated by channels and basin-like facies, rather than a simple marginal reef belt. To the north is a marginal reef complex around Castleton, while on the eastern flank are reefs of a rather different character including brachiopod-crinoid heaps showing quaquaversal dips, limestone breccias, coarse crinoidal limestones, and fine grained calcite mudstones and algal mounds. (Black 1954, Shirley 1959). Reef knolls enveloped by shale have proved to be favourable loci for ore deposition, (Shirley and Horsfield 1940, 1945), as Shirley has demonstrated at Mill Close Mine (1949).

The sequence is interrupted by both extrusive and intrusive igneous rocks, (Bemrose 1894, Wilcockson 1932) mainly in late D_1 and early D_2 times. Olivine basalt lavas, massive and amygdaloidal occur at two main horizons, and in several lesser ones. Associated with the lavas are tuffs and ashes, which have been subjected to widespread alteration, the ultimate product of which is a sticky clay substance forming 'wayboards', and in some horizons a mottled green rock known as toadstone. Waybaords and toadstones are almost impervious alike to ascending ore-solutions and descending water, and have exerted a very powerful contol upon the distribution of the mineral oreshoots, splitting up the massive limestones into relatively thin favourable beds (Ixer 1974).

Structurally the district as a whole is to be regarded either as a broad structural dome, or as an uplifted block limestone, with reef limestone screes and boulder beds (Simpson 1968), banked against the surrounding cliffs. Shirley (1945 and 1949) has shown that the dome is far from simple, having a broad flat axial region trending north-south near its western margin, broken by numerous faults, and having three smaller complex anticlines extending eastwards from the dome axis, the Eyam-Calver, Youlgreave, and Matlock anticlines, plicated by pitching cross folds of noth-south axial trends. Fearnsides (1933) showed that the east-west folds were already in existence during the Lower Carboniferous, and Shirley and Horsfield (1945) have shown that the master veins of the northern district run along the crests of the minor corrugations of the main structure.

Around all sides of the 'Dome' the limestone plunges under the Edale Shales, to reappear again to the east where a pitching north-south trending anticlinal ridge brings up two domal inliers of limestone at Ashover to the north and Crich to the South.

The Derbyshire massif and the Crich and Ashover inliers are traversed by innumerable mineral lodes, running within 45° of the general East-West direction practically all of them carry galena to some extent, sphalerite, a little pyrites and chalcopyrites, calcite, barytes or fluorspar. The mineral deposits are particularly rich and numerous at the northern and eastern flanks of the massif.

The deposits are classified as Rakes, Scrins, Flats and Pipes. Rakes are major fissure fillings, often extending for some kilometers, (Long Rake 11 Km.), and commonly 6m. wide. They often show horizontal slickensiding on the walls indicating final lateral fault movement. Scrins are small fissure fillings a few inches wide often occurring in swarms. Flats are horizontal ore bodies of similar length and width, while pipes are similarly horizontal but length considerably exceeds width. Both flats and pipes are replacement of limestone often with roof or floor of wayboards or toadstones.

In the rakes and scrins the minerals often show parallel banding on each wall with an occassional open vug in the centre, but a vug or cavity is much more common in the replacement deposits.

A study of Farey (1811), and Pilkington (1798) would show that fluorite is the predominant gangue mineral within a 2Km or so of the eastern boundary of the limestones, gradually giving way to barite gangue, then 2Km or so further west to calcite gangue, although in all three zones, all three gangue minerals are usually found together and this zonation is marked only by the dominance of one or the other. Wedd and Drabble (1908) suggested this zonation was largely statigraphically controlled, the fluorite being the earliest and hottest mineral was restricted to the highest beds of the limestone beneath the Edale Shales, and the restriction to the eastern margin was said to be due to the removal of the equivalent limestones by erosion further west. However, subsequent statigraphic work tends to show that these beds had in fact been removed by erosion prior to the deposition of Edale shales, and later mineralisation. Shirley and Horsfield confirmed (1945) that fluorite is more important under the anticlinal areas of the limestone, the ore solutions coming from a postulated granite magma beneath the east (Dunham 1934) and travelled up the tension fractures along the crests of the easterly pitching anticlines, in which tension fractures they subsequently crystallised. Mueller, (1954a) in his study of the distribution of fluorite varieties claimed that the north-south zones of Wedd and Drabble are partly lost in the synclines and thus confirmed Shirley and Horsfield's hypothesis concerning anticlinal control of mineralisation, and further subdivided the fluorspar zone into three distinct subzones which he claimed can be plotted with respect to each main vein and related side vein and thin stringers respectively. The subzone classification is based on colour of fluorite, and he equated colour with temperature of deposition, thus arriving at his temperature zones. The fluorite varieties he recognised are clear; colourless or yellow, containing pyrite or chalcopyrite inclusions and delimit his high temperature subzone, a medium temperature sub-zone with turbid faintly purple fluorite containing fluid inclusions, sometimes known as Bradwell or Crich spar, and a low temperature subzone recognised by fluorite with marked blue or purple colours. He ascribed the dark colours to hydrocarbons retained at lower temperatures within the fluorite, which can be driven off by the application of heat and made colourless. However, as was shown during the 1939-45 war when radium was stored in caverns containing purple fluorite, the colouration had been removed by radiation, and subsequently gradually returned, and subsequent work has shown the colouration to be a function of a lattice defect brought about by the excessive inclusion of calcium atoms in the cubic fluorite crystal lattice.

Mueller (1954b) further suggested pyrite and chalcopyrite generally are confined to the highest temperature sub-zone and drew an analogy with their distribution in Cornwall where they are usually found nearer the apparent source of the mineralising solutions. Mueller further stated he could temporally correlate fluorite and calcite crystals in different veins from similarity of shape, size, density and type of pyrite, chalcopyrite or gas bubble inclusions, and broad tendencies could be recognised throughout regions some miles across. (Mueller 1954c). However, the present investigation could detect no real evidence of colour subzones, or restriction of pyrite inclusions to one particular colour of fluorite. One explanation could be the unavailability of in-situ material, dump material being heterogeneous and inherently incapable of providing the accuracy of detail necessary to confirm Mueller's findings.

Material was collected from 69 locations in Derbyshire, and from 5 locations at Ecton, Staffordshire. Of the Derbyshire locations 55 contained bravoite or nickeliferous pyrite, 4 of which also exhibited an anomalously zoned marcasite and of the 5 from Ecton, one contained bravoite, and one a pinkish nickeliferous pyrite. Collections were made either from isolated dumps, or at intervals along the rakes. In the case of the former, the grid reference of the dump is given, in the case of the latter, the grid references of the extremities of the length of the rake collected along are given, together with the number of collections made. Purely for the purposes of this report the region has been divided into four areas of 10,000 hectares each, as shown on the key map.

Maps 1 to 4 show the boundary between the D_2 limestone and the overlying Edale Shales and the principal rakes and veins. Locations from which collected material contained bravoite or nickeliferous pyrite are shown thus, ●. Material containing no nickel is shown thus + .

Nomenclature: - 1.Bravoite and Nickeliferous Pyrite

The boundary between bravoite and nickeliferous pyrite has been assigned at 20% nickel/cobalt content. Nickel/cobalt content can only be determined by use of the electron probe. For the purposes of this research a subjective classification has been made. All crystals exhibiting pronounced colours and one or more colour zones being classified as bravoite if isotropic, or nickeliferous marcasite if distinctly anisotropic. Other iron pyrites exhibiting a very slight 'off-yellow' colour, with or without zoning were classified as nickeliferous pyrites.

2. Gangue

The term gangue is used to describe all non-sulphide minerals; fluorite, calcite, barite, quartz.

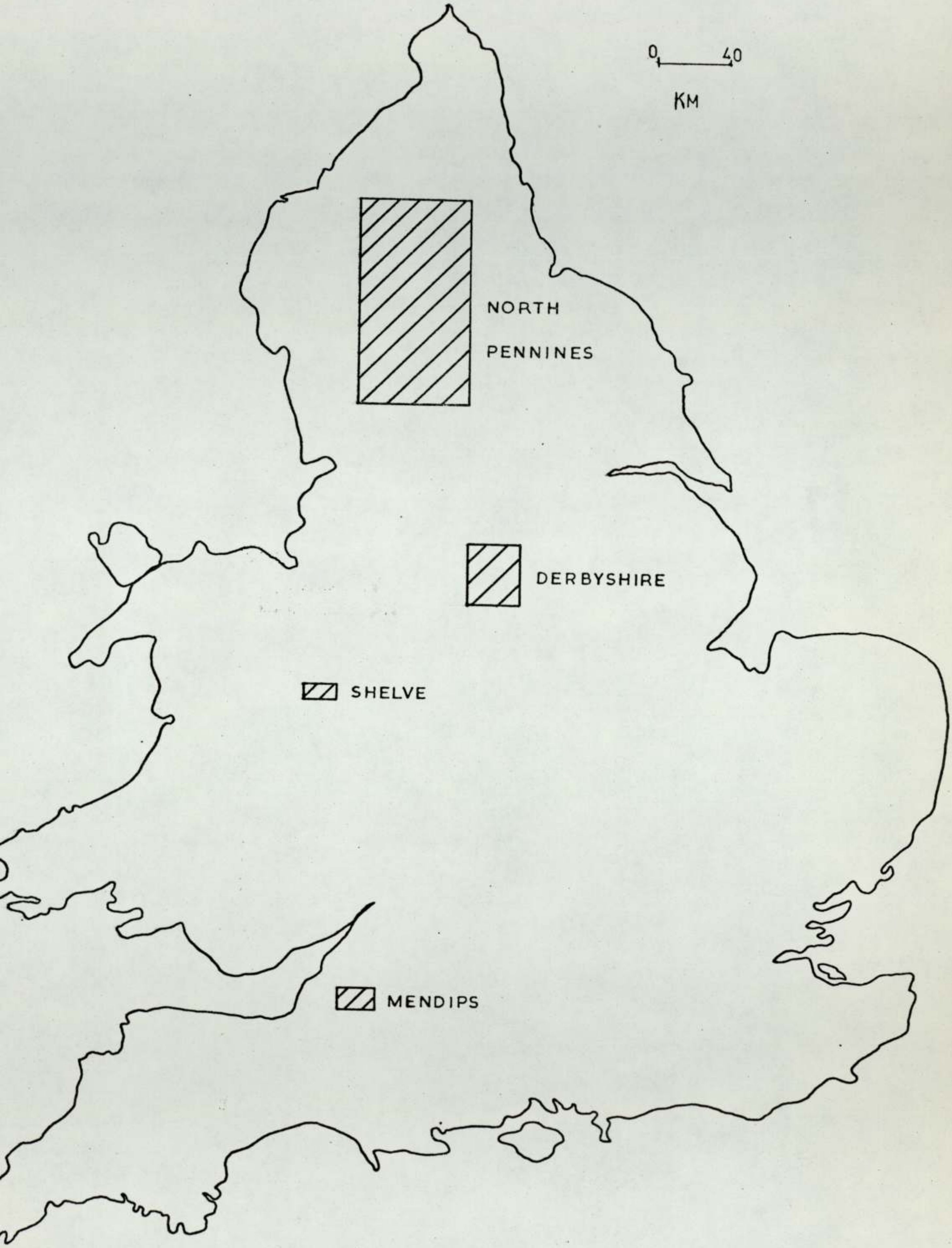


Fig. A. Sketch Map of the locations of the collecting areas.

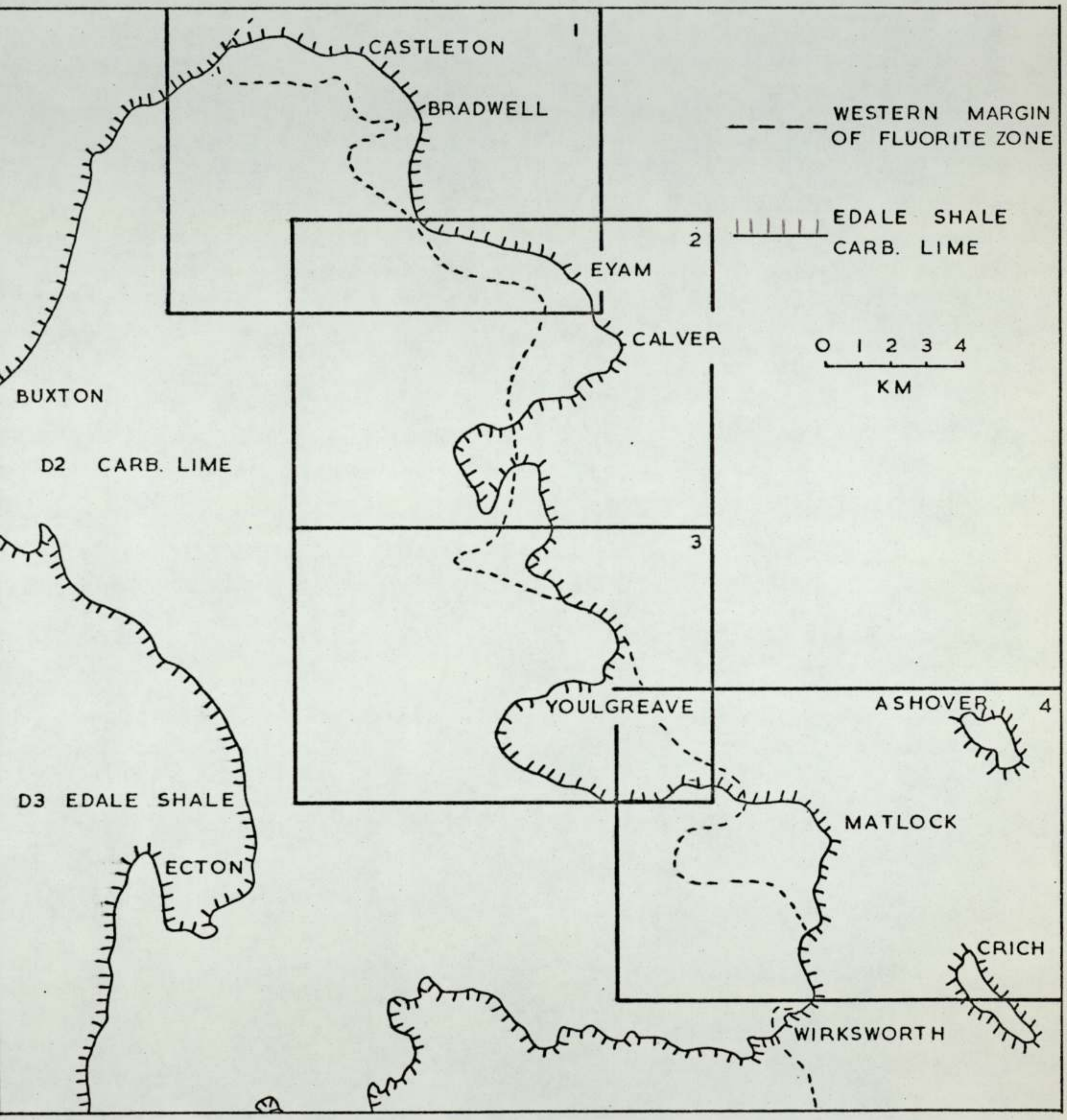


Fig. B. Sketch Map of the Derbyshire Dome showing the boundary of the limestone massif and the western margin of the fluorite zone.

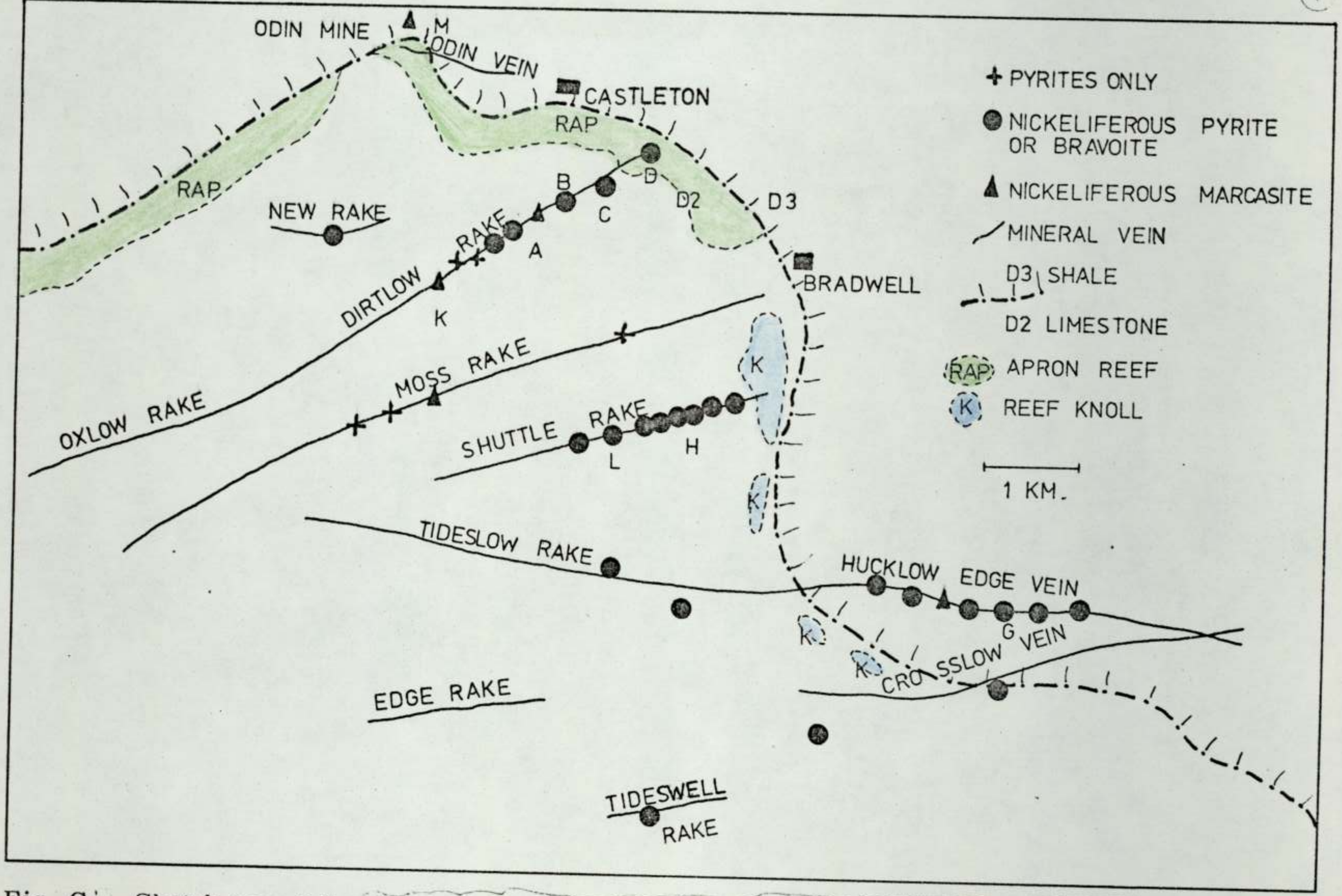


Fig. C$_1$ Sketch map of the Castleton Bradwell area, showing the distribution of the collecting sites.

②

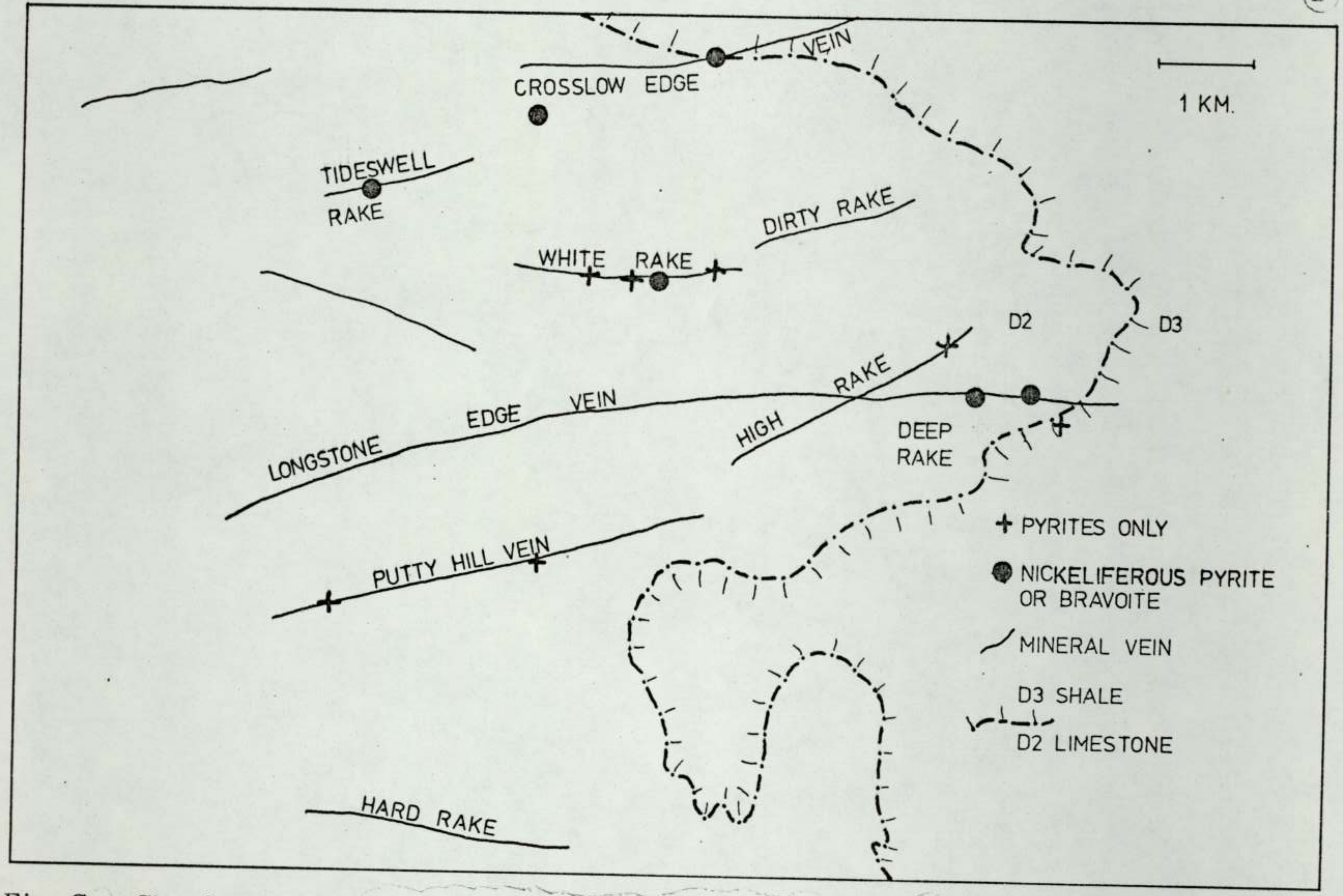


Fig. C_2 Sketch map of the Eyam Calver area showing the distribution of the collecting sites

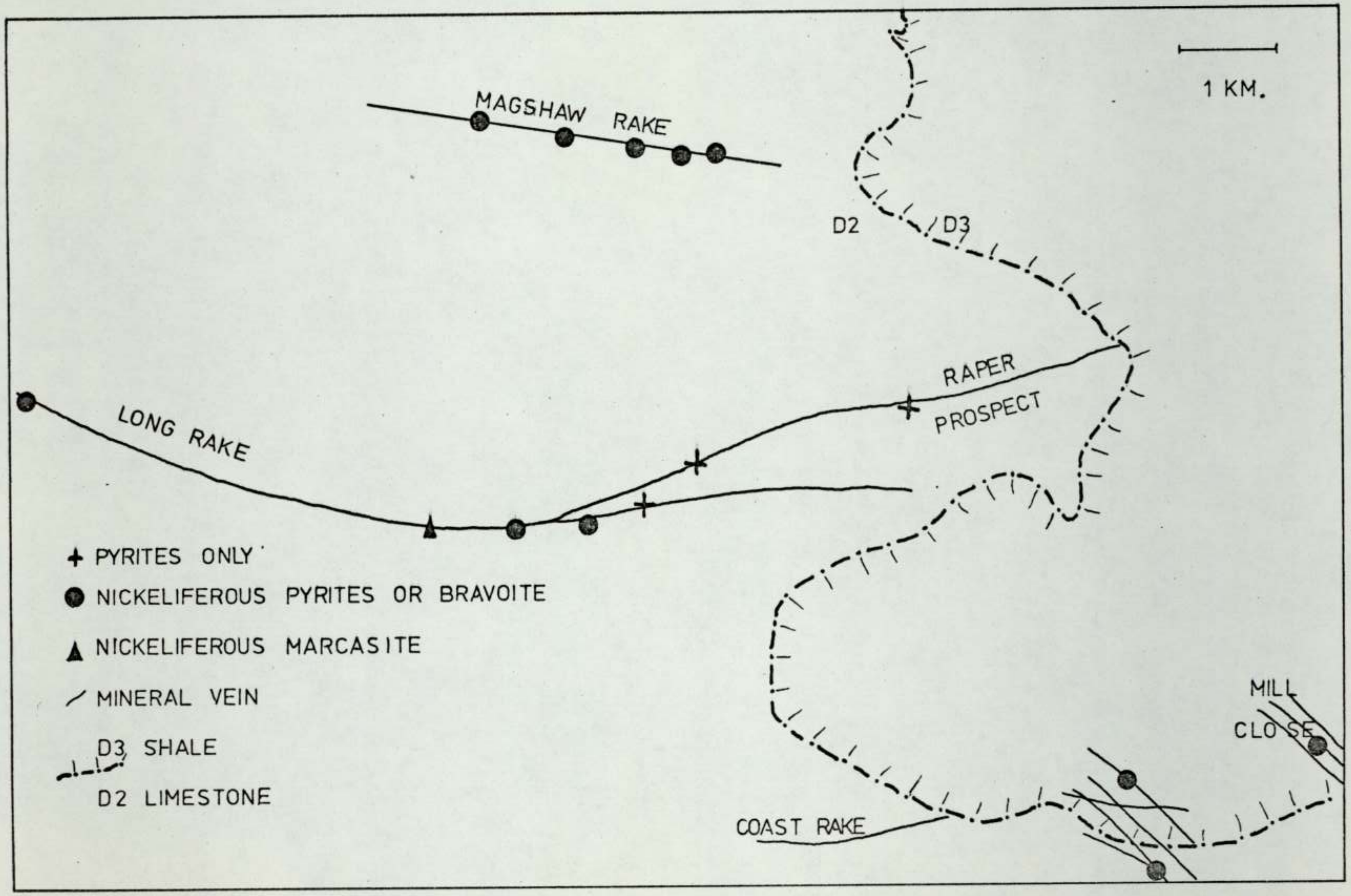


Fig. C3. Sketch map of the Youlgreave area showing the distribution of the collecting sites.

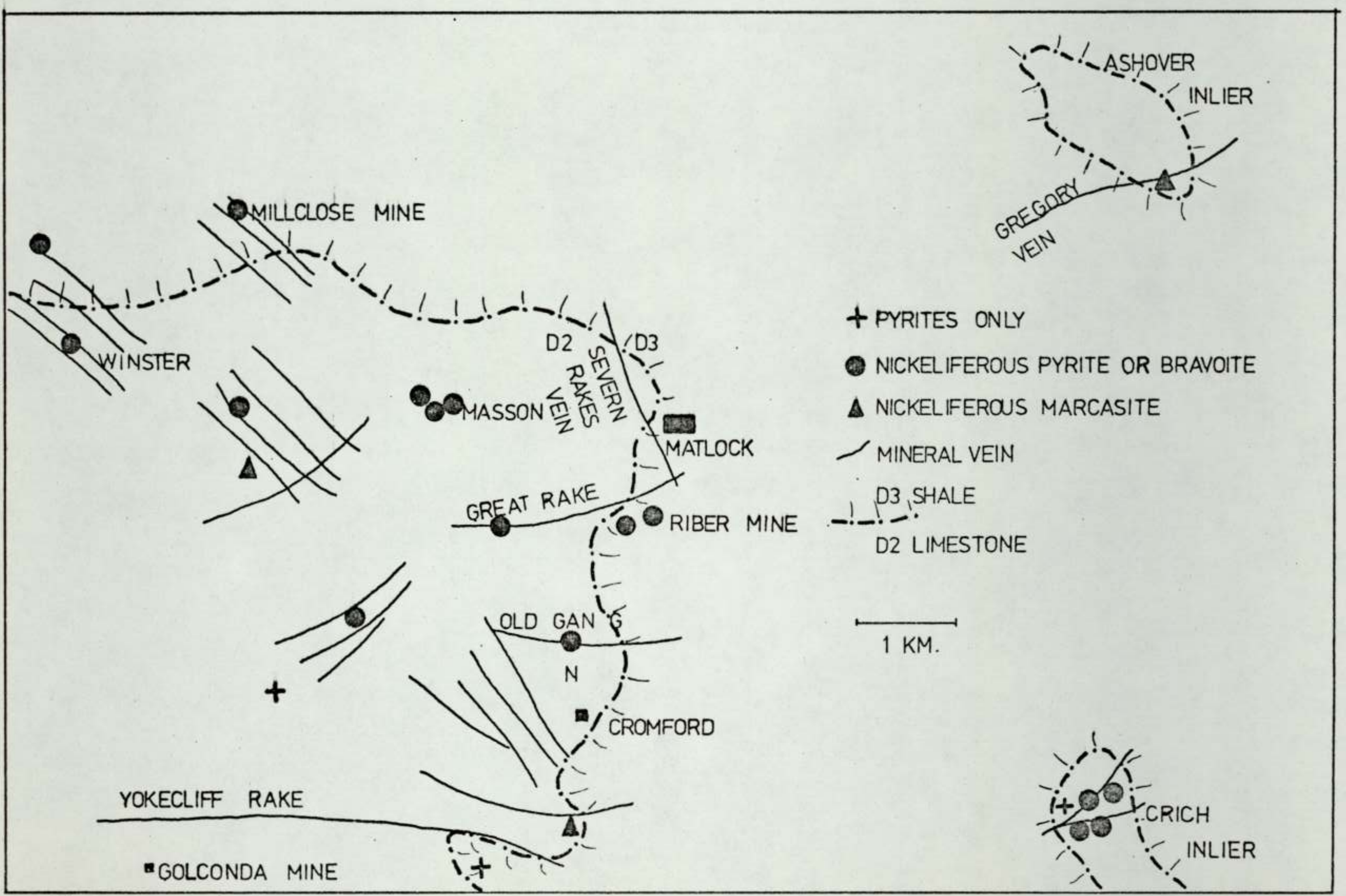


Fig. C4 - Sketch map of the Matlock Cromford area, showing the distribution of the collecting sites

A Description of the Derbyshire Specimens

Name	Ref.	Style	Nickel Species	Remarks.
1 Odin Mine	135837	Void infill	Zoned and unzoned bravoite	Common, unbanded, 50μ, 10μ euhedral to subhedral. Rarely associated with chalcopyrite and bornite.
			Ni. Pyrite	Pink, some faintly zoned. 20μ
			Ni. Marcasite	Associated with some bravoites. Gangue, calcite quartz, barytes.
2 New Rake	128816	Void infill	Zoned bravoite	Common, unbanded, 10μ, rarely clustered. Subhedral to euhedral. Faint brown. Chalcopyrite, rare. Calcite, fluorite.
3 Dirtlow Rake (1)	137813	Replacement	Zoned brown pyrite	Common, banded, 10μ triangular parallel edge fluor crystals. Associated with 10μ galenas.
			Zoned Ni. marcasite	Rare Assemblage in massive flourite.

A Description of the Derbyshire Specimens Continued

Name	Ref	Style	Nickel Species	Remarks
3 Dirtlow Rake (2)	140815	Void infill	Nil	Few chalcopyrite, subhedral galena, covelline, 5μ pyrites, calcite, subsiduary fluorite, barytes.
(3)	142816	Void infill	Nil	1μ pyrites common in calcite, with chalcopyrite, 5μ galena around calcite scalenohedra, banded. Subsiduary fluorite.
(4)	144817	Void infill	Zoned bravoite	Common, banded, 10μ inclusions in alternating bands of calcite and fluor.
(5)	148819	Void infill	unzoned bravoite	Rare, unbanded, 20μ, euhedral, as inclusions in barytes. Few marcasites.
(6)	149820	Void infill	Zoned and unzoned bravoite,	Common unbanded, 15μ, euhedral, inclusions in fluorite, rarely in barytes. Associated with pyrites.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
3 Dirtlow Rake (6) Cont...	149820	Void infill	Zoned marcasite	Rare, 30μ, surrounding anhedral bravoite, as inclusions in fluorite Gangue, blue, sugary fluorite.
(7)	151821	Void infill	Zoned and unzoned bravoite	Common, clustered, brown, purple 10-50μ. Inclusions in calcite and barytes. Associated with pyrites and marcasite. Calcite scalenohedral.
(8)	155822	Void infill	Zoned and unzoned bravoite	Very common, clustered brown, lilac some bizoned, 10-25μ. inclusions in calcite and fluorite. Associated with marcasite.
(9)	158825	Void infill	Zoned and unzoned bravoite	Common, clustered, brown, purple, 10-25μ, inclusions in fluorite and calcite scalenohedra.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
4 Moss Rake (1)	130795	Void infill	Nil	Few unbanded pyrites in calcite.
(2)	133706	Void infill	Nil	As Moss Rake (1) with rare cerrusite.
(3)	138798	Void infill	Zoned bravoites	Rare, banded and clustered 10u, along calcite crystal boundaries.
			Zoned marcasite	Rare, surrounding bravoite in pyrite 120μ. Marcasite crystal zoned in one region side only.
(4)	166805	Void infill	Nil	As Moss Rake (1).
5 Shuttle Rake (1)	152793	Void infill	Zoned bravoites	Common, banded and unbanded, 20μ Alternating bands of galena bravoite/ pyrite, and fluorite. Gangue, calcite and fluorite.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (2)	155795	Replacement See Remarks	Zoned bravoites	Common, unbanded, 20µ. euhedral and anhedral, alterations to goethite common except where inclusions are in fluorite. Associated with pyrite, rare chalcopyrite. 98% fluor, rare calcite and barytes. Relict transparent circular structures 50µ dia. of uncertain origin.
(3)	160796	Replacement	Zoned bravoites	Rare unbanded, 10µ euhedral, associated with rare euhedral 20µ chalcopyrite. Gangue fluorite replacing calcite.
(4)	162797	Undetermined	Zoned bravoites	Common, unbanded 20µ euhedral associated with pyrite, marcasite.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (4) Cont..	162797	Undetermined	Zoned pyrites	Rare, 5µ, pinkish gangue, calcite, fluorite. Calcite replacing fluorite?
(5)	165798	Replacement	Zoned bravoite	Common, unbanded, 3µ, very pale, some with pyrite centres. Bravoites mainly in fluorite. Relict crinoid ossicles, and transparent circular structures of uncertain origin, rarely showing incipient pyritisation.
(6)	166798	Undetermined	Zoned pyrite	Common, unbanded, 20µ, faint brown zoning, associated with normal pyrite and marcasite. Commonly inclusions in scalenohedral calcite. Gangue, calcite, fluorite, little barytes.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (7a)	167799	Void infill	Zoned bravoites	Common, unbanded, 30μ, hexagonal habit. Zoning complicated, esp. as inclusions in fluorite.
			Ni pyrite, zoned	Very rare, very pale brown, 2μ, euhedral inclusions in large (late?) calcites. Gangue, calcite, fluorite.
(7b)	"	Void infill	Zoned bravoite	Common, unbanded 30μ, brown. pentagonal habit, very irregular zoning with multiple re-entrant angles in euhedral crystals occur. Associated with pyrites, marcasite. Gangue, Calcite scalenohedra with rare fluorites on faces.
(8a)	168800	Void infill	Zoned bravoite	Common, banded, purple, 12μ, euhedral to subhedral inclusions in calcite. gangue, fluorite replacing calcite cross-cut by later fluorite.

A Decription of Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
5	Shuttle Rake (8b)	168800	Replacement?	Unzoned bravoite	Rare, unbanded, purple, 5µ euhedral. Associated with sphalerite, and rarely chalcopyrite. Gangue, calcite/fluorite bands.
6	Tideslow Rake (1)	156782	Undetermined	Zoned bravoite	Common, banded, 20µ euhedral, Inclusions in galena. Gangue calcite, rare fluorite.
7	Nr. Tideslow Rake	164776	Undetermined	Unzoned bravoite	Rare, unbanded pale brown 20µ euhedral, inclusions in fluorite. Lines of inclusions along bravoite crystal faces Gangue, fluorite with 25-50% replacement by euhedral quartz 20µ.
8	Tideswell	162756	Undetermined	Zoned bravoite	Rare, unbanded, brown 10µ pentagonal inclusion in fluorite. Associated with pyrite. Gangue calcite, being replaced by fluorite.

A Description of the Derbyshire Specimens Continued

	Name	Ref	Style	Nickel Species	Remarks.
9	Hucklow Edge Vein (1)	186779	Void infill	Zoned bravoite	Very rare, unbanded, 5µ euhedral inclusions in scalenohedral calcite.
	(2)	189778	Void infill	Zoned bravoite	Rare, unbanded purple 5µ euhedral, and common subhedral lilac 20µ, inclusions in fluorite. Associated with pyrite. Gangue, calcite, purple fluorite, barites, quartz. Rare dolomite. Semi-translucent single or multiple bodied structures 5-20µ dia. in fluorite.
	(3)	192777	Void infill	Zoned and unzoned bravoite.	Common, banded, and unbanded 40µ, euhedral. Generally as inclusions in fluorite. Associated with pyrite and marcasite.
				Ni pyrite	Rare, pink, 5µ.

A description of the Derbyshire specimens Contined

	Name	Ref.	Style	Nickel Species	Remarks
9	Hucklow Edge Vein (3) Cont.	192777	Void infill	Ni Marcasite.	Rare, zoned, infrequently associated with framboidal pyrite. Gangue, 90% fluorite, 10% calcite. All sulphides in fluorite.
	(4)	196776	Void infill	Zoned bravoite	Common banded, brown, 20µ associated with pyrite, marcasite, sphalerite. Alternating bands of calcite, fluorite galena, subsiduary barites.
10	Crosslow Vein	196770	Void infill	Zoned bravoite	Rare 20µ and common, banded, purple 6µ subhedral to euhedral, associated with covelline, pyrite, marcasite, in narrow band between galena.
				Ni pyrite	Rare pink.
11	1.6 Km South of Gt. Hucklow	178765	Void infill	Zoned bravoite	Rare unbanded, 15µ euhedral associated with pyrites, marcasite, sphalerite. Gangue fluorite, calcite, minor barite.

A Description of the Derbyshire Specimens Continued

MAP	Name	Ref.	Style	Nickel Species	Remarks
12	White Rake (1)	184748	Void infill	Nil	Massive calcite, pyrites, 3μ along fractures.
	(2)	189748	Void infill	Nil	Massive calcite, pyrites marcasite 300μ, along fractures in calcite.
	(3)	192748	Void infill	Zoned bravoite	Rare, unbanded, 20μ euhedral associated with pyrite as inclusions in calcite and fluorite in calcite/fluorite breccia.
	(4)	198749	Void infill	Nil	Rare pyrites 10μ euhedral in fluorite/calcite breccia recemented with barites
13	High Rake	222743	Replacement?	Nil	Marcasite 2μ enclosed in pyrite, gangue 80% fluorite, 18% calcite, 2% quartz. Many semi-transparent structures in calcite, rarely mineralised by framboidal pyrite.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks.
14	Deep Rake (1)	225735	Void infill seen in situ	Zoned and unzoned bravoites	Common banded, 50µ euhedral and 5µ euhedral inclusions some with pyrite centres in alternating fluorite/galena/calcite bands associated with covelline. Common unbanded 10µ bravoites in calcite scalenohedra.
	(2)	229735	Void infill	Zoned and unzoned bravoites	Common, banded, violet streaked, 50µ, euhedral, habit change in crystals common. Inclusions in fluorite. Associated with pyrites, chalcopyrites Gangue 100% fluorite.
15	White Coe Mine	233734	Void infill	Nil	Calcite cleavage flake. Pyrite, marcasite, chalcopyrite. (3 specimens examined, nil result).
16	Putty Hill Vein (1)	178718	Void infill?	Nil	Fluorite with unbanded chalcopyrite, pyrite and marcasite in clusters. Chalcopyrite rarely in galena. Fluorite exhibits sugary texture.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
16	Putty Hill Vein (2)	158713	Void infill	Nil	Similar to Putty Hill vein (1) overleaf.
17	Magpie Mine (1)	173681	Void infill	Zoned bravoite	Common banded purple 150μ euhedral part goethitised inclusions in calcite. Associated with pyrite, marcasite sphalerite. Alternating bands of calcite pyrite/bravoite, galena, Gangue 100% calcite.
	(2)	"	Void infill	Zoned bravoite	As (1) above. Pyrite wedges in bravoite preferentially goethitised.
	(3)	"	Void infill	Zoned bravoite	As (1) above. Host rock limestone.
	(4)	"	Replacement	Zoned bravoite	Rare unbanded, 10μ, associated with sphalerite and framboidal pyrite, some framboids coelescing. Gangue, re-crystallised micrite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
18 Magshaw Rake (1)	183680	Undetermined	Zoned and unzoned	Common, unbanded, lilac 10µ pentagonal showing habit change in pyrite Associated with pyrite as inclusions in barites. Gangue fluorite, barytes barytes replacing fluorite. All sulphides in barytes.
(2)	189678	Void infill	Unzoned bravoite	Rare, unbanded, pale, 15µ on galena/fluorite boundary, rarely in galena. Alternating bands of fluorite and galena.
(3)	193677	Void infill	Zoned and unzoned bravoite	Common, unbanded, multi-coloured, multi-zoned 60µ inclusions in fluorite. Associated with pyrite, goethite, Goethitised bravoite darker blue than goethitised pyrite. Gangue fluorite and calcite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks.
18 Magshaw Rake (4)	19677	Void infill	Zoned and unzoned bravoite	Rare, banded, 10μ associated with marcasite and pyrite as alternating bands in fluorite gangue.
19 Long Rake (1)	127653	Replacement	Unzoned bravoite	Very rare, unbanded, lilac 5μ, in pyrite. Gangue fluorite, with replaced relict coral containing bravoite. Cherty limestone replacement.
(2a)	167640	Undetermined	Zoned bravoite	Common banded, 20μ euhedral, associated with pyrite, marcasite. Chalcopyrite.
			Ni marcasite.	Very rare, 2μ, showing optical continuity with bravoite. Gangue, calcite.
(2b)	"	Void infill?	Nil	2μ-50μ pyrite, rare quartz inclusions, and euhedral to subhedral quartz gangue containing pyrite inclusions, Milky neomorphic spar.

A. Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks.
19 Long Rake (3)	176640	Void infill?	Ni pyrite	Rare, unzoned, pink 50μ associated with pyrite and marcasite, in calcite scalenohedra intersected by later quartz vein of subhedral crystals.
(4)	183640	Void infill?	Unzoned bravoite	Rare, brown, 10μ anhedral associated with chalcopyrite, pyrite, marcasite, in calcite scalenohedra.
Youlgrave Mine on Long Rake (5)	188643	Void infill?	Nil	Fluorite inclusions in galena in calcite scalenohedra.
Long Rake (6)	195645	Void infill	Nil	Pyrite 0.8μ rare associated with 30μ galena in massive calcite.
20 Raper fluorspa Opencast (1)	216652	Replacement	Nil	Massive fluorite with chert (hand specimen) Rare pyrite 10μ.
(2)	"	Replacement	Nil	Sugary fluorite, goethite.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
21	Portaway Mine	234614	Void infill	Zoned and unzoned Bravoite	Common repetitive banding purple 5μ-30μ, euhedral to subhedral, associated with alternating bands of pyrite and marcasite with rare chalcopyrite as inclusions in calcite flake.
				Ni pyrite	Rare pink pyrite, 10μ
				Ni marcasite?	Rare marcasites show traces of zoning. Five sections all very similar.
22	Near Winster	Unknown not in situ	Void infill	Zoned and unzoned	Common banded and unbanded, 5μ-150μ euhedral to subhedral, multi-habit associted with pyrite and marcasite and rare chalcopyrite.
				Ni pyrite	Pink pyrite, adjacent to bravoites.
				Ni marcasite	Rare, generally partially or completely enclosing bravoite/pyrite. All as inclusions in calcite flake. Four sections, all very similar.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
23 Shaft at Mill Close Mine (a)	258617	Replacement	Nil	Pyrite, 10μ-100μ euhedral to subhedral as inclusions in calcite, and a vermiform incrustations around relict titanomagnetite reticulated structures in calcite. Rare pyrrhotite, haematite, rutile (after ilmenite). Rare fluorite and barytes. Later pyrite in fractures. A replaced lava.
(b)	"	Void infill	Zoned and unzoned bravoite	Rare, banded, 15μ associated with alternating bands of chalcopyrite and minor pyrite with rare marcasite as inclusions in calcite flake. Four specimens all similar.
24 Slack Mine	258597	Undetermined Void infill?	Zoned and unzoned bravoite	Common, banded, lilac and purple, below 10μ and between 50μ-75μ euhedral to anhedral, rarely interdigitating with pyrite, associated with rare chalcopyrite, along calcite crystal faces. Gangue 100% calcite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
25 Oxclose Mine (a)	275599	Replacement	Zoned bravoite	Common, unbanded, purple, 10μ-40μ zoning concentric, rarely radial. Associated with pyrite, marcasite, as inclusions in fluorite. Gangue 80% fluorite, 20% calcite Sulphides mainly in fluorite.
(b)	"	Void infill	Zoned bravoite	Rare, unbanded, 20μ associated with pyrite and chalcopyrite in calcite flake.
26 Jughole (a)	279598	Replacement	Zoned bravoite	Rare unbanded, 20μ associated with pyrite. marcasite. Gangue, calcite, dolomite, fluorite.
(b)	"	Void infill	Zoned and unzoned bravoite	Common, euhedral unbanded 10μ, associated with pyrite and marcasite as inclusions in calcite flake.
27 Masson	284592	Replacement	Zoned and unzoned bravoite	Rare unbanded, brown, 20μ associated with pyrite in fluorite gangue.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks.
28	Bonsall Moor	258592	Undetermined	Zoned bravoite	Rare, unbanded, brown, 4μ associated with pyrite in calcite with minor fluorite, and quartz porphryblasts.
				Ni marcasite	Rare, 5μ, faint zoning.
29	Low Mine (a)	283586	Void infill	Zoned bravoite	Common unbanded, 10μ purple associated with pyrite, marcasite and chalcopyrite 5μ and rarely 40μ, in fluorite gangue.
				Ni pyrite?	Rare pinkish unzoned pyrite species in fluorite.
	(b)	"	Void infill	Zoned and unzoned bravoite	Common, banded, 30μ euhedra to anhedral, associted with alternating bands of galenz and fluorite/calcite. Minor Chalcopyrite adjacent to galena.
				Ni pyrite?	Pink (?) pyrite, 30μ.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
30 Riber Mine	299588	Void infill	Zoned bravoite	Rare, unbanded, euhedral and anhedral 25µ associated with pyrite, marcasite, sphalerite, rarely enclosed by sphalerite, in massive, fractured calcite infilled with quartz.
31 Tip Nr Riber Mine (a)	296584	Void infill	Zoned and unzoned bravoite	Rare, unbanded, 5µ-100µ inclusions in calcite, rarely replacing cerrusite Associated with pyrite and chalcopyrite.
			Ni pyrite, unzoned	Rare, unbanded, pale pink 8µ-20µ. Gangue calcite, fluorite, rare euhedral quartz.
(b)	"	Void infill	Zoned bravoite	Common, unbanded, brown, 5-10µ, euhedral interdigitating with pyrite, commonly ringing galena, associated with chalcopyrite in a fluorite/calcite matrix.
32 Slaley	268576	Undetermined replacement?	Nil	Rare marcasite in brecciated fluorite, fluorite being replaced by calcite, later,

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
	Slaley Cont.				marcasite-bearing quartz cross-cutting both earlier phases.
33	Old Gang Vein	291574	Replacement?	Unzoned bravoite	Rare, unbanded brown, 20μ interdigitating with pyrite, Gangue, recrystallised micrite, minor fluorite.
34	Near Cromford	292558	Void infill	Unzoned bravoite	Rare, unbanded, 5μ euhedral associated with sphalerite pyrite, marcasite, and barite replacing minor fluorite.
				Ni. marcasite ?	Anomalous pink, low bi refringence, very rare.
35	Middleton	282552	Replacement	Nil	Marcasite common, 50μ altering to goethite Rare chalcopyrite, covelline. Matrix, recrystallised limestone with barites replacing shell fragments and crinoid ossicles.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
36 Ashover (1)	351621	Undetermined	Zoned and unzoned bravoite	Common, banded, lilac, 50µ euhedral, inclusions in fluorite.
			Ni marcasite zoned.	Rare, associated with bravoite. Gangue fluorite, minor barites.
(2)	"	Replacement	Nil	Pyrites, marcasite, galena, malachite, cuprite, covelline, recrystallised micrite.
37 Crich (1)	343559	Void infill	Zoned and unzoned bravoite	Common, grey/brown, unzoned in fluorite, lilac, zoned in barites, altered to goethite in barites only. Alternating bands of barite, fluorite, galena, fluorite replacing galena?
(2)	345560	Void infill	Zoned bravoite	Common, pale lilac, unbanded, 10µ anhedral associted with 150µ pyrite and sphalerite in 100% calcite matrix.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
37 Crich (3)	340558	Replacement	Nil	Common 150-300µ euhedral pyrite, galena. covelline, gangue, recrystallised limestone, fluorite replacing fossil debris, minor barites laths.
(4)	342556	Void infill	Zoned bravoite	Common, unbanded, 40µ, euhedral, inclusions in barite and fluorite. Bravoite in barites much goethitised. Associated with pyrite. Gangue, alternating bands of barite and fluorite.
(5)	344556	Undetermined	Zoned bravoites	Very common, 80µ euhedral inclusions in fluorite and barite. Associated with chalcopyrite, covelline, pyrite, Gangue black fluorite, interpenetrated by barites laths. Bravoite much altered to goethite in barites.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
38 Ecton (1)	095577	Void infill	Zoned bravoite	Rare, unbanded, 10μ anhedral inclusions in calcite associated with chalcopyrite. pyrite, marcasite and sphalarite.
(2)	096585	Replacement?	Nil	Pyrite, chalcopyrite, galena, sphalerite, covelline, chalcocene, in calcite with rare euhedral quartz, and pyrite framboids.
Ecton (3)	"	replacement?	Nil	As (2) above, but including barites.
(4)	"	replacement?	Nil	Pyrite, chalcopyrite, marcasite, sphalerite in dolomite gangue.
(5)	"	replacement	Ni pyrite	Rare, faintly zoned pyrite, pink, or different habit to normal associated pyrite. Marcasite, chalcopyrite, galena, sphalerite. Gangue; alternating bands of creamy and brown dolomite with rare euhedral quartz.

4.3 Description of the Northern Pennine orefield.

The Northern Pennine orefield is divided structurally into two rigid blocks, the Alston block to the north and the Askrigg block to the south underlain by Devonian granites, (Dunham 1974), which are separated by the Stainmore syncline. To the north the region is bounded by the Northumbrian trough, and to the west and south by the Pennine, Dent and Craven fault systems. To the east, the mineralised Lower Carboniferous of the stable blocks plunges beneath the Carboniferous and Permian rock higher in the succession. The Carboniferous deposits over the rigid blocks are thin and may be regarded as having accumulated in a shelf area, those of the Alston block being primarily of typically Yoredalian facies of the Lower Carboniferous, and those of the Askrigg block having a tendency towards showing rhythmic sedimentation in the higher horizons, but dominated by the D_1 and S_2 Great Scar Limestone at the base of the succession.

The major quartz dolerite igneous intrusion of the Whin Sill is present in the Alston block, and is believed to be the source of silica and iron necessary for the silicification and ankeritisation of much of the limestone. In places the Whin is altered to the "White Whin", a rock composed of secondary carbonates, clay minerals, anatase, residual quartz and apatite, (Wager, 1929; Smythe, 1930). formed by the removal of iron, magnesium, silica, and soda, and addition of potash and carbonates. The fluids responsible for this metasomatism are considered to represent the first phase of mineralisation, introducing ankerite, chalybite and silica to the limestone, the second stage of mineralisation introduced sulphides, fluorite, barite and carbonates, and a late phase is characterised by the deposition of calcite.

In the North Pennine orefield, ore occurs either in mineralised fissures seldom deviating more than 20° from the vertical, or as metasomatic flats, owing their form to replacement of flat-lying favourable beds of limestone. The orefield is remarkable for the perfect conjugate pattern of vein fissures it exhibits, these representing mineralised faults. Generally faults having a displacement greater than 12 metres are un-mineralised, being filled and rendered unsuitable by shale gouge dragged in, but those less than this width in hard limestones, dolerite, and sandstones that remained open to the mineralising fluids are ore-bearing, with the greatest concentrations of mineralisation in and near the Great Limestone at the bottom of the Upper Limestone Group. In general, veins in the limestone are wider that those in the sandstone due to widening during mineralisation by solution and metasomatism. (Dunham 1949).

The minerals of the Askrigg block deposits include fluorite, galena, sphalerite, quartz, chalybite, ankerite barite and calcite, the distribution of fluorite and barite follows a crude zoning pattern as shown on map Fig. D. The innermost fluorite zone centred around St. John's Chapel, and Weardale, yields only minor quantities of sulphides, except for a unique occurrence of payable chalcopyrite. Quartz is generally most abundant in the innermost parts of the fluorite zone. Towards the periphery of the fluorite zone galena becomes important, with sphalerite appearing in places. In certain areas, a zone whose predominant mineral is barite follows next, but in other areas intermediate zones where the predominant minerals are galena, or galena and sphalerite with or without witherite are significant. (Dunham 1934, 1937.) Within the fluorite zone, the purple or green fluorite gives way to amber as the edge of the zone is approached, and, unlike Derbyshire, where the gangue mineral zoning describes only the predominant gangue mineral, visible barite is absent in the fluorite zone, and similarly, fluorite is not found in the barite zone.

The typical veins of the area exhibit a banded texture, paralleling the vein walls. The bands normally consist of pure or nearly pure minerals, with crystal faces developed on that side of the band nearest the centre of the vein, indicating that the veins were filled from the walls inwards. Bands of matrix material, fluorite, quartz or barite are generally continuous but the sulphide bands may be broken. Post-mineralisation movements are shown by slickensliding accompanied by narrow belts of brecciated vein material, but are seldom if ever accompanied or followed by the deposition of new primary minerals. The veins exhibit many repetition of bands, followed by several minor phases of reopening. Under these circumstances no general "order of deposition" of minerals can be acceptable. Dunham (1934), has however showed that marcasite and chalcopyrite were generally "early" sulphides, and that the crystallisation of fluorite was completed before the deposition of barite in the few instances where these minerals are associated in the field.

The Great Sulphur Vein, more properly described as a lode, is unique among the veins of the orefield. Its total length is 15 Km as shown on map Fig D. Its greatest width is 350 metres decreasing downwards to 33 metres where seen in the valley bottoms, and from structural evidence, it is known to post-date the Whin Sill. (Thompson 1933). The dominant mineral introduced is quartz, mainly present as a replacement of limestone, shale and sandstone within the lode, but making a few shoots of massive vein quartz which stand out as ribs. In the higher regions it is almost completely unmineralised but at the lowest exposed horizon, that of the Tynebottom Limestone there is what may be presumed to be a continuous zone of sulphides of tabular form containing pyrrhotite, pyrite and marcasite with in places a little chalcopyrite. A sequence of replacement is seen, pyrite replacing earlier pyrrhotite, marcasite replacing both minerals. Polished sections reveal that the tabular form of the sulphides is due to replacement of small slabs of argillaceous limestone derived from above which is considered to have collapsed during the metasomatism of the lower more calcitic beds. Structural arguments have been advanced to show that the Great Sulphur Vein is of a younger age that the remainder of the Pennine Veins, (Dunham 1934), yet it both shifts and is shifted by Sir John's Vein, (a normal mineralised vein) so the problem of its age remains open for the present.

The Askrigg block, consisting of Arkengarthdale, Swaledale, Wharfdale, Wensleydale and Midderdale is patchily mineralised. In Swaledale, Arkengarthdale and Wensleydale the rocks are of the rhythmic Yoredale facies, which thin towards the south at the same time the sandstones and shales decrease in significance with a marked increase in thickness of limestones until at Grassington a predominantly limestone sequence represents the D_2 subzone, and at Greenhow, the Great Scar limestone, (D_1 and S_2), or its lateral equivalent prevails. The southern margin of the mineral field lies in the vicinity of the Craven fault system, which also marks the strucutral change from 'block' conditions (Hudson 1924), to the basin of Bowland Shale and thick Millstone Grit sedimentation.

The limestones of the southern part of the Askrigg block are noted for the abundant and luxuriant growth of corals and crinoids, (Rayner 1946), probably induced by their favourable position in the shallow and clear waters immediately bordering the basin. (Ramsbottom, 1974).

The mineralisation is of veins in fissures, with the rare 'flat' and 'pipe' in the Greenhow area. The gangue minerals are fluorite, calcite, quartz and barytes, with galena, and fluorite occurring in strictly localised occurrences as shown on the map. Having regard to the well-defined central fluorite zone in the Alston Block (Dunham 1934), these areas may be considered to be adjacent to feeding centres. The most productive galena deposits occur in or marginal to these areas, as in the Alston Block.

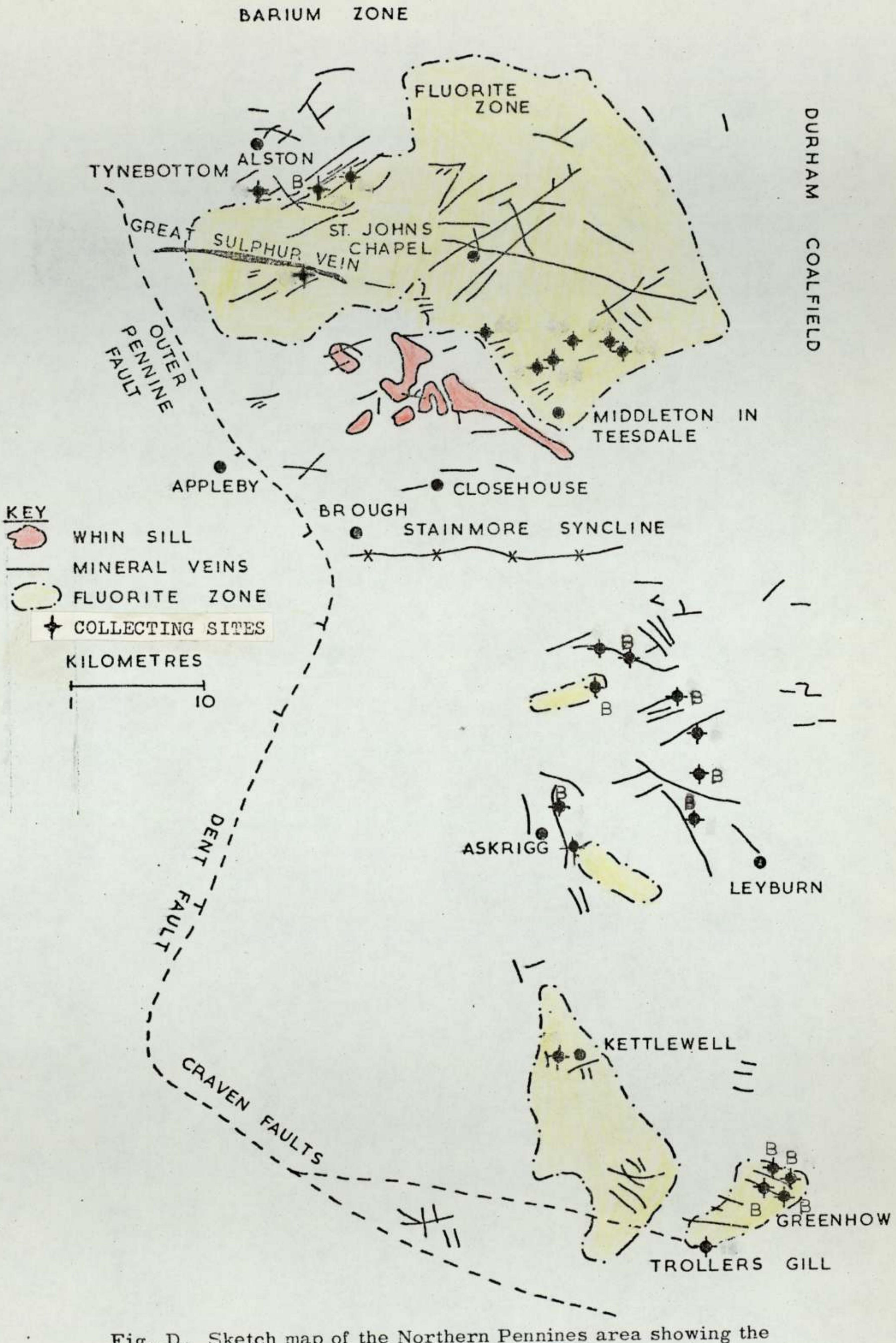


Fig. D. Sketch map of the Northern Pennines area showing the distribution of the collecting sites. B. indicates Bravoite.

A Description of the North Pennine Specimens. A. Askrigg Block.

Name	Ref.	Style	Nickel Species	Remarks
1 Swaledale				
Warton Hall	955905	Replacement	Nil	Pyrite, two generations, euhedral crystals of coelescing framboids in micrite, and later, large non framboidal pyrite in vein-filling calcite. Smithsonite. Gangue, recrystallised limestone, relict crinoids, rare euhedral quartz.
2 Redmire Scar	059931	Void infill	Zoned bravoite	Common, banded, brown, 50μ associated with pyrite, marcasite, sphalerite, as inclusions in barites, rarely in fluorite. Alternating bands of fluorite barites, galena. Bravoite frequently follows barite/fluorite boundaries.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
3	Summerlodge Moor (a)	946944	Replacement	Unzoned bravoite	Rare, unbanded, pale brown smudgy 10μ, anhedral, associated with very rare pyrite and marcasite. Gangue, brecciated dolomite.
	Summerlodge Moor (b)	946944	Replacement	Ni. pyrite	Rare, very pale lilac, pyrite in calcite. Gangue, calcite re-cemented limestone breccia.
4	High Faggergill	989062	Undetermined	Nil	Massive marcasite bands replaced by hematite. Marcasite rarely radical.
5	Langthwaite (a)	980030	Undetermined	Zoned and unzoned bravoite	Common unzoned unbanded lilac 15μ euhedral inclusions in barites, rarely in fluorite then zoned. Very pale lilac, 3μ in galena. Associated with rare chalcopyrite, pyrite, anglesite. Gangue, barites laths in fluorite.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
5	Langthwaite (b)	980030	Undetermined	Unzoned bravoite	Extremely rare brown, unbanded, 5µ in barites. Alternating bands galena/barites. Galena framboid. Gangue 100% barites.
6	Copperthwaite Mine	063005	Undetermined	Zoned bravoite	Common unbanded brown 50µ euhedral, inclusions in barites, associated with pyrites, marcasite.
				Ni. marcasite	Rare marcasites show possible zoning. Gangue; fluorite and barites.
7	Hurst	045023	Undetermined	Zoned bravoite	Common, unbanded, brown, 15µ, subhedral, as inclusions in fluorite. Rare bravoite in fluorite in galena. Gangue, barites and fluorite.
8	Greenhow Hill (a)	108640	Undetermined	Unzoned bravoite	Rare, lilac, unbanded, 5µ inclusions in fluorite associated with pyrites in barites/fluorite gangue.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
8	Greenhow Hill (b)	108640	Undetermined	Unzoned bravoite	Rare, brown, unbanded, 5μ inclusions in fluorite, associated with 20μ euhedral pyrite in brecciated flourite with later fluorite cementing.
	Greenhow Hill (c)	108636	Undetermined	Unzoned bravoite	Rare pale lilac, unbanded, 5μ associated with 100μ pyrites and rare marcasites,in barites with subordinate fluorite gangue.
	Greenhow Hill (d)	108636	Undetermined	Zoned and unzoned bravoite	Rare, pale lilac, 10μ, unbanded, associated with pyrite and marcasite, as inclusions in barite gangue.
	Greenhow Hill (e)	108636	Replacement	Nil	Pyrite, common, euhedral, 5μ associated with rare anhedral chalcopyrite, 5μ, in a calcite matrix with fossil debris and quartz porphryblasts.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
8	Greenhow Hill (f)	108636	Replacement	Nil	Rare, 2μ pyrites, euhedral associated with galena 100μ, in calcite gangue.
9	Trollers Gill	066621	Undetermined	Nil	Rare 5μ pyrites in fluorite gangue.

A Description of the North Pennine Specimens, B.Alston Block.

	Name	Ref.	Style	Nickel Species	Remarks
	Nent and South Tyne.				
1	Nenthead (a)	790436	Void infill and replacement	Zoned bravoite	Rare, unbanded, brown, 5μ inclusions in quartz around limestone fragments. Associated with 100μ chalcopyrite. Gangue, quartz, ankerite, chalcedony.
	Nenthead (b)	790436	Undetermined Replacement	Ni. pyrite	Common, unbanded, zoning concentric, purple, very faint and fine, 10μ, euhedral, inclusions in quartz. Associated with chalcopyrite, pyrite, in quartz gangue with minor barites.
	Nenthead	790436	Void infill	Nil	Pyrite, 10μ euhedral, chalcopyrite, galena, sphalerite around chalcopyrite. Quartz inclusions in sulphides common. Gangue, quartz, chalcedony barites, around limestone breccia. Later quartz

A Description of the North Pennine Specimens, B. Continued.

Name	Ref.	Style	Nickel Species	Remarks
				replacing galena.
2 Great Sulphur Vein (a)	739381	Replacement	Nil	Chalcopyrite, euhedral; chalcocene, covelline, in quartz matrix.
(b)	739381	Replacement	Ni. pyrite	Pyrite, 1cm., with marcasite inclusion, galena with pyrite inclusion. Rare pyrite, 10μ with possible very faint zoning. Gangue, quartz.
3 Garrigill (a)		Replacement	Nil	Arsenopyrite with minor euhedral pyrite 10μ, gangue ankerite, calcite quartz.
(b)		Replacement	Nil	As (a) above.
(c)		Replacement	Nil	Chalcopyrite, pyrite, euhedral; gangue, replacing ankerite.

A Description of the North Pennine Specimens, B. Continued.

	Name	Ref.	Style	Nickel Species	Remarks
	Teesdale.				
4	Newbiggin Common Lodgesike-Manorgill Vein 6.5Km	903314	Undetermined Mineralised shatterbelt with replacement.	Nil	Sphalerite, galena, goethite in fluorite matrix.
5	Coldberry	942290	Void infill	Nil	Galena, graphite, pyrite of two generations, framboidal in limestone breccia pieces; late in quartz matrix. Gangue; ankeritic limestone breccia, quartz.
6	Lodgesike Mine	955293	Void infill	Nil	Chalcopyrite, 40µ euhedral; sphalerite, galena, in shattered quartz matrix around siliceous breccia containing framboidal pyrite and 5µ marcasite.

A Description of the North Pennine Specimens, B. Continued

Name	Ref.	Style	Nickel Species	Remarks
7 Eggleshope Mine (1)	977307	Void infill	Nil	Pyrite, euhedral 120μ; chalcopyrite euhedral 100μ. Galena, containing and contains chalcopyrite. Gangue, quartz, cemented siliceous breccia.
(2)	997308	Void infill	Nil	Coelescing framboidal pyrite in ankerite breccia, cemented by sphalerite-bearing quartz.
(3)	013308	Void infill	Nil	Framboidal pyrite in shale breccia cemented by quartz bearing pyrite, sphalerite and galena.

4.4 Description of the Central Mendip lead-zinc orefield.

The Central Mendip area is included in the Wells Sheet (280) of the 1" to the mile Geological Survey Maps. (New Series).

The geology consists of two main elements, a relatively complex basement of upper Palaeozoic rocks, and a strongly unconformable cover of gently folded lower Mesozoic rocks. (Welch 1929).

The ore-bearing rocks are the limestone facies of the Carboniferous Limestone Series and the massive facies of the Dolomitic Conglomerate (Keuper in age). The limestones are described by Green (1958) and Green and Welch (1965), and are of the order of 800m thick.

The Dolomitic Conglomerate is typically a breccia or conglomerate largely composed of fragments of Carboniferous Limestone with some scattered Upper Palaeozoic sandstone and quartzite. The matrix varies from a marl in the finer grained varieties to a calcareous rather angular gravel in the coarsest varieties. The Conglomerate has a variable thickness and has been proved to over 120m.

The main structures in the Palaeozoic rocks, described by Welch (1929), are three en-echelon periclines aligned east-west, and contemporary faults and thrusts. Folding had ceased by Mesozoic times, and a landscape of great relief was buried by the Dolomitic Conglomerate and subsequently Keuper Marl. (See Map Fig. F)

The controlling factor in ore deposition was local structure rather than lithology. The whole of the limestone and conglomerate are mineralised, especially adjacent to the faults and on the flanks of the periclines, which are in places overturned.

Examination of the debris thrown out from old workings shows the dominant gangue mineral is calcite, usually coarsely crystalline and milky white or red and yellow stained. It is sometimes banded, sometimes veined with barite. Fluorspar is present as very rare traces. Schnellman and Wilson (1947), have suggested the spatial distribution of gangue minerals corresponds to a rough temperature zoning, in order of decreasing temperature, fluorite, barite, calcite, and it is noteworthy that in the Mendips, the strongest mineralised zone contains abundant barite, whilst peripheral to this, barite is unknown in the calcite.

The galena is widespread, both as specks and small crystals scattered in the calcite and barite, and as occasional nodules of many kilograms (Green 1958). Trace quantities of sphalerite are widespread, the main ore of zinc is calamine (smithsonite $ZnCO_3$). Much very siliceous 'brown haematite' is present, whether it is much later or an oxidation product of pyrites contemporary with the other sulphide mineralisation, is unknown. Kingsbury (1941), gives a detailed account of mineral localities on the Mendip Hills, many of these were visited, but in the greatest majority agricultural and natural processes have completely covered and rendered non-locatable the sites he records. It was with the greatest difficulty that any mineralisation was found; all mining activities having ceased at the beginning of the century, and no re-working having taken place subsequently to expose the material. Calcite pieces were fairly widespread in ploughed fields, and especially so in one recently shown to be the site of Roman smelting operations, but none revealed any trace of metalliferous mineralisation. Because of the problems of finding suitable material the number of samples studied is small.

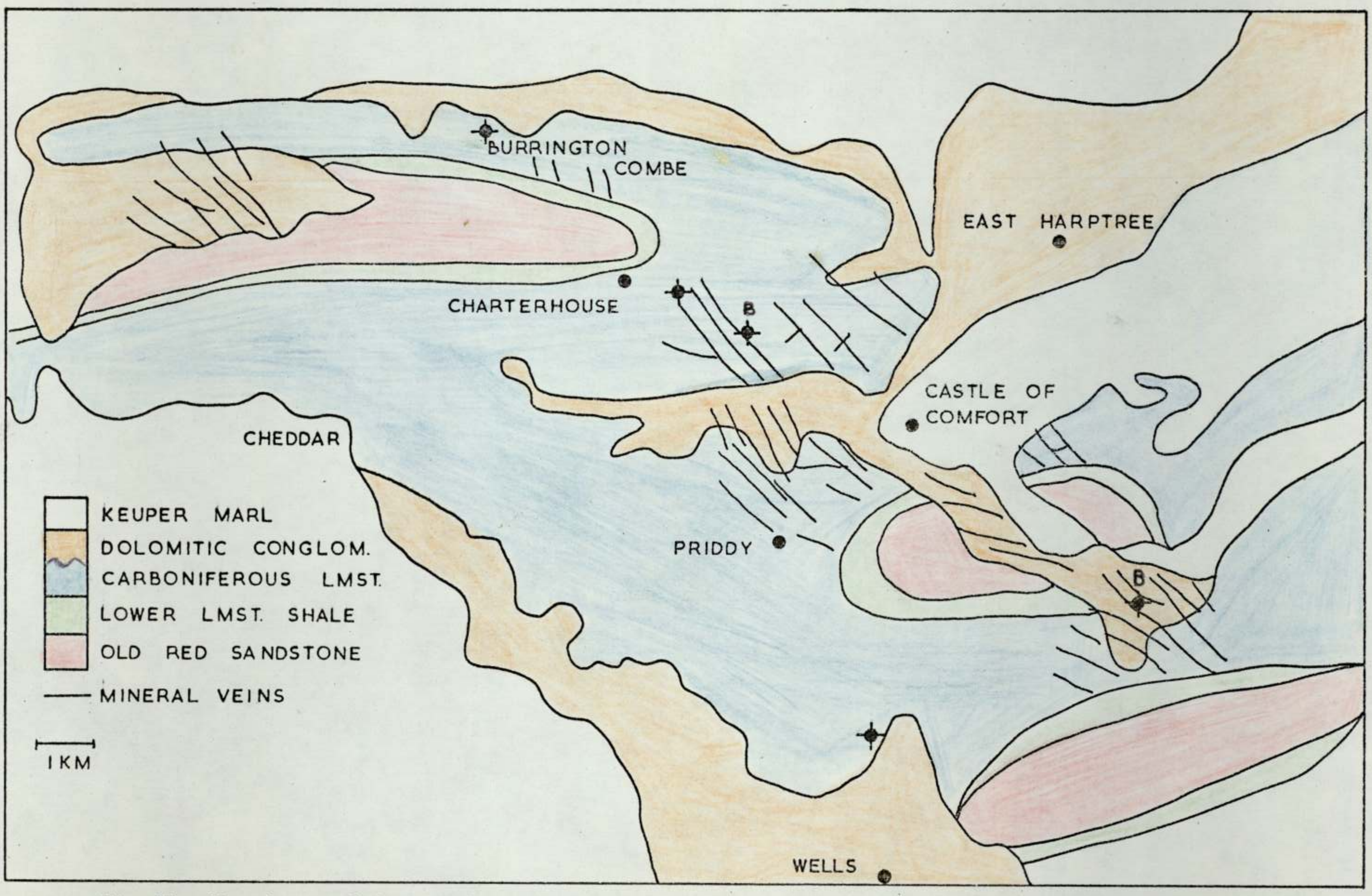


Fig. F. Sketch map of the Mendips, showing the chief mineralised areas and distribution of the collecting sites. Bravoite marked B.

A Description of the Mendip Specimens.

Name	Ref.	Style	Nickel Species	Remarks
Charterhouse	504555	Void infill	Nil	Rare anhedral pyrite, 75% goethitised, associated with cerrusite; gangue, calcite, much brecciated and weathered.
Haydon Grange	518548	Replacement	Unzoned bravoite	Rare, unbanded, 3μ, euhedral lilac, associated with 3μ pyrite in a recrystallised brecciated limestone with secondary calcite matrix.
Green Ore	560505	Undetermined	Unzoned bravoite	Extremely rare, brown, 4μ euhedral, enclosed by 10μ euhedral pyrite, associated with framboidal pyrites, occasionally having darker inner zone. Gangue calcite.
1.6 Km. E. of Wookey Hole	548482	Void infill	Nil	Very rare, pyrite, 3μ euhedral in calcite gangue.

4.5 Description of the Shelve-Habberley mining region, West Shropshire.

The ore-field lies roughly within a radius of 10Km around Shelve village, 22Km south-west of Shrewsbury, but is confined almost exclusively to the Mytton Beds of the Arenig Series, Ordovician. (Geol. Surv. sheet 152, new series). In this area the sequence of Ordovician rocks seems to be nearly complete (Whittard 1958). except for the absence of the Ashgill series. The Mytton Stage commences with the Stiperstones quartzite, a very hard, siliceous, in part conglomeratic sandstone. The Mytton Beds, which follow, consist of hard flags and shales of which all the spoil heaps of the lead mines are composed. These are overlain by the Hope Shales, the base of the Llanvirn Series, and succeeded by the Stapeley Volcanics, an inter-bedded series of tuffs, breccias, lavas, and shales. In general the strike is to the north-north-east, with Mytton Flags cropping out either side of the Ritton Castle syncline, in which the unmineralised Hope Shales and Stapeley Volcanics appear at the surface. To the east the mineralised area is bounded by the Stiperstones Quartzite, forming the very prominent ridge and crags of the Stiperstones. To the west the beds plunge underneath, as successively higher Series of the Ordovician come in.. A transgressive sill of dolerite is present in the area. The mineralisation is confined to regions in the most competent rock shattered by a series of parallel east-north-easterly trending and north westerly trending faults. In the shaly strata, where the softer rock has been comminuted and reduced to a pug, filling the fault fracture, the mineralising solutions have been unable to penetrate, and the beds are barren.

The mineralisation occurs as galena, sphalerite, and rarely pyrite, in a gangue of crushed country rock with quartz, calcite, barytes, and occasional fluorspar. Although the veins show no direct connection with the igneous intrusions, they may be related to a concealed mass of granite.

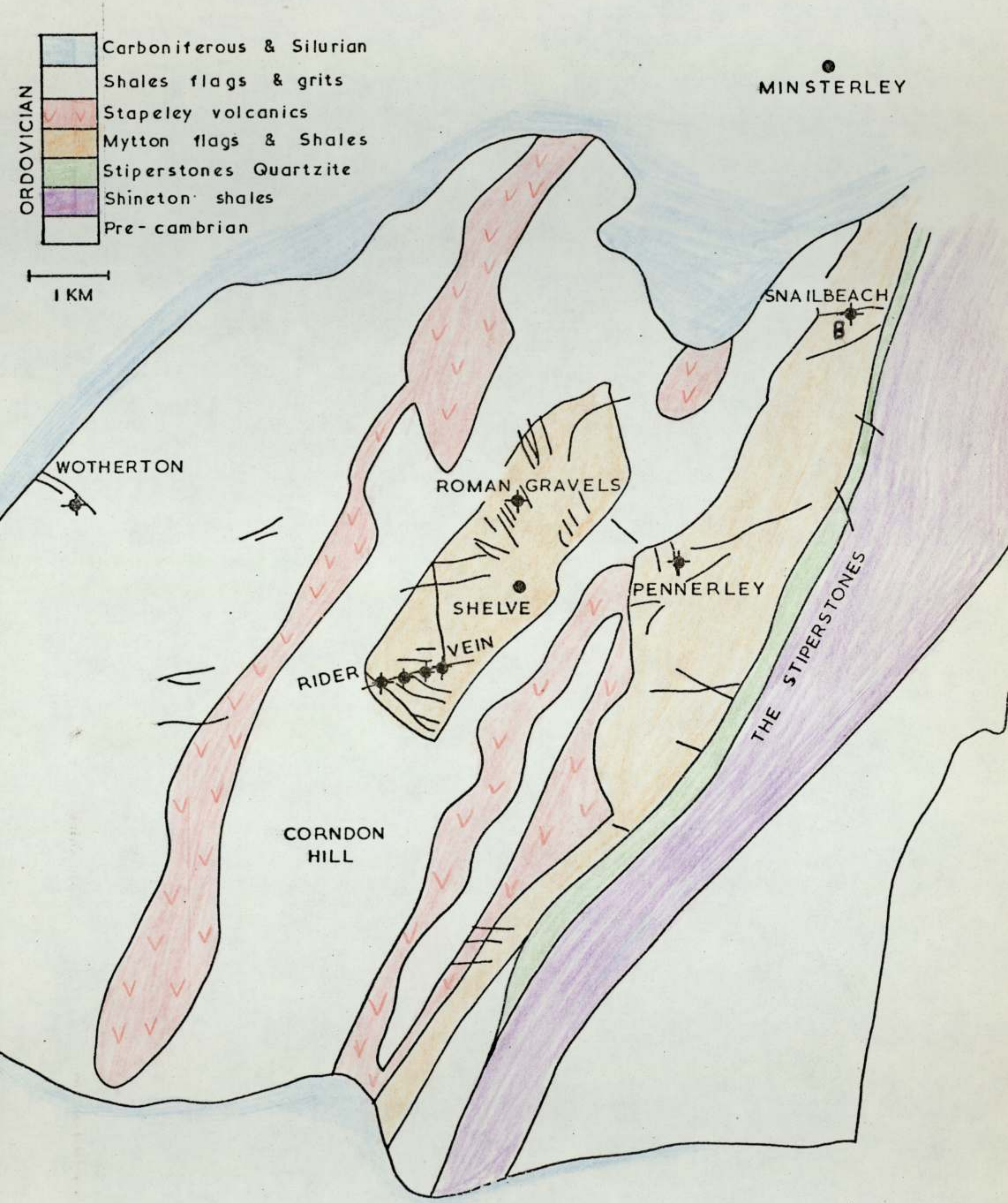


Fig. E. Sketch map of the Shelve, Shropshire, area, showing the chief mineral veins and distribution of the collecting sites. B. indicates Bravoite.

A Description of the Shelve-Habberley Specimens.

Name	Ref.	Style	Nickel Species	Remarks
Snailbeach Mine	374023	Void infill	Unzoned Bravoite	Rare, unbanded 5μ, brown, as inclusions in sphalerite, associated with chalcopyrite in a calcite gangue being replaced by quartz.
Roman Gravels	335002	Replacement	Ni. pyrite	Rare, pale pink pyrite, 5μ, associated with pyrite, pyrrhotite, graphite, rutile, Hematite, Sphalerite, anatase.
Pennerley Mine	355995	Undetermined	Nil	Pyrite, chalcopyrite, graphite, sphalerite, pyrrhotite, gangue; quartz.
Whitegrit	319979	Undetermined	Nil	As above, with ruby blende.

PHOTOGRAPHS OF POLISHED SECTIONS

All the photographs are of specimens found in Derbyshire unless otherwise stated. The columns headed 'Location' and 'Number' refer to the description tables.

Plate No.	Photo. No.	Location	Number
1	1	5 Shuttle Rake	7b
	2	14 Deep Rake	2
	3	25 Oxclose Mine	(a)
	4	37 Crich	1
2	1	9 Hucklow Edge	3
	2	5 Shuttle Rake	7b
	3	9 Hucklow Edge	2
	4	37 Crich	2
3	1	1 Odin Mine	
	2	5 Shuttle Rake	2
	3	9 Hucklow Edge	2
	4	2 New Rake	
4	1	14 Deep Rake	2
	2	2 Redmire Scar (Askrigg)	
	3	9 Hucklow Edge	3
	4	9 Hucklow Edge	3
5	1	14 Deep Rake	2
	2	1 Odin Mine	
	3	7 Hurst (Askrigg)	
6	1	22 Near Winster	
	2	22 Near Winster	
	3	9 Hucklow Edge	3
	4	9 Hucklow Edge	3

Plate No.	Photo. No.	Location	Number
7	1	9 Hucklow Edge	3
	2	9 Hucklow Edge	3
	3	22 Near Winster	
	4	22 Near Winster	
8	1	22 Near Winster	
	2	22 Near Winster	
9	1	3 Garrigill (Alston)	(a)
	2	3 Garrigill (Alston)	(a)
	3	3 Garrigill (Alston)	(a)
	4	3 Garrigill (Alston)	(a)

PLATE 1

No. 1 U.L.	Two brown bravoites in calcite with pyrite rims on three sides only. Zoning in right hand grain very irregular. X 350.
No. 2 U.R.	Euhedral lilac bravoites showing faint concentric and radial zoning, partially rimmed with pyrite. X 750.
No. 3 L.L.	Euhedral lilac bravoite in fluorite partially rimmed with pyrite. Characteristic pentagonal habit with concentric and radial zoning. X350.
No. 4 L.R.	A double bravoite crystal showing concentric zoning, with a dark nickel-rich centre adjacent to a pale pyritic centre. X400.

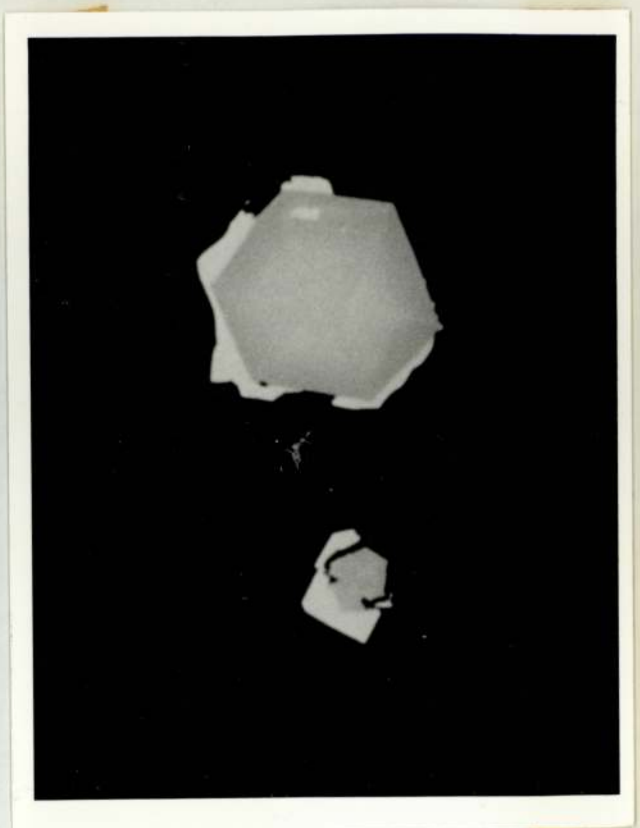
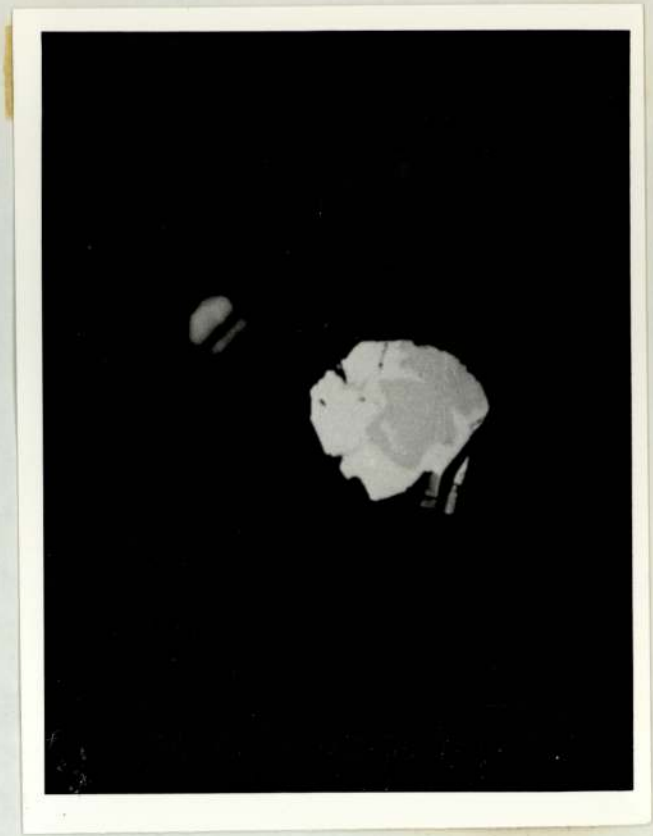


PLATE 2

No. 1 U.L.	Elaborately zoned bravoite in fluorite showing faint concentric zoning and below, a well defined sub-parallel zoning with a superimposed fine structure and 'cross zoning'. X250. Compare with 3 below.
No. 2 U.R.	Elaborately zoned bravoite partially surrounded by pyrite, in fluorite. X700.
No. 3 L.L.	Subhedral chalcopyrite separating anhedral pyrite from very euhedral bravoite. Bravoite shows pale streaks sub-parallel to long face. X250. Compare with No. 1 above.
No. 4 L.R.	Lilac bravoite in fluorite, partially enclosed by a 1 to 2u rim of pyrite, with an irregular pyritic zone in centre. X700.



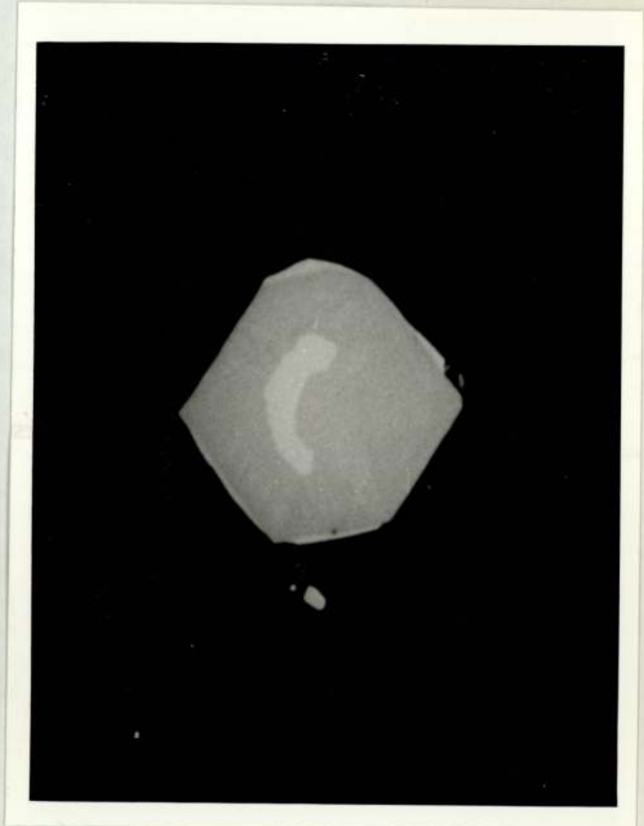


PLATE 3

No. 1 U.L.	Scalenohedral pentagonal bravoite with faint concentric zoning, and nickel rich rim in nickeliferous pyrite. Outer zones of bravoite being preferentially replaced by goethite. Quartz gangue. X500.
No. 2 U.R.	Concentrically zoned subhedral bravoite with nickel rich centre and pyrite rim, in calcite. X1000.
No. 3 L.L.	Double zoned purple bravoite surrounded by pyrite on three sides. The bravoite crystal is growing on the face of a fluorite crystal. X750
No. 4 L.R.	Bravoite in fluorite showing three main subhedral zones. The central euhedral hexagonal darker zone contains 1µ wide fine zoning structure. X500.

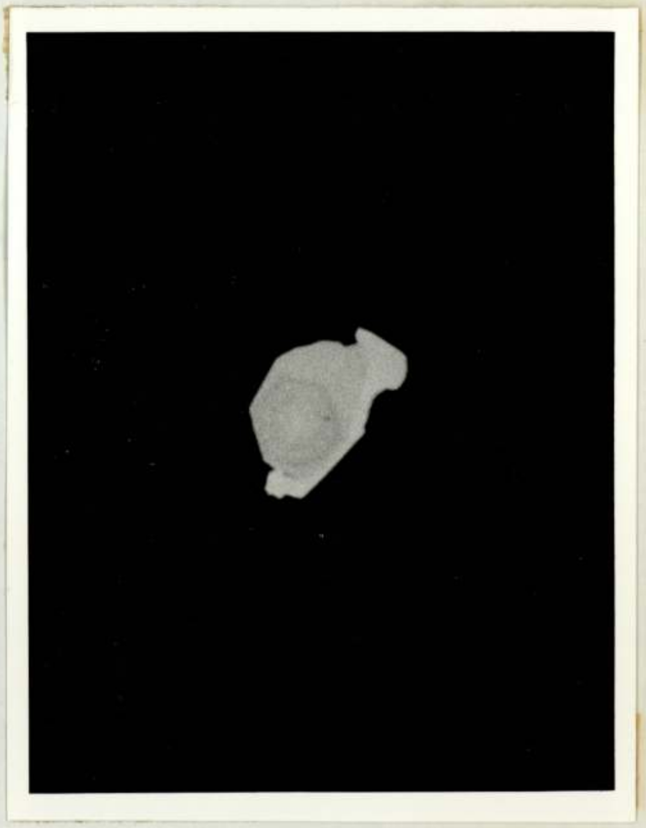


PLATE 4

No. 1 U.L.	Two bands of bravoite crystals in fluorite, and some scattered inclusions. These are generally small and unaltered, but the larger bravoite crystals on the fluorite crystal faces are being replaced by goethite in some instances. X50.
No. 2 U.R.	Bands of bravoite crystals following barites-fluorite junction. The bravoites are confined to the barites. Large pyrite crystal on left. X30.
No. 3 L.L.	Assemblage of bravoite, pyrite and marcasite in fluorite. Bravoite dark grey and streaky grey; marcasite pale grey; fluorite black. X250
No. 4 L.R.	As lower left. X250

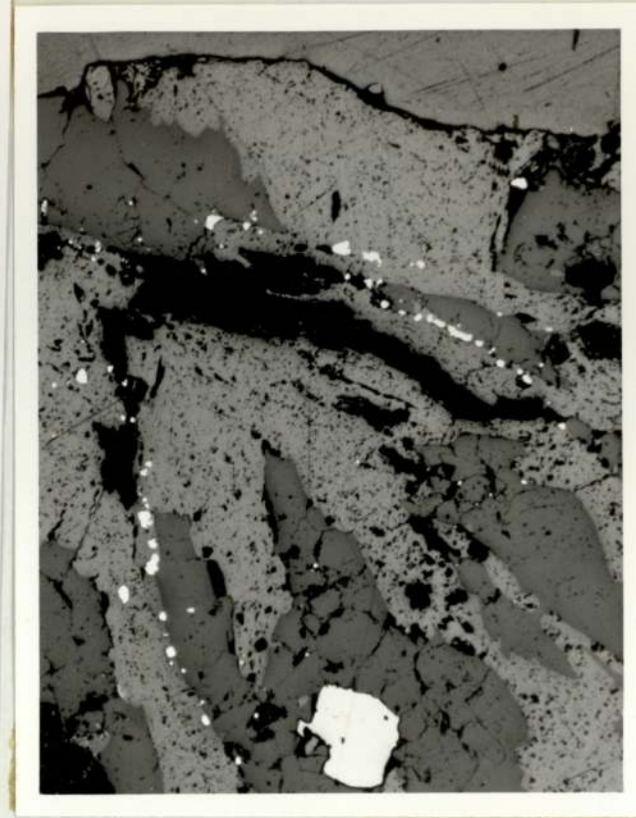


PLATE 5

No. 1 U.L.	Zoned goethite pseudomorphing bravoite on fluorite crystal faces. Small unaltered bravoite in centre of fluorite crystal as inclusion. X250
No. 2 U.R.	Pyrite white, chalcopyrite pale grey, bornite dark grey. Marcasite grain below. From Odin Mine, Derbyshire. X100.
No. 3 L.L.	Bravoite in fluorite being replaced at centre and radially by goethite. X300.

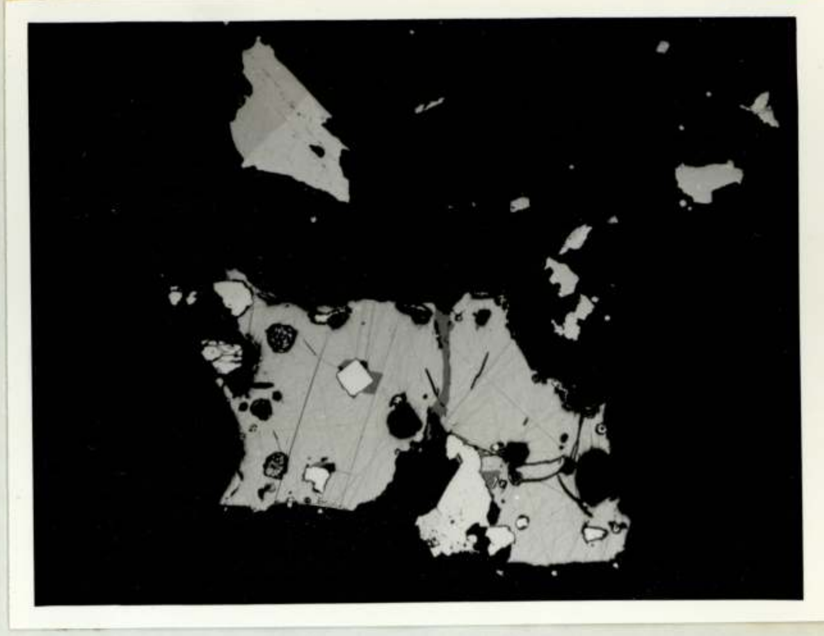
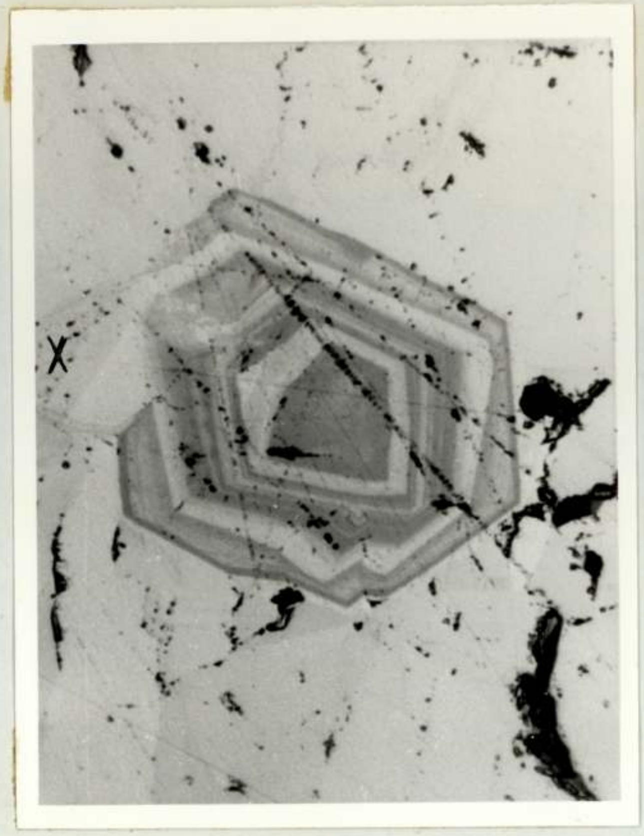


PLATE 6

No. 1 U.L.	Nickeliferous marcasite. Fine multizoned bravoite in marcasite in calcite flake. Note continuation of bravoite zoning into marcasite on left. Polars uncrossed. X300.
No. 2 U.R.	As left. Polars crossed. Note anisotropy at left where bravoite zoning continues into marcasite. X200.
No. 3 L.L.	Nickeliferous marcasite. Bravoite crystals separated by marcasite. The upper bravoite has a fainter outer zone, with intermittant pyrite boundary, and a dark inner zone. The continuation of the darker inner zone is seen as a relatively darker band crossing the marcasite and joining up with the adjacent bravoite. Polars uncrossed. X250.
No. 4 L.R.	As lower left. Polars partially crossed. Note the marcasite and the dark band joining the bravoites cut by the marcasite crystal boundary. X250.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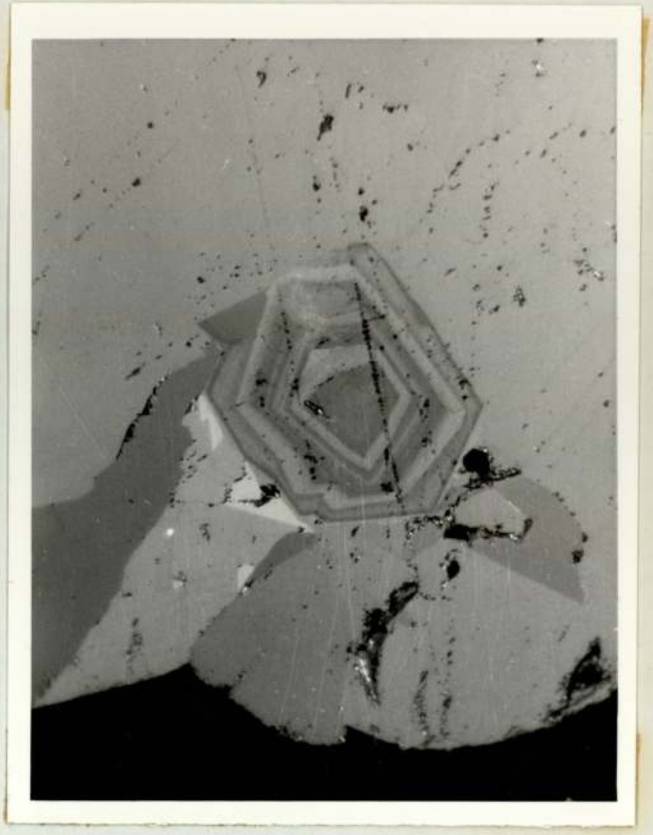
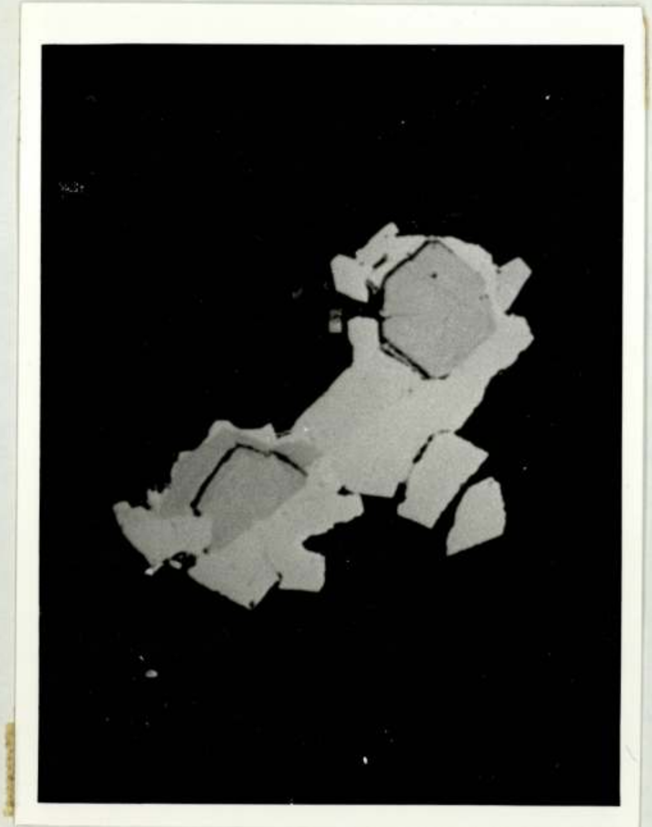




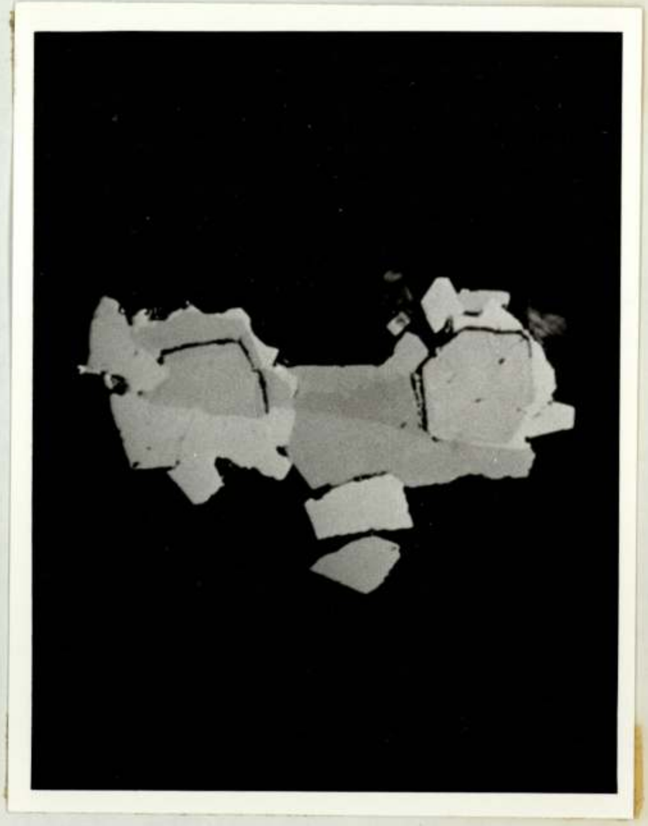


PLATE 7

No. 1 U.L.	Zoned marcasite. Marcasite showing bravoite-type colour zoning. This is purple, and not pleochroism. Polars uncrossed. X300
No. 2 U.R.	As above, polars crossed. Zoning remains, but anisotropy changes it to a deep purple. X300
No. 3 L.R.	Multizoned bravoite surrounded by marcasite and pyrite. Polars half crossed. X250.
No. 4 L.L.	Multizoned bravoite in pyrite. Gangue, calcite flake. Bravoite colours, from top; pale lilac, centre and lower, brown, separated by dark lilac, V shaped zone. X500.

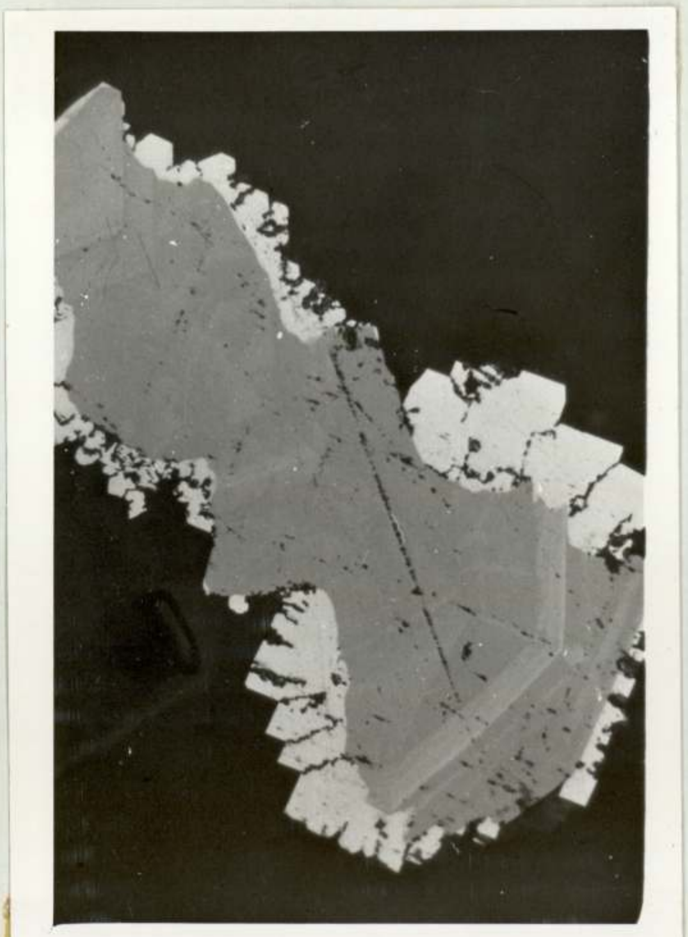
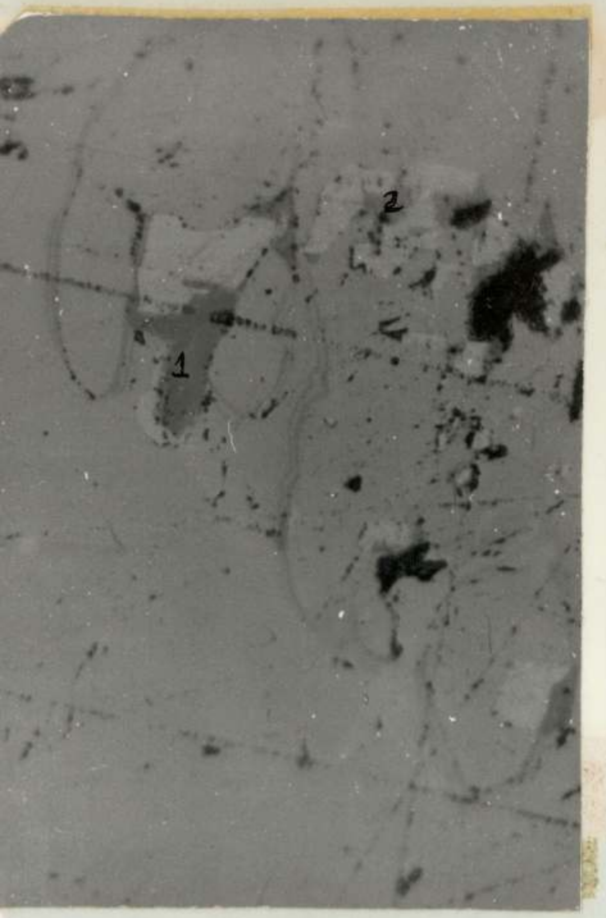


PLATE 8

No. 1 U.L.	Nickeliferous marcasite. Deep purple bravoites in marcasite with sinuous purple band cutting marcasite crystal boundaries. Dark grey; bravoite, Pale grey; marcasite, light grey; pyrite. Polars uncrossed. See Fig. 3. X500.
No. 2 U.R.	As left, polars partially crossed. Marcasite anisotropy seen, with coloured bands cutting across it. X500.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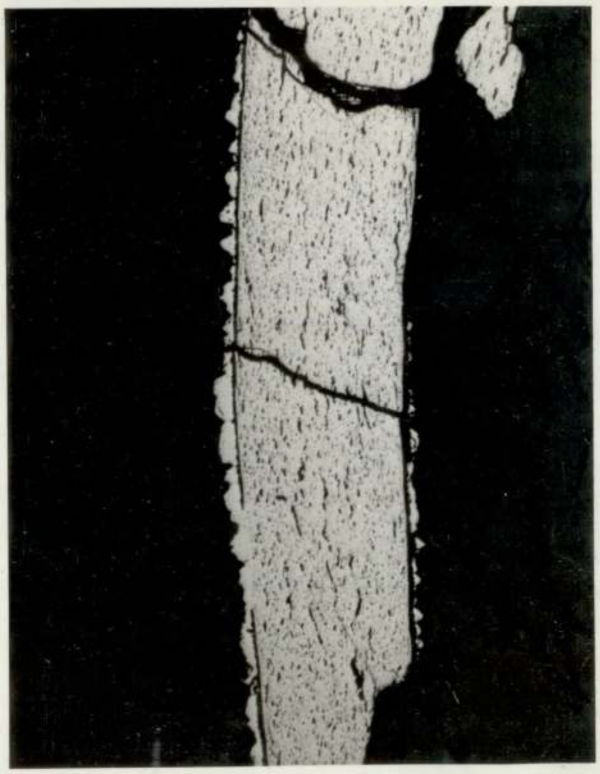


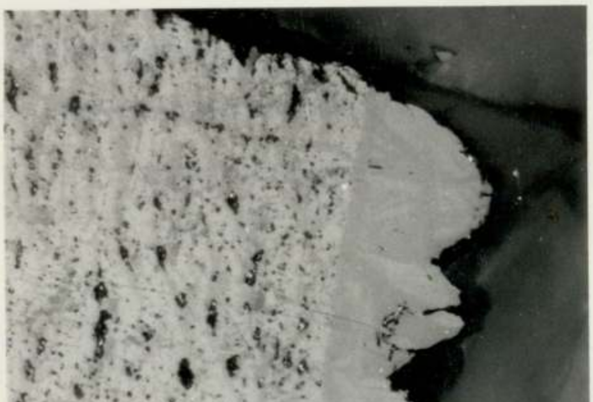


PLATE 9

No.1 U.L.	Much fractured arsenopyrite in quartz. Tynebottom Limestone. X25
No. 2 U.R.	As left, showing anisotropic rim of different phase. X100.
No. 3 L.L.	As above, showing various unidentified phases. X250.
No. 4 L.R.	As above, polars crossed. X300

CHAPTER 5

DISCUSSION OF RESULTS.

5.1 Classification.

The nickel species observered were classified as

1. Bravoite
2. Nickeliferous pyrite
3. Nickeliferous marcasite.

5.1.1. Bravoite.

Colour — brown, violet, mauve, lilac, grey.

The colours varied both as indicated above, and in depth or saturation, from a faint tinge to moderately and rarely very, deep. The determination of the colours was very subjective except in the case of the rare deep hues.

Zoning — Zoned or unzoned. An extremely common form of zoning was the bizoned pentagonal form which consisted of an inner coloured core surrounded on four sides with a narrow rim of yellow pyrite, groups of similar crystals often arranged in semi-parallel bands, and had a certain orientation of the zoning. This is discussed later. (Fig 2).

Zone widths varied from less than 0.5μ to almost the complete width of the crystal. Zone boundaries were generally sharp, rarely diffuse. Rare instances of a zonal boundary gradually disappearing by gradual convergence of the colours either side to one common colour are known.

Zones were generally regular, often exhibiting some coarse symmetry. (Plates 1,2,3) Completely irregular zoning patterns were rare, but ranged from interdigitation to those which approximated in appearance to a myrmekitic intergrowth.

A regular variation of zone width linked with a similar regular variation of zone colour often occured. This led to an appearance of a coarse symmetry about some point in the crystal.

Pl.2.1 illustrates a unique cross-hatched pattern.

Superimposed on a course zoning pattern was commonly a finer pattern, which consisted of subtle variations within the zone of the dominant zone colour. The widths of this fine zoning extended down to the limit of resolution of the microscope.

Isotropy	Isotropic, rarely slightly anistropic.
Twinning	Not apparant.

5.1.2 Nickeliferous Pyrite

Colour	Faint pinkish superimposed on yellow pyrite.
Zoning	Not present, or very faint.
Isotropy	Generally isotropic, rarely showing faint anisotropy.
Twinning	Not apparant.

5.1.3 Nickeliferous Marcasite Plate 6.

Colour	Similar to bravoites, less intense, less variation in one crystal.
Zoning	Usually zoned or 'streaky', zones or 'streaks' which cut across crystal or twin boundaries.
Isotropy	Strong anisotropy.
Twinning	Often present.

5.2 Detailed description of Bravoite.

5.2.1 Bravoite distribution.

Bravoite was found throughout all the geographical locations where the study was made. There was no-where any detectable difference in colour, shape, zoning pattern or mode of occurrence. Regional variations that were found in the distribution are shown below:

Locality	Collection	Number with			Percentage of sites	Specimens	Number with
	sites	Br	Py	Mc	with bravoite	made	bravoite
Derbyshire	79	56	14	10	71	93	70
Askrigg Block	10	7	1?	1?	70	16	10
Alston Block	10	1	2	-	10	14	1
Shelve, Salop	4	1	1	-	25	4	1
Mendips	4	2	-	-	50	4	2

5.2.2 Bravoite associations - other sulphide minerals.

	Pyrite	Chalcopyrite	Marcasite
% of all specimens containing	86	30	50
% of all bravoite - bearing specimens containing	97	37	38

These figures show that bravoite had a very strong tendency to be associated with pyrite and chalcopyrite, and less so with marcasite. A possible reason for copper to show a preference for co-precipitation with nickel as the sulphide is that the chemical and physical conditions required by both were similar for the precipitation of chalcopyrite and bravoite, respectively; and were not so favourable for the precipitation of marcasite. An interesting point arises as to why the nickel/iron sulphide favoured precipitation from numerous nuclei from many small crystals, and the copper/iron sulphide favoured fewer nucleation sites but produced much larger crystals.

Insufficient samples were studied from regions other than Derbyshire to be able to construct a similar analysis concerning relative mineral occurrences.

5.2.3 Bravoite associations - gangue minerals.

Bravoite was found in all three common "gangue" minerals; fluorite, calcite and barytes. Rare occurrences in quartz were also noted. Where a banding of gangue occurred, bravoite had a tendency to be located at or just adjacent to the contact zone between the gangues. Where the admixture of gangues was heterogenous especially as between fluorite and calcite, no preferential host could be determined. However in a mixture of fluorite and barites, the barite appeared to be the more favourable host. No reason is offered for this. See Plate 4, No. 2.

5.2.4 Textural Relationship.

1. Banding. See Plate 4, No. 1.

In many polished sections, a marked banding of bravoite was observed in the gangue mineral. This was particularly apparent in fluorite and scalenohedral and rhombohedral calcite. Parallel and sub-parallel bravoite bands were commonly of the order of 10 to 20 microns wide, composed of 5 micron bravoite crystals which exhibited diverse crystal forms. Each band had characteristically its own modal size of crystal, although there was considerable scatter about the mode with the distribution being skewed towards the smaller sizes. The crystals were either found predominantly on the gangue mineral crystal faces, or predominantly as inclusions inside the gangue mineral.

2. Bravoite and Pyrite.

The relationship of the pyrite to the bravoite varied from one of being a completely enclosing mineral, to merely rimming the bravoite on one face only. As an enclosing phase, the widths of rim on all faces commonly varied, not only in relation to the width on adjacent faces, but also along each face. A very common relationship was that of a pentagonal bravoite, generally not exceeding 10 microns, having a pyrite rim well developed on four faces, but missing on the fifth face. A statistical analysis of the angular direction of the normal to the faces of the bravoite that was nickel free was carried out, the angle subtended by the normal through the bravoite produced was measured with respect to some arbitrary direction as reference on the polished section. A bimodal distribution was commonly found, having maxima less than 90° apart particularly when the crystals were growing in a fluorite gangue. Since a crystal will grow in a direction normal to the substrate on which it commences growth, assuming unimpeded flow of ions in solution to all exposed faces, the directions of the measured normals will in fact be the direction of growth, and since the pyrite follows the bravoite spatially, it is therefore later than the bravoite in the paragenetic sequence. See fig 2 .

3. Bravoite and other sulphides.

Other sulphide minerals, galena, sphalerite, and chalcopyrite are seldom hosts for bravoite, There is further, a special and marked association between bravoite and marcasite which will be discussed in a later chapter. Notwithstanding the rarity of bravoite as inclusions in galena, sphalerite or chalcopyrite, there is exhibited a marked tendency for bravoite to be located in bands adjacent to galena separating it from the associated gangue mineral. Although the evidence is by no means free of ambiguity,

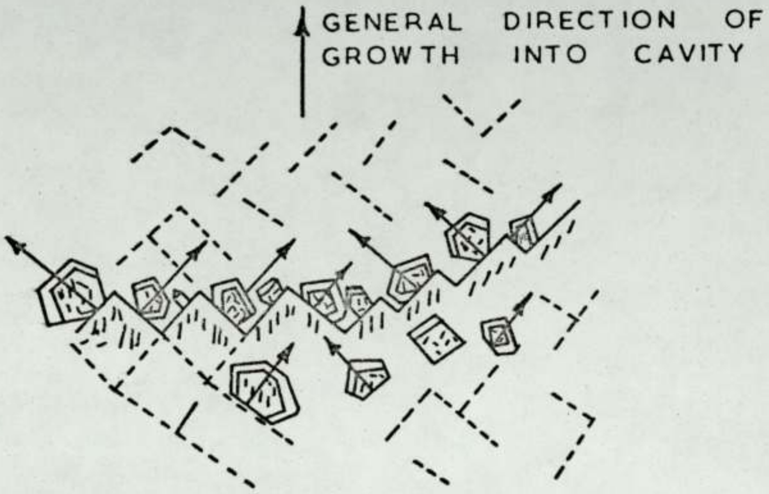


Fig. 2. Sketch showing the arrangement of bravoite in pyrite growing on fluorspar crystal faces, indicating the direction of growth. The bravoite is shaded inside the pyrite.

there is a tendency for bravoite to be associated with minor purple fluorite showing contact colouration adjacent to galena, in an otherwise colourless fluorite field.

5.2.5 Physical Properties.

1. Size

Bravoite crystals range in size from a minimum diameter of 2 microns to a maximum of 150 microns, the commonest size would appear to be about 10 to 20 microns. There appeared to be no correlation between size and colour, nor between size and crystal habit. The smaller crystal is commonly more euhedral than the larger, because adjacent crystal growth is less likely to interfere.

2. Colour.

Bravoites range in colour from grey, lilac, violet, mauve, to brown, or any intermediate hue of varying saturation. They can be of one colour, two, or many, and if not monochromatic, the colours form zones, either continuous or discontinuous, concentric or radial, or both. In one crystal successive colour zones or groups of zones commonly show a change of outline for example, from pentagonal dodecahedral to cubic. Similarly, colours, successive order of colours, width and arrangement of colours and zones commonly changes radically from crystal to crystal within a few microns. An attempt was made to classify the colours exhibted by bravoite crystals using the Munsell Colour Charts, but it was found impossible to obtain reproducible results. This is believed to be due to the combined effect of the relatively dark background and the oil immersion lens on the extremely small crystals, compared with the size and illumination of the colour chart.

3. Zoning.

The great variation in zonal patterns displayed has been shown by El Baz (1963), to be incapable of mathematical analysis; the variation in the geometric shape of the successive zones was originally believed to reflect a change in crystal habit brought about by the change in composition also indicated by the change in colouration, but considerations of crystal geometry of the pyritohedral class of the cubic system in which bravoite crystallises show that the pentagonal dodecahedron, the common form it exhibits, will give figures of three, four, five and six sides in cross section, depending on how many faces are cut by the section and when this form is combined with the octahedron, can give figures of eight sides. Thus there appears to be no need to postulate a change in habit with composition, (Vaughan 1969).

Zones in bravoite crystals are very often irregular, occasionally discontinuous or cut by radial boundaries, seldom curved, and commonly exhibit an ultra-fine discrete, or some-times a gradational, zoning within the courser zoning pattern as described earlier. This internal, superimposed assymetric zoning within a given zone can be explained by invoking a differential supply of nickel or cobalt (or copper) ions to each crystal face.

4. Reflectivity.

Reflectivity measurements using a Reichert reflex microspectrophotometer were attempted on various of the nickel species, but because of their small size, no reproducible results were obtained. This confirmed the finding of other workers who have stated that the optimum size for reflectivity measurements is 100μ, and accuracy is greatly reduced at sizes below 40 μ.

5. Hardness.

Again because of the small size of the bravoite crystals no Vickers hardness tests were carried out. Using optical methods, some bravoite zones showed a positive relief against pyrite, others negative.

5.2.6 Bravoite Alteration Products. Plate 5, Nos. 1 and 3.

Bravoite was commonly seen to be altering to goethite. In many cases the goethite pseudomorphs the bravoite zoning. Goethite after pyrite shows no regular structure. Often in one section no unoxidised pyrite or bravoite remained, but the former presence of bravoite was revealed by the goethite pseudomorphs. There was some evidence to suggest that goethite after bravoite is of a deeper red or blue than geothite after pyrite which was often pale blue or grey.

Bravoites as inclusions in fluorite, and to a lesser degree as inclusions in calcite, altered to goethite far more rarely than bravoite lying along fluorite or calcite crystal boundaries. This would reflect the relative ease of ingress of water along crystal boundaries rather than crystal cleavage planes or fractures. The difference between degree of oxidation of bravoite in calcite of those lying along the crystal boundaries and those found as inclusions was not so marked as in the case of fluorite, this probably reflects the greater solubility of calcite leading to wider and longer solution channels into the crystal up which the water can travel, and oxidise the bravoitic and pyritic inclusions.

5.3 Nickeliferous Marcasite

A mineral species believed to be nickeliferous marcasite was discovered at 10 different randomly distributed locations in Derbyshire and at one possible location in the Alston Block. Two types were found. In one, Pl.6, No1, a deep lilac bravoite 15μ by 8μ , very euhedral, surrounded on two sides by normal pyrite varying from 5μ to 10μ in width is situated in a large marcasite field, the boundary on one side of the pyrite crystal forming a continuation of the adjacent marcasite on the left. Plate 8, No. 1, plane polarised light, shows the bravoite in the lighter coloured pyrite, with smaller scattered bravoites and associated pyrites to the right, set in grey marcasite. See Fig 4 . A series of lilac lobes, in places double or triple bounded, having vague crystal outlines cut across the marcasite field and in general emanate from or terminate in the deep lilac bravoites. The fine double or triple bands defining the lobes are 1μ wide, in places widening out to 3μ. Pl 8 No 2 (crossed nicols), brings out the marcasite boundaries which in places cut directly across the lilac lobes, and in one place becomes contiguous with them. Electron micro-probe studies showed the lilac bravoite to have up to 57.44% nickel and no cobalt, whilst the lilac band had between 13.37 & 13.72% nickel. The uncoloured regions across which the band lay had 0.24% Nickel. The second type of nickeliferous marcasite appeared under plain polarised light to be a normal zoned bravoite, euhedral, with well marked colour zoning, but which exhibited a pleochroism on rotating the stage, superimposed

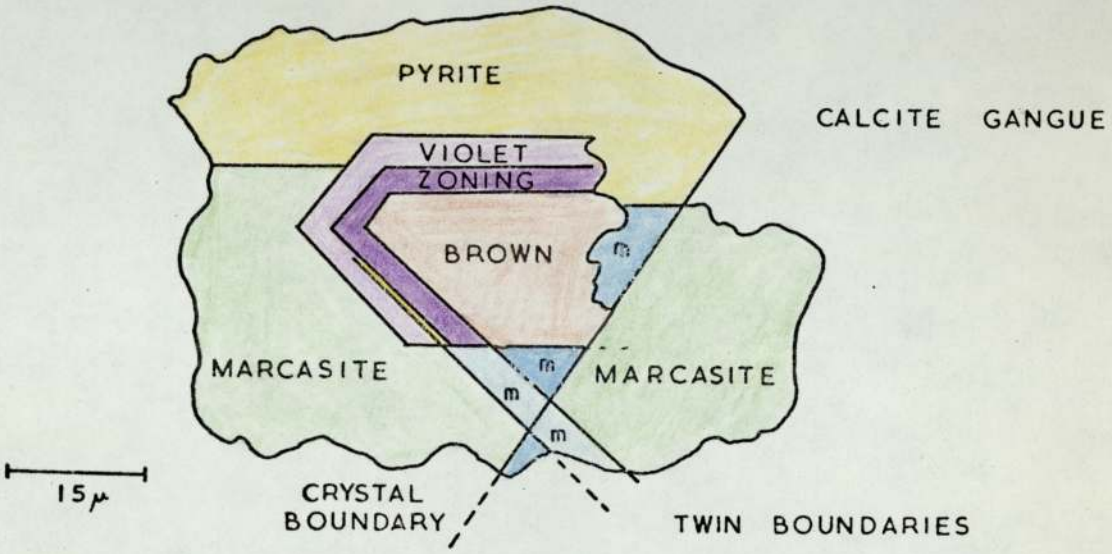


Fig. 3 . A typical nickeliferous marcasite showing twin boundaries as an extension of a coloured zone of the included bravoite. Seen under crossed nicols.

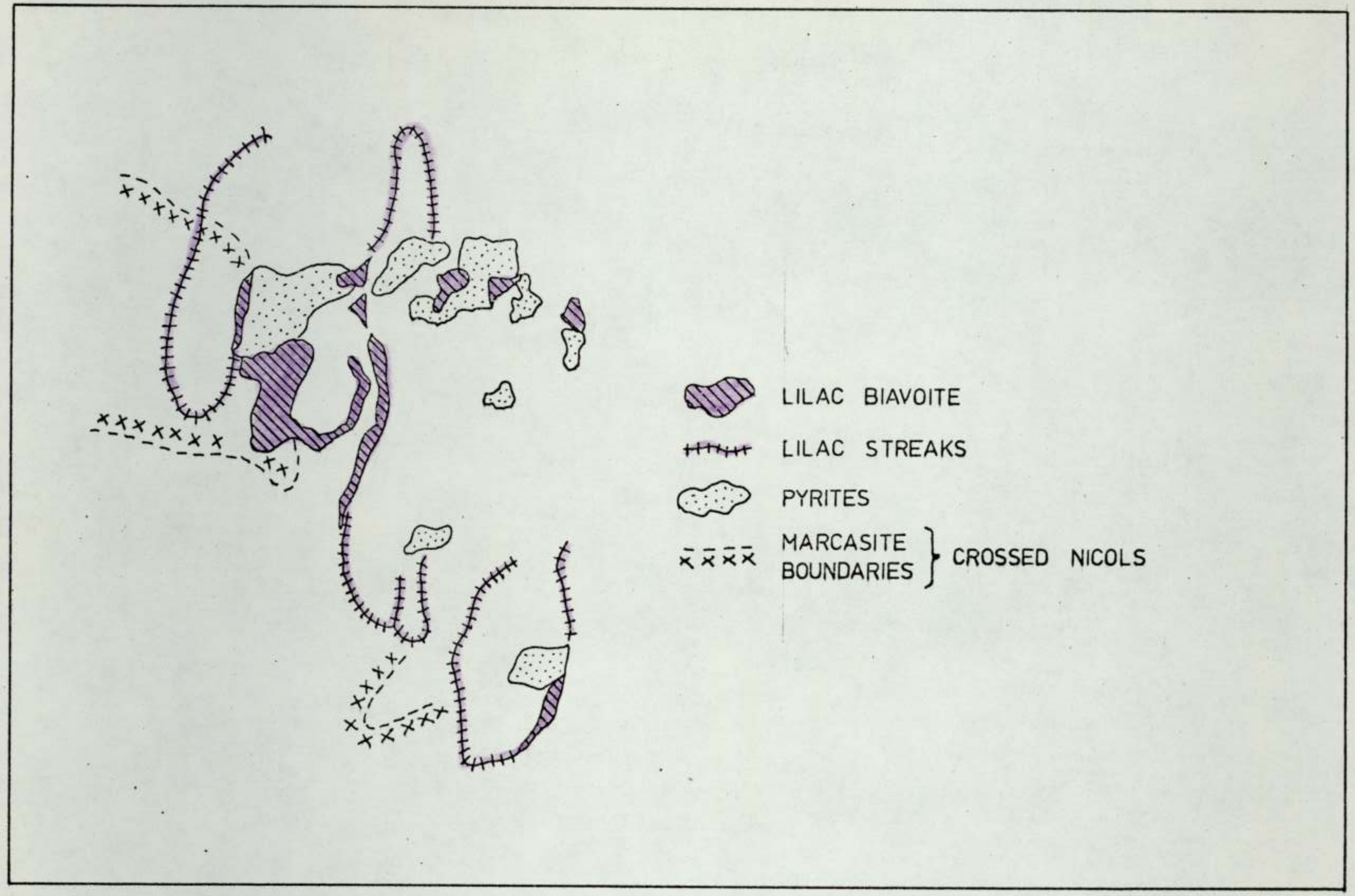


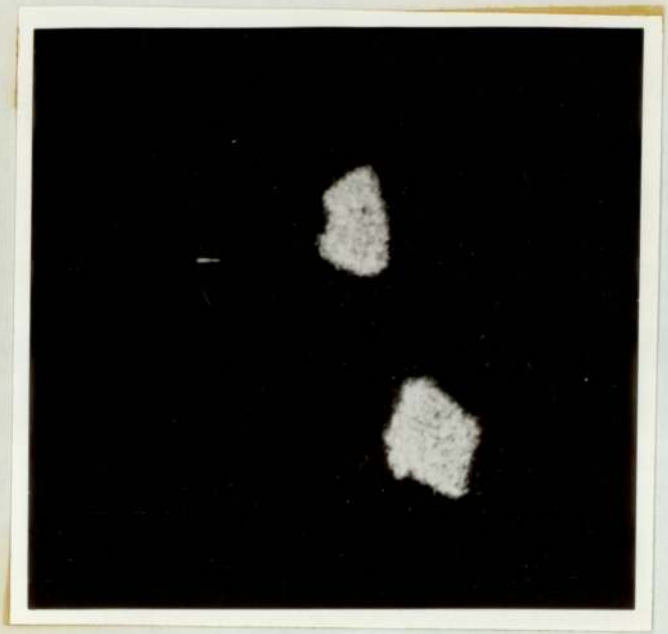
Fig. 4. A nickeliferous marcasite, as in Plate 8 Photo 2 , showing the lilac nickel rich streaks crossing the marcasite boundaries when seen under crossed nicols.

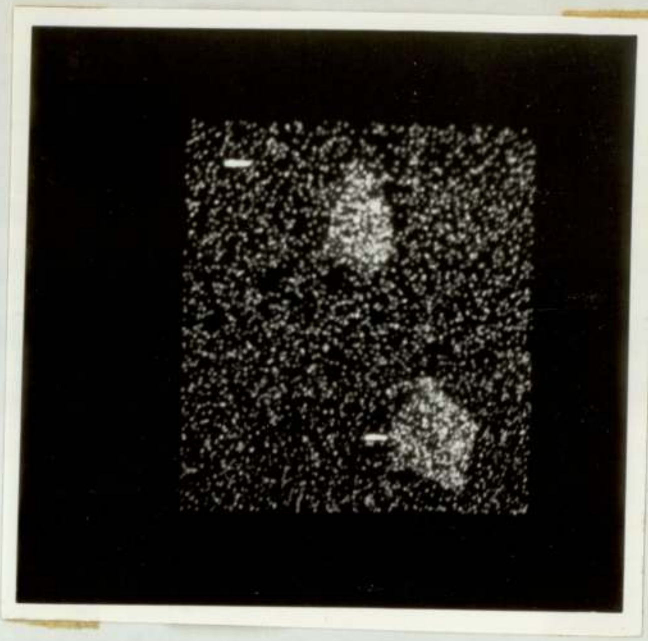
on the colour zoning. With crossed nicols, strong anisotropy with contrast across a twin plane appeared, whilst the colour banding still could be seen. Other examples of this type had a marcasite twin or crystal boundary as an extension of a colour zone boundary of an included bravoite. See Fig 3 and Plate 6, Nos. 3 and 4, and Plate 7, Nos. 1 and 2.

There is slight evidence that these nickeliferous marcasites show their best development in large, void-infilling, rhombohedral calcite.

The first described marcasite, (Plate 8) is most remarkable. A possible explanation is that the whole complex of crystals were originally a group of zoned bravoites of a normal type, but subsequently the (unstable) zoned bravoites established equilibrium by exsolving the greater part of the nickel which migrated to the now nickel-rich areas with a minor portion migrating to the previous bravoite boundaries. Either simultaneously, or later, parts of the newly formed nickel-free pyrite converted to the marcasite structure, but leaving within them nickel pseudomorphs or relict structures of the old bravoites. See Plate 13, No. 4 electron probe nickel picture.

Pl 6,1 shows a large, 80µ zoned bravoite where one part of the rim appears to have lost its nickel and gone over to marcasite. In this vicinity other parts of adjacent zones appear to be 'decaying' also.





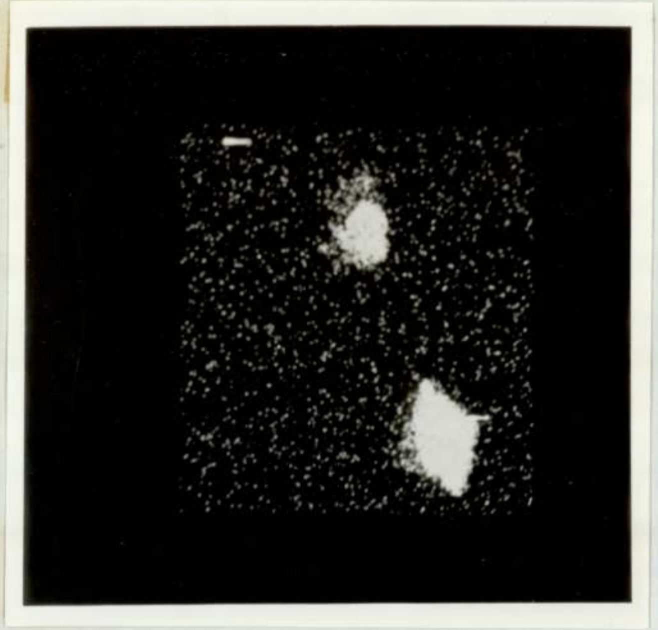
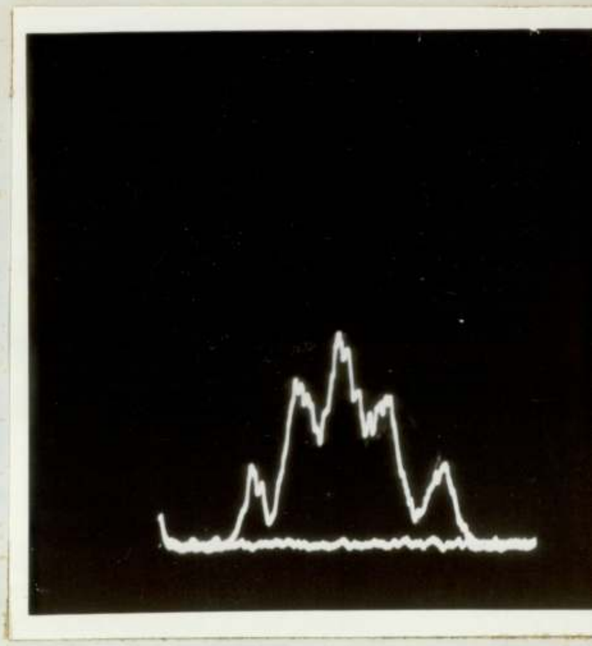
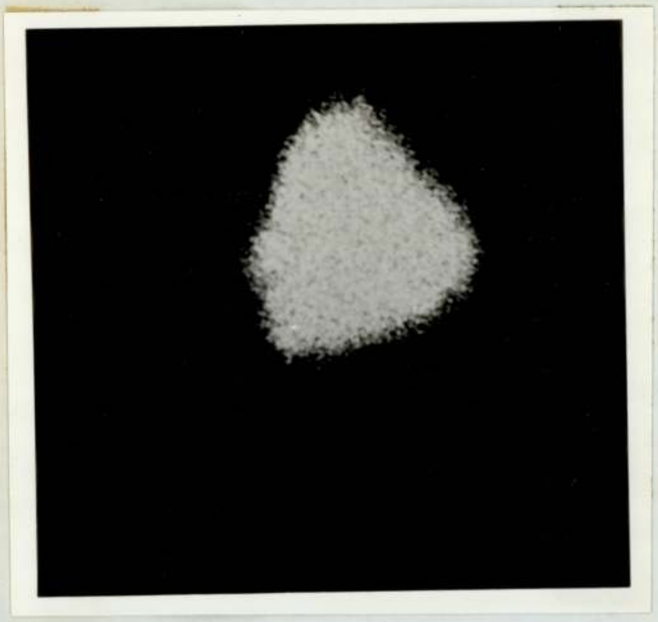


PLATE 10

No. 1 U.L.	Nickel X-Ray picture of specimen in Plate 1, No. 1.
No. 2 U.R.	Cobalt X-Ray picture.
No. 3 L.L.	Iron X-Ray picture.
No. 4 L.R.	Nickel X-Ray picture of specimen E in table 2. E_1 is the central area, E_2 is the left hand boundary, rather diffuse.





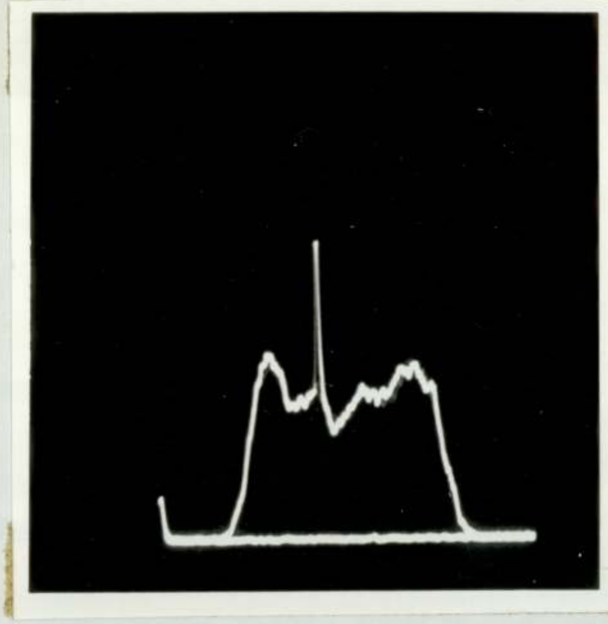
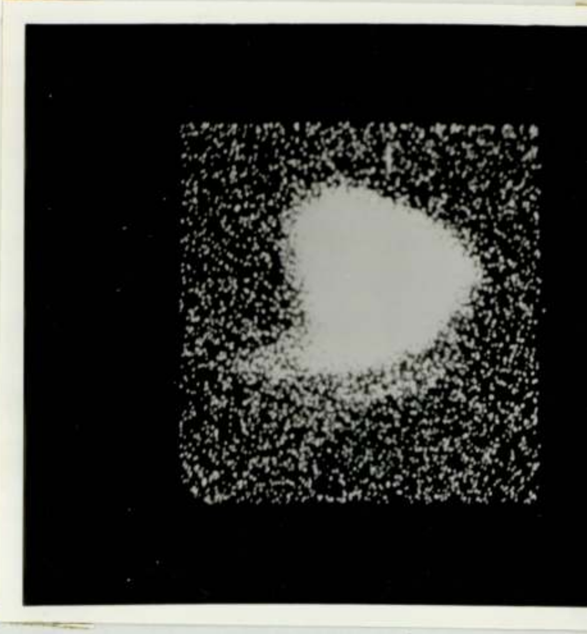
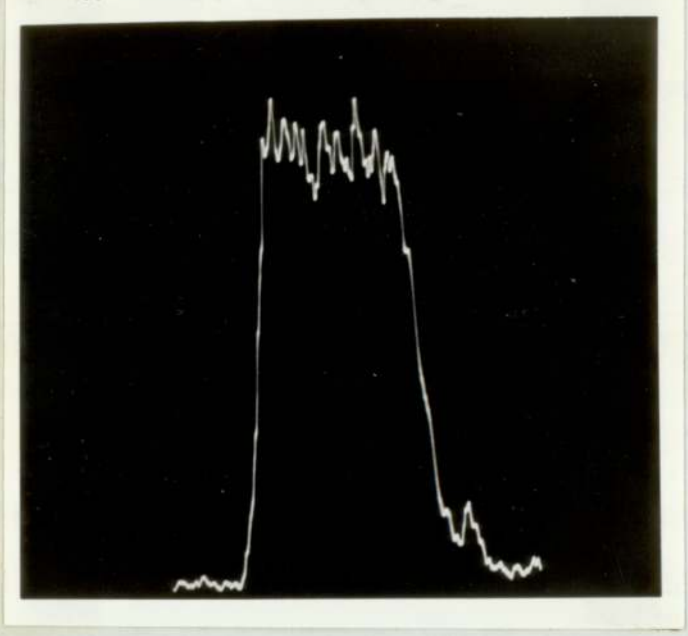
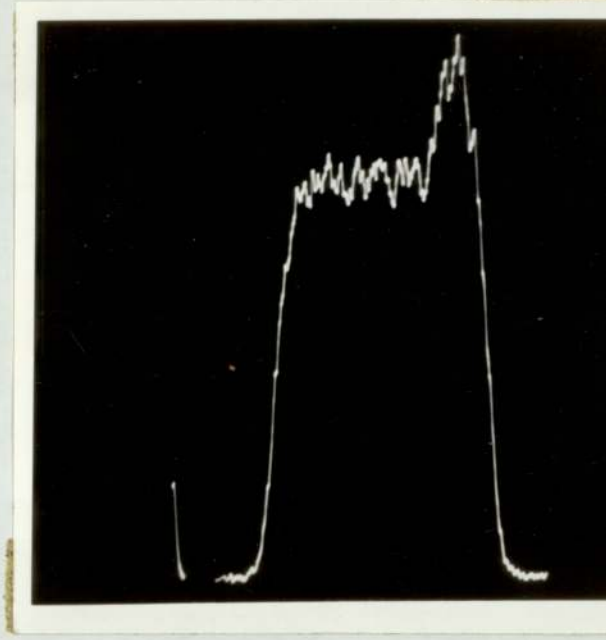


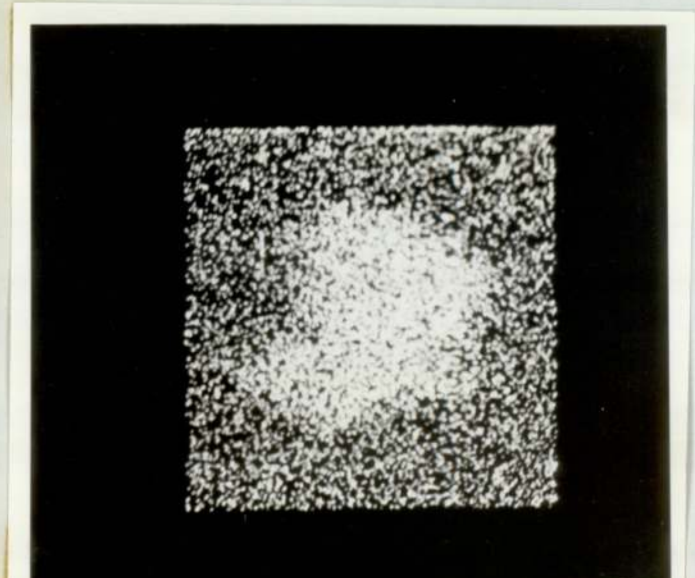
PLATE 11

No. 1 U.L.	Nickel X-Ray picture of specimen in plate 3, No. 2.
No. 2 U.R.	Nickel X-Ray trace. .
No. 3 L.L.	Iron X-Ray picture.
No. 4 L.R.	Iron X-Ray trace.









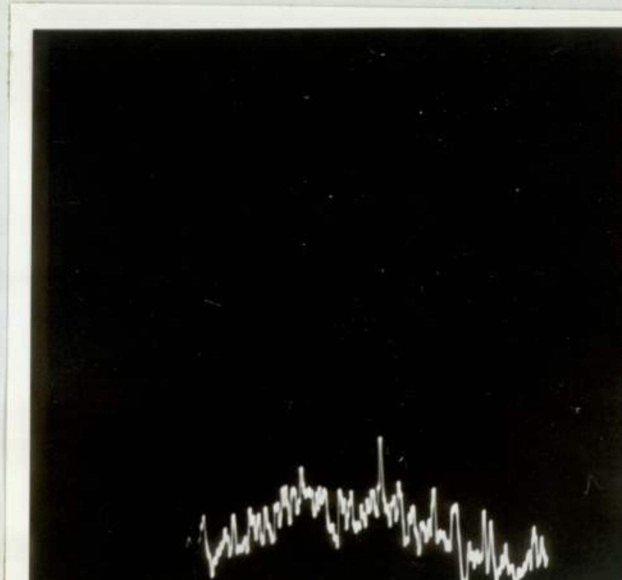
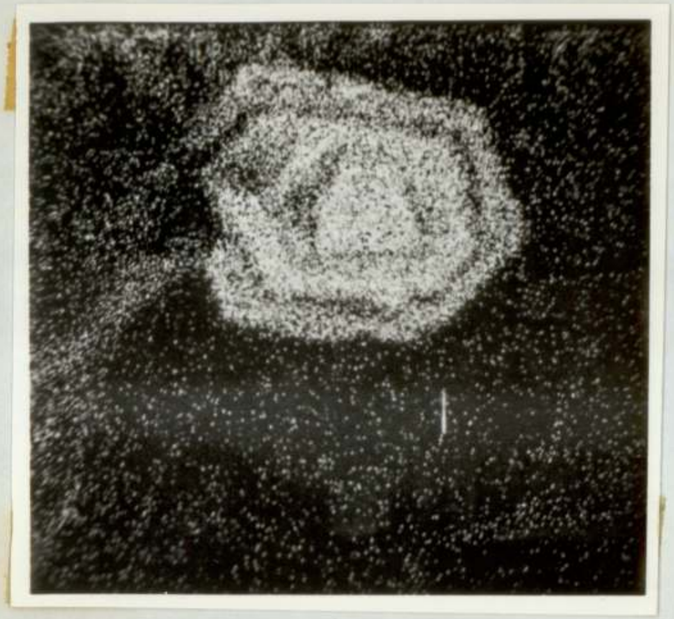
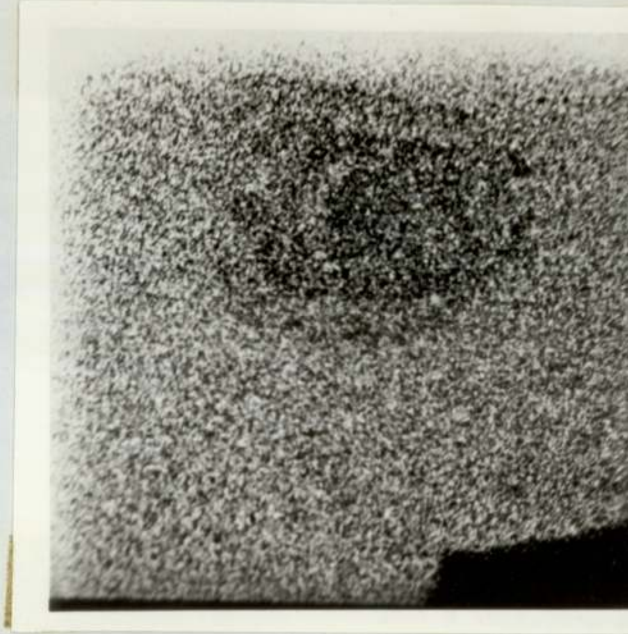
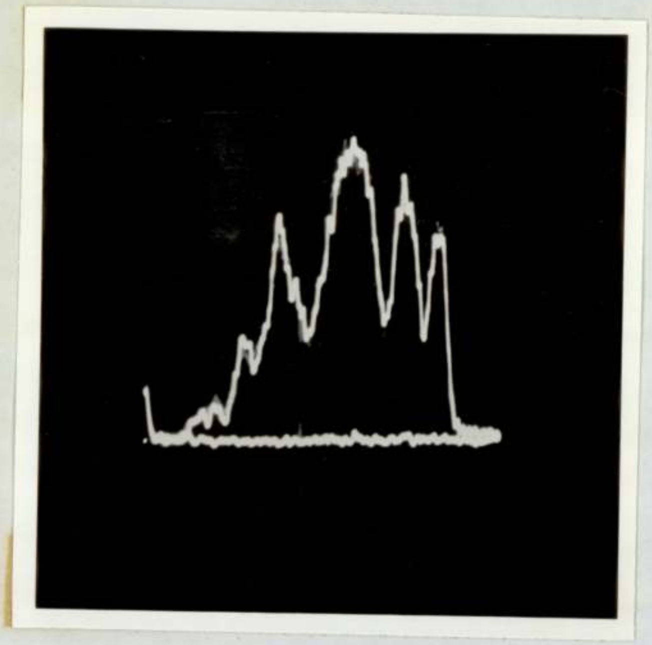


PLATE 12

No. 1 U.L.	Bravoite having partial rim of pyrite. Trains of inclusions of unknown type. X2000.
No. 2 U.R.	Nickel X-Rays electron picture. Note lesser concentration along lower boundary, but slight increase at extreme edge.
No. 3 C.L.	Nickel X-Ray trace.
No. 4 C.R.	Iron X-Ray trace. Note greater iron where nickel decreases along pyrite boundary.
No. 5 L.L.	Cobalt X-Ray picture. No variation in cobalt can be detected.
No. 6 L.R.	Cobalt X-Ray trace. Concentration appears to increase towards the centre, but the crystal is so small and the concentration so low, that background effect is noticeable.







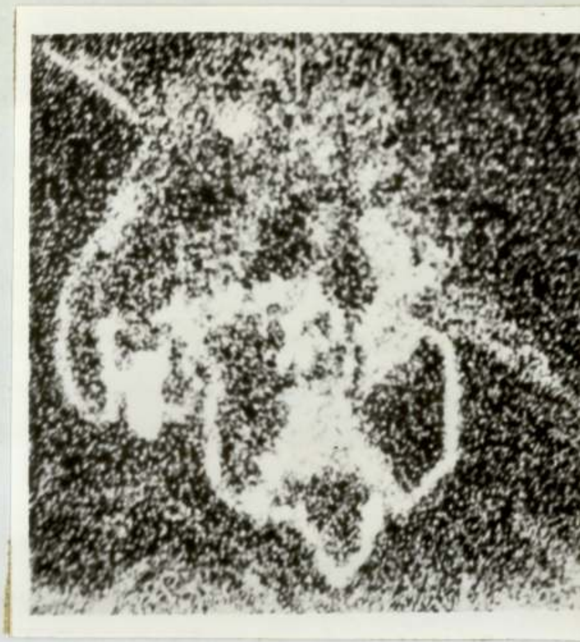
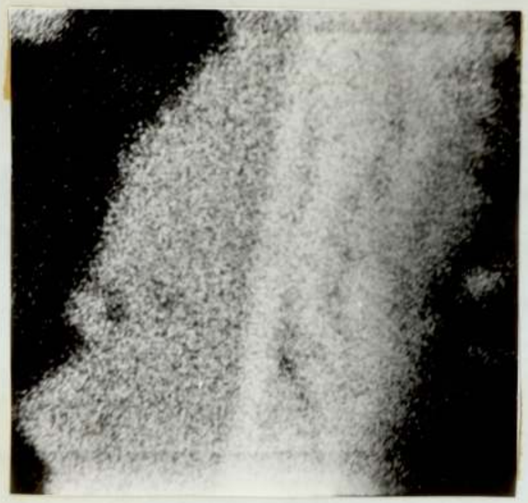
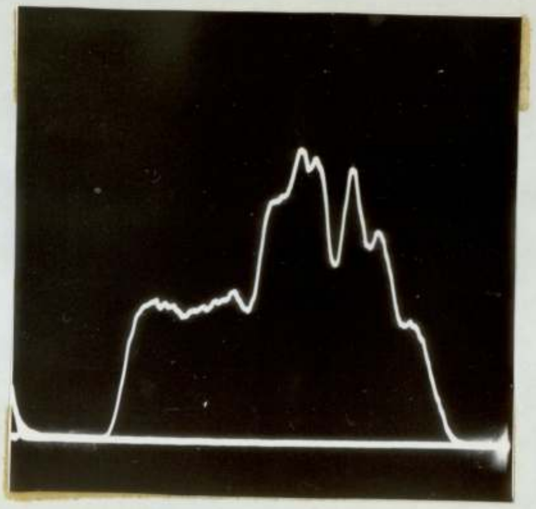
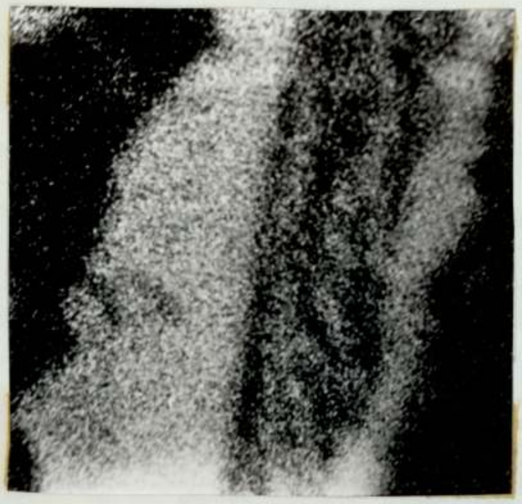


PLATE 13

No. 1	U.L.	Nickel X-Ray picture of specimen in Plate 6, Nos. 1 and 2. Notice break in outer nickel zone, with a diffuse region of nickel of lower concentration situated in the marcasite. X250.
No. 2	U.R.	Iron X-Ray picture. X250
No. 3	L.R.	Nickel X-Ray trace from right to left across the specimen.
No. 4	L.R.	Nickel X-Ray picture of specimen in Plate 8, showing sinuous nickel rich band. X250.







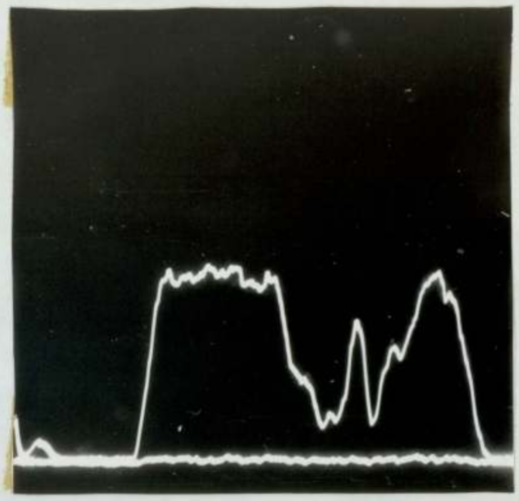
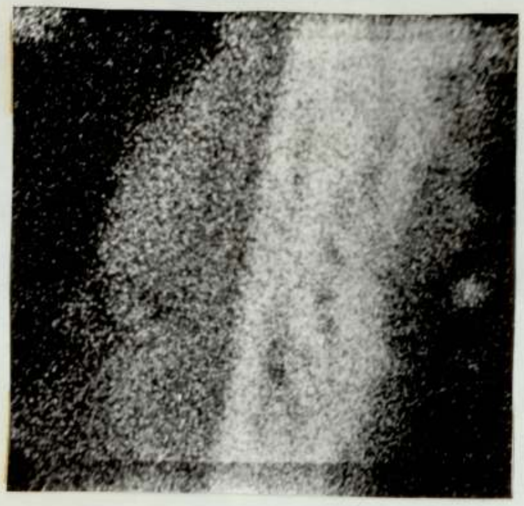
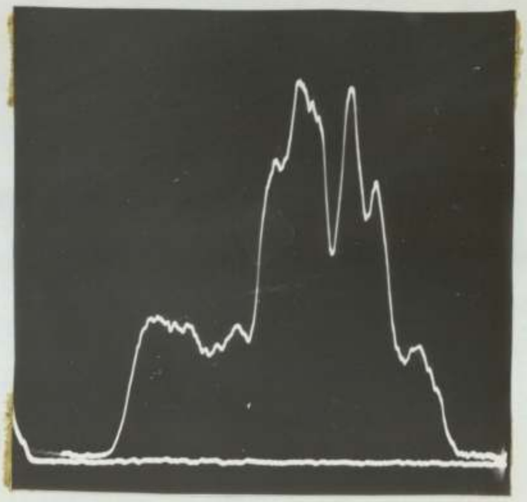


PLATE 14

No. 1 U.L.	Sulphur X-Ray picture of specimen similar to that in Plate 9, No. 2. Note central region, and boundary regions.
No. 2 U.R.	Sulphur X-Ray trace.
No. 3 L.L.	Arsenic X-Ray picture
No. 4 L.R.	Arsenic trace.





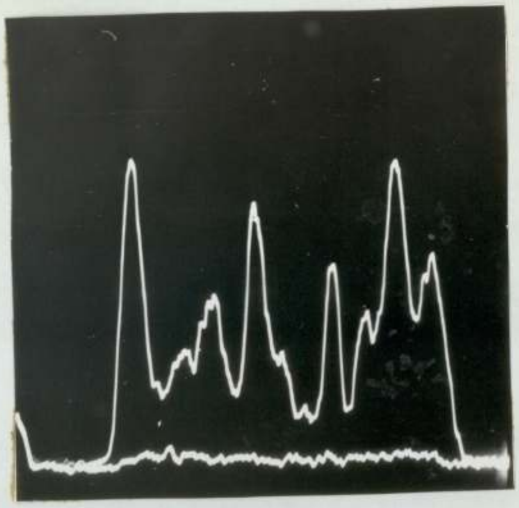
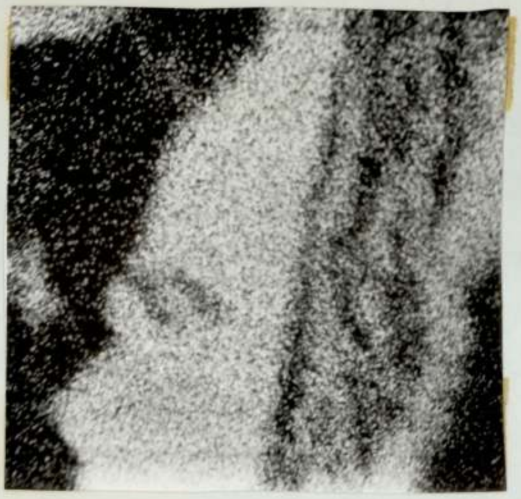


PLATE 15

No. 1 U.L.	Iron X-Ray picture of specimen similar to that in Plate 9, No. 2.
No. 2 U.R.	Iron X-Ray trace.
No. 3 L.L.	Nickel X-Ray picture.
No. 4 L.R.	Nickel X-Ray trace.



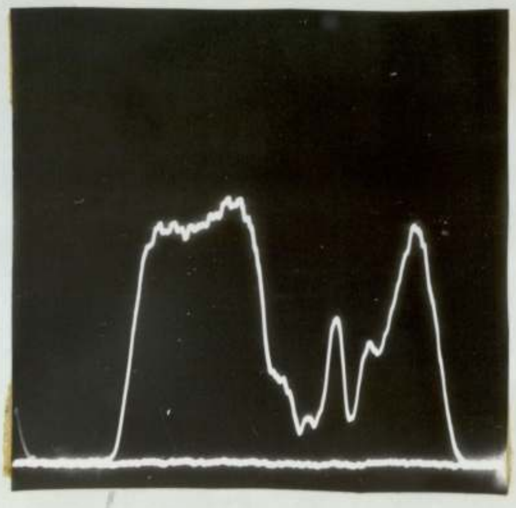


PLATE 16

No. 1 U.L.	Cobalt X-Ray picture of specimen similar to that in Plate 9, No. 3.
No. 2 U.R.	Cobalt X-Ray trace

CHAPTER 6

ELECTRON MICROPROBE

6.1 Introduction

A Cambridge Mk V electron probe microanalyser was used to analyse material from fifteen sites in Derbyshire, one site in the Mendips, and one site in the Alston Block, North Pennines.

27 quantitative and 25 qualitative measurements were made by the author using a voltage of 15Kv and specimen current of 100 mA for the first 29 analyses and a tube voltage of 20 Kv and a specimen current of 100 mA for the remaining 23 analyses. The standards used were metallurgical ones consisting of the pure elements for iron, copper, nickel, cobalt and arsenic, and zinc sulphide for sulphur.

Many of the specimens analysed were less than 10μ across, and they included zones narrower still. In these circumstances, the actual depth of crystal in to which the electron beam penetrated was very small and in fact may be less than the actual depth to which the beam penetrated. This occasions errors in the results since the intensity of X-rays generated is reduced, but cannot be allowed for in the calculations.

Results lying in the range 96.5% to 103.5% were used and are tabulated under three headings,

Nickeliferous pyrites and bravoites	Table 2
Nickeliferous marcasites	Table 3
Arsenical nickel/cobalt/iron sulphides from Tynebottom limestone	Table 4

The results in Tables 2 and 3 were recalculated to 100% and plotted on triangular diagrams firstly as plots of composition be weight of sulphur, iron and nickel/cobalt, Figs 5 and 8, and then as plots of composition by molecular proportions of FeS_2, NiS_2, and CoS_2, with a greatly exaggerated scale in the CoS_2 direction. The analyses quoted by Bannister Table 1 are also plotted for reference on Fig. 6.

The percentage of sulphur recorded was in the majority of cases rather higher than that reported by previous workers on these iron/nickel/cobalt sulphides. This is believed to be due to the use of a zinc sulphide standard rather than the more usual iron pyrites one. The relative proportions of iron, cobalt and nickel are unaffected.

Table 2 Ni Pyrites and Bravoite

Designation	S%	Fe%	Ni%	Co%	Total	Notes
B	55.99	53.162	12.266	-	101.424	Pale Brown
C	55.61	29.575	11.400	0.206	96.800	Pale Brown
D	51.85	35.252	10.071	-	97.173	Very Pale Lilac
E_1 Plate 11	57.19	20.397	24.827	0.092	102.510	Centre Brown
E_2 No. 4.	56.90	35.384	9.659	-	101.952	Edge Purple
E'_1	57.09	24.173	20.408	0.046	101.722	Centre Brown
E'_2	56.44	35.941	7.604	0.011	99.997	Edge Purple
G	55.85	31.983	10.607	0.286	98.726	Centre
K_1	51.72	29.729	14.588	0.905	96.951	Inner Brown
K_2	48.91	34.523	12.127	0.451	96.020	Outer Brown
L_1	51.19	32.359	13.012	-	96.585	PurpleCentre Zone
L_2	51.13	38.098	8.538	-	97.770	Purple Outer Zone
L_3	54.12	35.949	5.994	-	96.072	Purple Middle Zone

ELECTRON MICRO-PROBE ANALYSES

Collection sites of specimens probed are given below.

Table 2 Nickeliferous pyrites and Bravoite

Specimen designation	Location
B	Dirtlow Rake 7
C	Dirtlow Rake 8
D	Dirtlow Rake 9
E	Near Winster
G	Near Winster
K	Dirtlow Rake 1
L	Shuttle Rake 2

Table 3 Nickeliferous Marcasite

Specimen designation	
A	Dirtlow Rake 1
F	Near Winster
F'	Near Winster

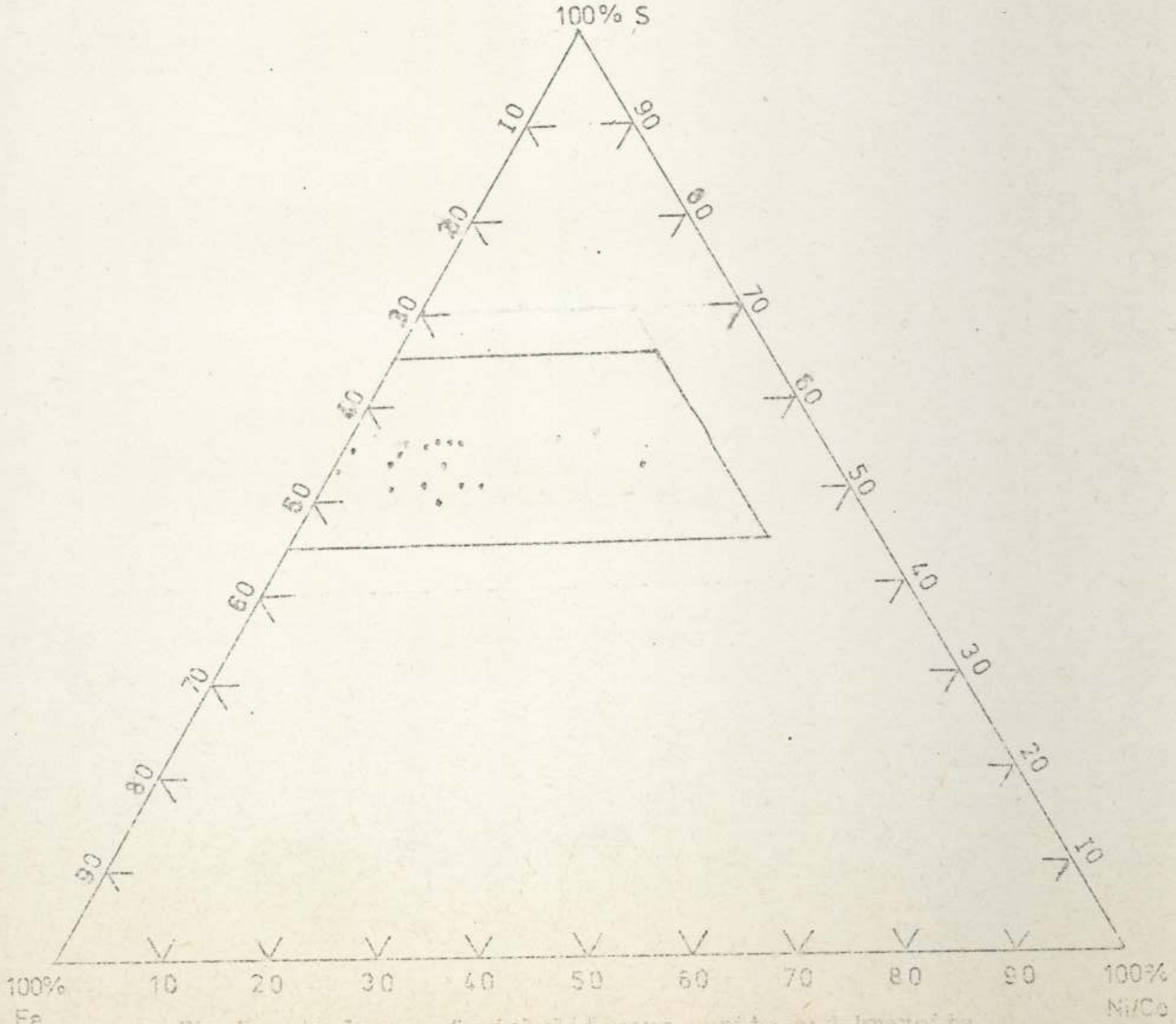


Fig 5. Analyses of nickeliferous pyrite and bravoite.

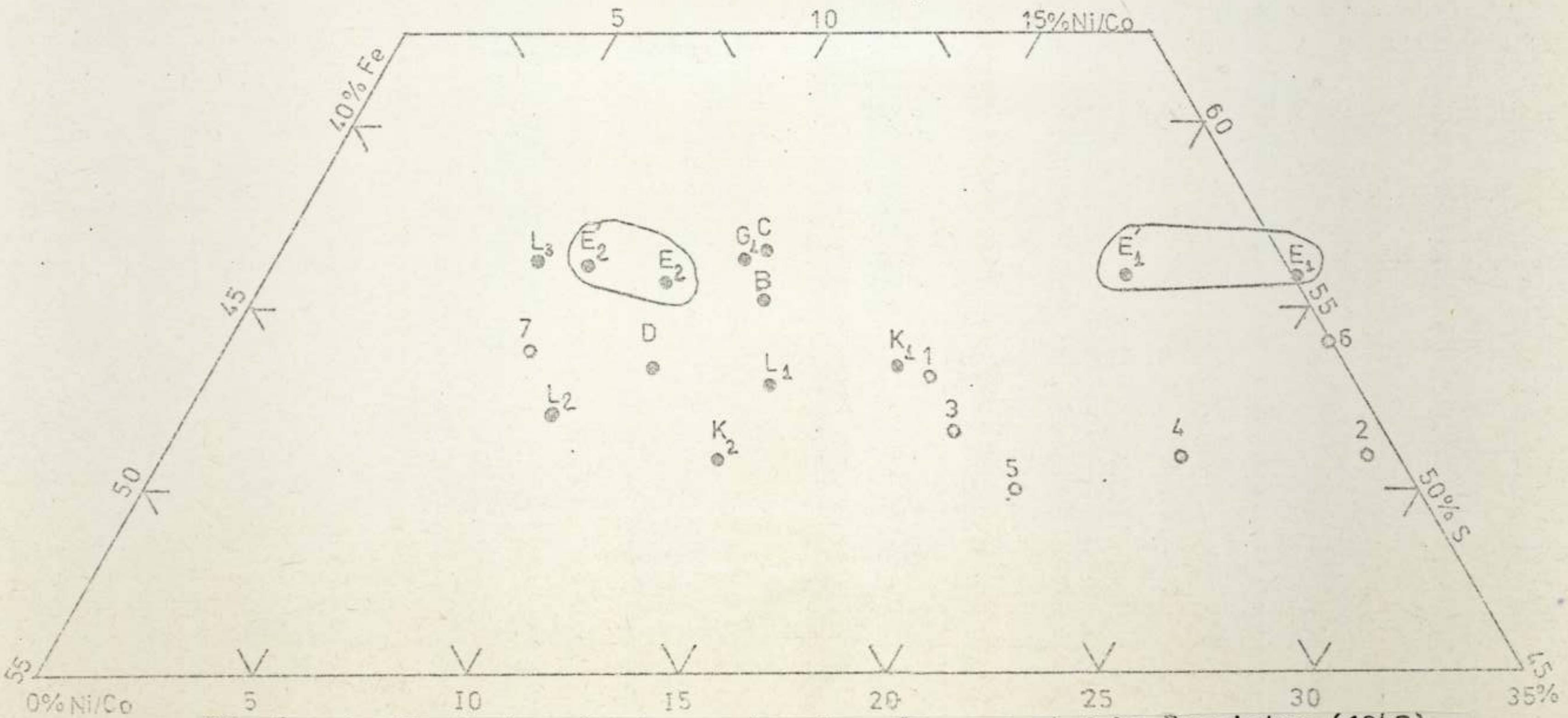


Fig 6. As Fig 5 also showing numbered analyses quoted by Bannister (1940).

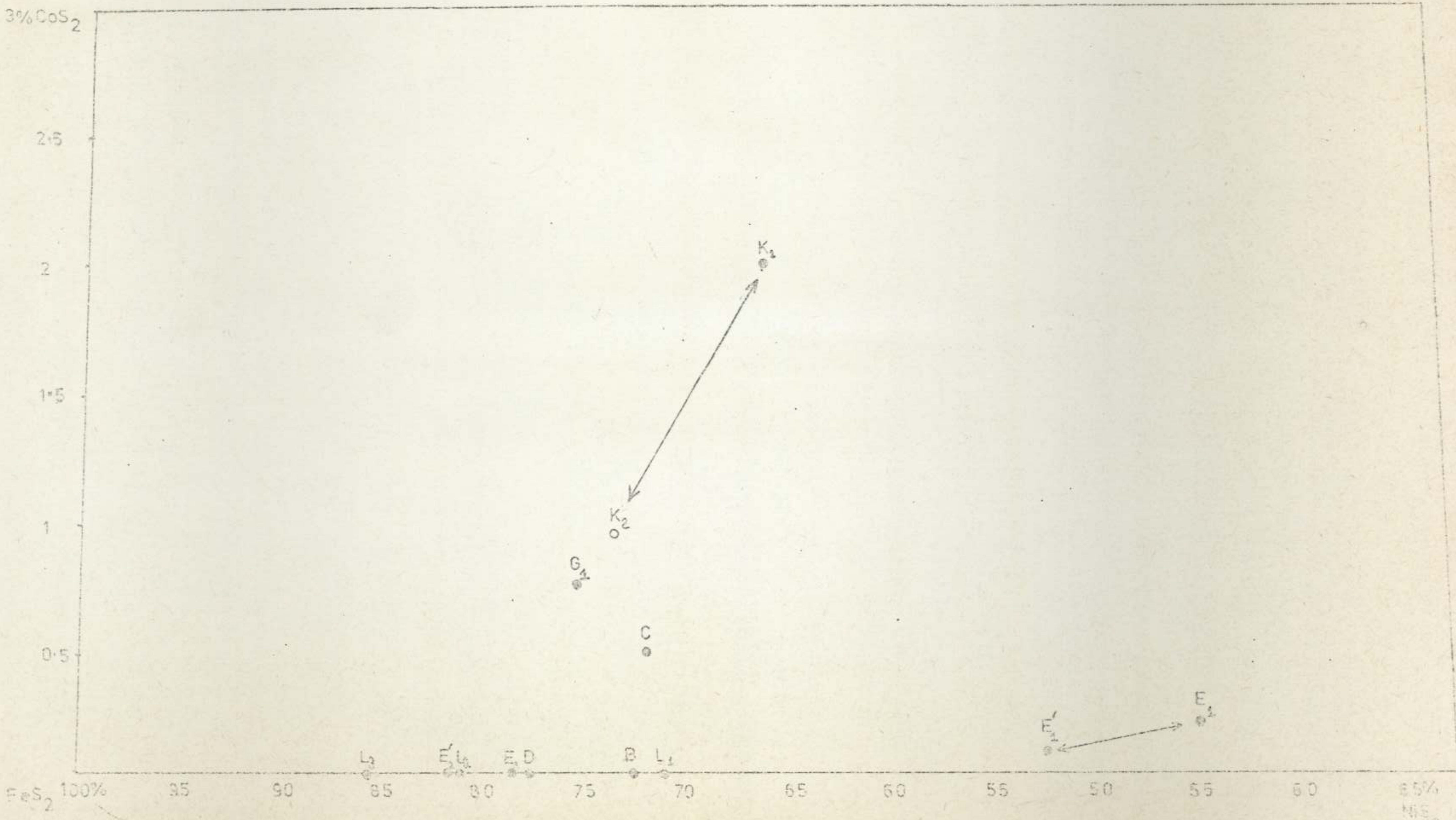


Fig 7. Analyses of nickeliferous pyrite and bravoite as nickel, iron, and cobalt sulphides.

6.2 Nickeliferous Pyrite and Bravoite

Analytical results are presented in Table 2 for 8 crystals obtained from seven different localities in Derbyshire. Fig 5 shows the general field occupied by these results. The modal value for nickel/cobalt concentrations was around 12%, with a maximum value of 24.9%, the modal value for cobalt alone being around 0.15%.

Results for specimens B, C, D, G, were single valued, these being very small, either non-zoned, very faintly zoned, or zoning so close together as to be outside the resolving capabilities of the electron probe.

Results for specimens E_1, E_2, E_1', E_2', K, L, were multi-valued, being values for different colour zones in each specimen. In the case of specimen E two crystals on the one polished section were probed, designated E and E' respectively. The maximum nickel/cobalt values are plotted on Fig 6 and lie relatively close to each other at around 23%. The correlation between the minimum values of the E crystals, at around 8%, is also shown on Fig 6.

The colours of the crystals and included zones cannot be correlated with composition except for a general tendency towards a lower reflectance as the percentage of iron decreases. Table 2 illustrated that nickel/cobalt concentrations above about 12% produced a tendency towards brown, becoming darker with decrease in iron.

The specimen pictured in Plate 3, No. 2, and the associated nickel X-Ray picture, Plate 11, No. 1, illustrates the correlation between reflectance and nickel concentration.

The correlation between maximum nickel concentration shown by two sets of adjacent crystals, E and E', are evidence to support Vaughan (1969) who stated that zoning is probably the result of very local variations in conditions.

Fig 7 illustrates the general increase in cobalt found to occur with an increase in nickel.

6.3 Nickeliferous Marcasite

Analytical results are presented in Table 3 for 3 crystals from 2 different localities in Derbyshire. Fig 8. shows the general field occupied by these results, which fall into two well-defined areas, that had modal values of nickel/cobalt concentrations of 4% and 26% respectively. Fig. 9 plots the nickel/cobalt values.

Specimen A was classed as a marcasite because it exhibited marked pleochroism cutting across the colour zone boundaries. Specimens F and F' occurred in massive calcite within 3000μ of each other. Crystal F is illustrated in Plate 6, Nos. 1 and 2, and F' in Plate 8.

Plate 6.1 shows the nickel-rich streak seen faintly and marked X in a violently anisotropic region as shown by the photographs taken with polars crossed and uncrossed respectively.

Specimen F'; Plate 8, Nos. 1 and 2, polars crossed and uncrossed respectively, shows a coloured banding cutting the anisotropic boundaries, and which showed on the nickel X-ray picture Plate 13, 4; the coloured streak contained 5.98% nickel and no cobalt, and the violet regions marked 2 on plate 8, 6.385% nickel and no cobalt. The dark coloured central part marked 1 on Plate 8, No. 1, has an approximate nickel content of 29% corresponding with the 28.8% nickel of the central zone of crystal F.

The Nickel X-ray photograph Plate 13 No. 4, appears to show nickel delineating crystal boundaries. The author is hesitant to suggest this depicts some form of migration of nickel from an excessively rich nickel core towards the boundary, assuming a nickel concentration of 29% is unstable.

Table 3 Nickeliferous Marcasite

Designation	S%	Fe%	Ni%	Co%	Total	Notes
A	53.29	43.010	1.574	-	97.876	Faint Zoning
F_5	54.92	43.964	0.450	-	99.343	
F_2	51.79	20.628	25.285	Trace	97.716	Brown
F_3	53.78	36.948	6.471	Trace	97.217	
F_6	51.75	14.744	28.881	1.244	96.623	
F'_1	53.68	40.165	6.385	-	100.232	Centre Deep Violet
F'_2	53.37	38.776	5.984	-	98.135	Coloured Streak
F'_3	51.67	47.069	0.133	-	98.860	Uncoloured Region

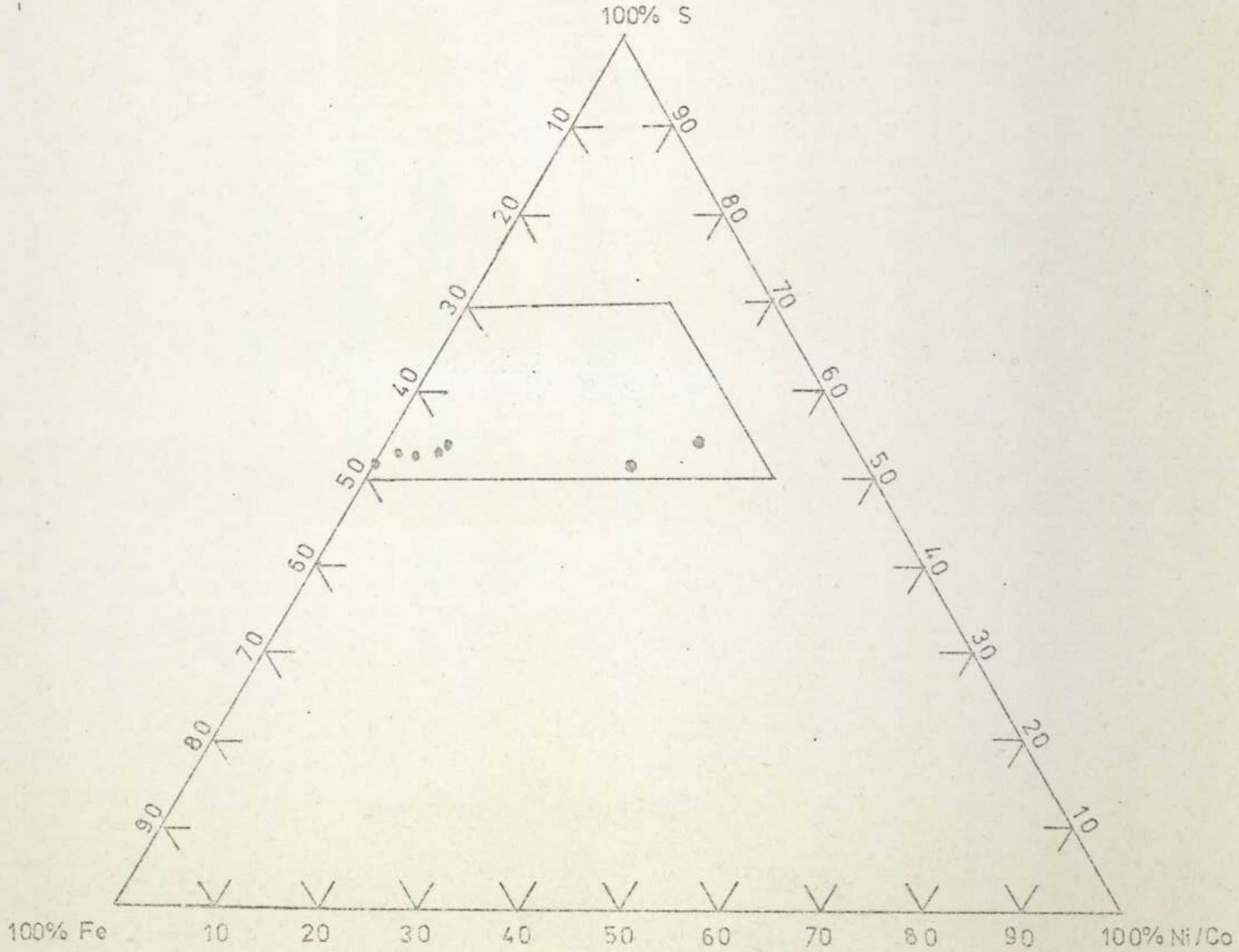


Fig 8. Analyses of nickeliferous marcasite.

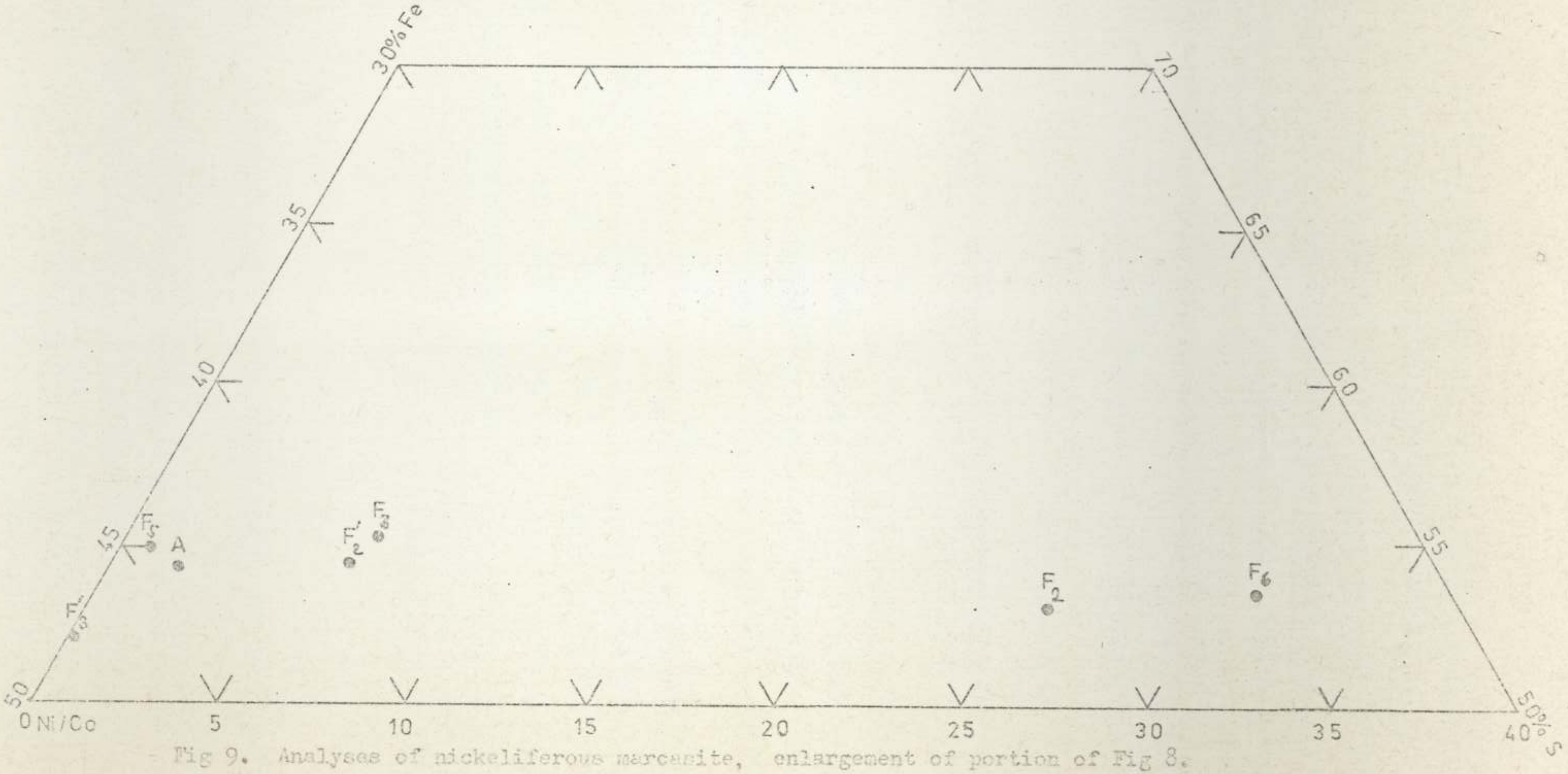


Fig 9. Analyses of nickeliferous marcasite, enlargement of portion of Fig 8.

6.4 Arsenical nickel/iron/cobalt sulphides, Alston Block

Arsenic rich sulphides were found in pieces of Tynebottom Limestone near Garrigill, which exhibited a characteristic pink cobalt bloom. Optical examination revealed bundles of sheaf-like anisotropic crystals, each crystal bounded by a narrow rim of anisotropic pale yellow material. The central part of each crystal was much fractured, and frequently bent. Chemical analysis of whole sample showed 38.2% arsenic, and the electron probe results are presented in table 4. Sulphur, Arsenic, Iron, Nickel and Cobalt X-ray traces are shown, together with the respective X-ray pictures. Plates 14, 15, 16.

The analyses fall into two groups, high arsenic, around 45% and low arsenic around 8.5%. High arsenic occurs with high cobalt and nickel, and vice-versa. In the low arsenic group, sulphur at 46.5% is over twice the value in the high arsenic group. In the low arsenic group iron is high at 39.8% whereas in the high arsenic group it is lower and variable, and antipathetic towards cobalt and nickel.

It is inferred that there are probably two or more phases present. X-ray diffraction studies demonstrated the presence of marcasite. The phases containing the high cobalt and nickel are as yet unidentified.

Table 4 Arsenical Nickel/Cobalt/Iron Sulphides.

Designation	S%	As%	Fe%	Ni%	Co%	Total
51	20.64	45.689	12.037	2.217	22.025	102.616
53	20.02	46.697	4.857	19.277	11.448	102.301
55	21.93	43.979	9.856	5.795	21.055	102.622
56	21.13	31.395	19.215	6.589	21.394	99.723
52	46.671	8.597	39.833	1.244	3.336	99.682
54	46.443	8.676	39.770	1.144	3.754	99.788

6.5 Bornite, Odin Mine

A semi-quantitative probe analysis of a brown isotropic phase revealed the presence of copper and suggested the presence of bornite. (See Plate 5, No. 2.)

CHAPTER 7

CONCLUSIONS

Main Research Findings

From the results of this research and the literature search, it is confirmed that bravoite and nickelian pyrite are common accessory minerals in the majority of Mississippi Valley Type low temperature hydrothermal deposits. (Heyl, 1956).

Previous Research

Examination of the literature revealed two main associations of bravoite, 1) Magmatic associations where it occurred as an alteration product of pentlandite. 2) Low temperature hydrothermal associations where it occurred as an accessory mineral in the Mississippi Valley type and 'Red Bed Sandstone' type deposits.

Nomenclature

Nomenclature of nickel iron cobalt sulphide is very unsatisfactory and one based entirely on appearance is proposed.

Distribution

Bravoite and nickeliferous pyrite are found commonly throughout all the mineralised areas of Derbyshire and the Askrigg Block of the North Penninnes. They occurred more rarely in the Mendips and the Alston block of the North Pennines, and the Shelve area of Shropshire. An examination of one specimen from Strontian, Scotland, revealed a zoned nickelian pyrite.

Nickel Concentration and Geographical Location

No significant correlation could be found in the Derbyshire Dome between nickel concentration in the iron sulphides and geographical location. Apart from confirming a general tendency towards a coarse overall calcite, barite, fluorite zoning, no evidence to support Mueller's hypothesis concerning the subdivisions of the fluorite zone could be detected on the basis of fluorite colour or of concentration of pyrites.

Bravoite Host Minerals

Bravoite and nickelian pyrite, and more rarely, nickelian marcasite occurred equally in calcite, fluorite, and barite, and much more rarely in quartz, galena, chalcopyrite and sphalerite. They are frquently found as many minute (5μ to 50μ) crystals in calcite, fluorite or barite which is otherwise completely devoid of other mineralisation.

Bravoite Physical Properties

Nickel cobalt pyrites exhibited a range of colours ranging from pale yellow through lilac, violet and purple to brown of varying shades and saturation. Electron probe studies enabled a subjective assessment of the reflectance to be correlated with nickel/cobalt content, but no correlation could be arrived at between colour and nickel cobalt composition. However, in general, the deeper the colour, the less the iron content. This agreed with other worker's findings (Vaughan, 1969).

They exhibited diverse habits and zoning patterns, often zoned and un-zoned crystals co-existing together, except when as inclusions in a single non-metallic crystal. The 3,4,5,6, and 8 sided figures exhibited by the crystals and the complicated zoning patterns are all derived from different sections of the basic pyritohedral form.

Bravoite Solid Solution Series

No major discontinuity in the iron nickel/cobalt solid solution series between a nickel/cobalt content varying between 0% and 25% could be detected. The concentration of results for nickel cobalt concentration between 6% and 15% probably reflected the choice of the deepest coloured specimens for electron probe examination. In general nickel and cobalt exhibited a sympathetic relationship, cobalt not usually coming in until the nickel content reached greater than 15%.

Nickeliferous Marcasite

Certain nickel rich iron sulphides varied from weakly to violently anisotropic and were identified as nickeliferous marcasite. Colour zones cut directly across crystal or twin boundaries delineated by the anisotropic boundaries, and in certain specimens sinuous violet coloured bands were superimposed on apparently normal marcasite crystals, and enclosing one or more highly nickeliferous, (up to 65% nickel cobalt sulphides), centres. Further investigation is needed to determine the structure and nature of these apparently anomalous findings.

Nickeliferous Arsenical Pyrites

An arsenic rich nickel iron cobalt sulphide was found in the North Tyne Valley in Tynebottom Limestone of the Alston Block. Micro-probe analyses revealed the presence of two phases, with arsenic and nickel cobalt showing an antipathetic relationship. X-ray diffraction showed the presence of marcasite, but the presence of other cobalt and nickel rich phases are suspected. Further work is necessary to resolve this problem.

Paragenesis

In every specimen of a nickel cobalt iron sulphide examined, bravoite or nickeliferous pyrite was always the earliest metallic phase, preceeding pyrite and marcasite. This paragenesis confirmed that of Ixer (1974).

Owing to the obvious limitations of the study it is impossible to say definately whether bravoite mineralisation could be used as a pointer towards locating economic deposits of lead and zinc, since all the collecting was carried out in areas rendered accessible by previous mining activities for these minerals. The existence of bravoite in other areas has not been conclusively disproved, but failure to detect the iron/nickel sulphide otherwise than in material associated with mineralised vein material was suggestive that the hydrothermal fluids, when mineralised conveyed simultaneously all the mineral species without selection and distributed them all in a fairly uniform manner in the now mineralised areas.

Economical Exploitation

There is no possibility that either cobalt or nickel are present in anything approaching economic quantities.

APPENDIX A REFERENCES

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THE DISTRIBUTION AND PARAGENESIS OF LOW TEMPERATURE NICKEL/IRON/COBALT SULPHIDES IN CENTRAL BRITAIN

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the degree of

Master of Philosophy

in accordance with the special regulations

of

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by

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CONTENTS

ABSTRACT

The previous literature on the nickel cobalt species and particularly bravoite is reviewed. The major associations of bravoite are 1) As an alteration product of pentlandite and 2) As a low temperature hydrothermal mineral commonly found within the Mississippi Valley Type deposits and a 'Red Bed Sandstone' type deposit.

An investigation of the occurrence and paragenesis of low temperature species of this type in the Central U.K. has been carried out. The areas covered were the lead-zinc mineralised deposits of Carboniferous Limestone in Derbyshire, North Pennines, the Mendips and additionally the mineralised Ordovician of the Shelve, Shropshire. The main minerals found were galena, sphalerite, chalcopyrite, pyrite, marcasite,bravoite, goethite, and very rarely nickeliferous marcasite. The non-metallic minerals, here referred to as 'gangue', were calcite, fluorite and barite. The bravoite was found mainly in the gangue as small inclusions.

Bravoite was found to occur throughout virtually all the low temperature lead, zinc, calcite, fluorite assemblages characteristically less than o.1% and rarely greater than 1% of it. Size, colour range and zoning characteristics are described but apart from vague similarities, no definate correlation between geographical location and appearance of the bravoites can be detected. The mineral paragenesis shows it to be the first mineral precipitated.

The optical properties of the bravoites are described and 13 quantitative electron probe analyses of bravoites from 6 localities are presented. Total nickel content ranges from 5.99 to 24.8 weight percent. The bravoites do not show any regional zoning, and are generally cobalt poor, not greater than 0.9%.

The optical properties of the nickeliferous marcasites are described and 8 quantitative electron probe analyses of the nickeliferous marcasites from 2 localities are given. No regional zoning is found, and the nickel content ranges from 0.1 to 28.8 weight percent. Maximum cobalt is 1.2 %.

An anisotropic arsenic-rich nickel/iron/cobalt mineral exhibiting a number of phases, from the Tynebottom Limestone of the Alston Block is described, and 6 electron probe analyses are presented. The chemical analyses are consistent with the phases being Nickel Iron Cobalt Arsenic Sulphides.

CHAPTER 1

INTRODUCTION

Hillebrand, (1907), whilst studying small isometric crystals associated with the vanadium ores of Minasragra, Peru, discovered a pyrite like mineral which contained 18.23% nickel. After a complete analysis he assigned the fomula $(FeNi)S_2$, and suggested the name Bravoite, after Senor Jose Bravo, a mining engineer, who had described the remarkable vanadium occurrence. Later Hewitt (1909), in a general description of the same ores showed a photo-micrograph of a polished surface in which the roughly square outlines of bravoite crystals (1-1.5mm) appeared to stand out in moderate to strong relief from a soft ground mass of patronite, VS_4.

Buddington (1924), identified a nickel iron sulphide from the vicinity of Chitina, Alaska, which corresponded to the bravoite of Hillebrand. The Alaskan material contained substantially more nickel than iron. (Table 1 No. 5.) Kalb and Meyer (1926), studied polished sections of a crushed ore from Mechernich, Germany, and observed small isometric crystals with a cross section which indicated a pyritohedral habit, and exhibited distinct zonal banding. Yellow-poor bands were nickelian pyrite, whilst steel-grey bands containing 3.28% cobalt, 24.73% nickel and 17% iron were classed as bravoite. (Table 1 No. 2.) This material was later X-ray diffracted by De Jong and Willems (1927) who determined the cell edge and the pattern to be of pyrite type. (Table 1. No 7.)

The first British report was by Bannister (1940) who described bravoite from Mill Close Mine, Derbyshire. Table 1. No. 1 shows the mineral contained 16.69% nickel. The specific gravity, 4.82, was higher than both the Peruvian and Alaskan material. Bannister also described a pinkish grey granular mixture of bravoite which surrounded pyrite and which had a 12% nickel content. This bravoite gave double lines on X ray powder photographs, and the same cell edge as the Mechernich material that contained 24.73% nickel. Bannister suggested that the double lines indicated that the material was a mixture of pyrite and bravoite and that if this bravoite contained the same proportion of nickel (24.73%,) as the Mechernich bravoite, a mixture of 43% bravoite and 57% pyrite was needed to yield the overall 12% nickel content.

By 1945 there were sufficient analyses for Kerr to propose a system of nomenclature for the iron nickel cobalt sulphides of the pyrite type.

Table 1. - Analyses of bravoite, after Bannister (1940)

	1	2	3	4	5	6	7
Fe	29.30	17.08	29.46	25.19	20.68	38.54	.
Ni	16.69	24.73	18.23	25.42	24.81	6.50	45.6
Co	trace	3.28	trace	0.35	--	--	
S	53.40	51.15	52.31	49.04	54.51	51.39	54.4
Totals	99.39%	95.24%	100.00%	100.00%	100.00%	96.43%	100.00%

1. Mill Close Mine, Derbyshire
2. Mechernich, Prussia
3. Minisragra, Peru
4. Main Creek, Tasmania.
5. Canyon Creek, Alaska.
6. Nickeliferous Pyrite, Denison Mine, Sudbury, Ontario.
7. Artificial nickel disulphide, de Jong and Willems (1927)

CHAPTER 2

BRAVOITE NOMENCLATURE

2.1 Nomenclature Presently Employed

RS_2 sulphides of pyritohedral symmetry with varying amounts of nickel, cobalt and iron forming an isomophous series have been described under the names of pyrite, nickelian pyrite and bravoite. Where minerals belong to isomorphous groups, the distinction between species of like structures is of course arbitrary and problems of nomenclature arise. Palache, Berman and Frondel (1944), in their review of the series NiS_2-FeS_2 proposed to apply the name bravoite only to members which contained more nickel than iron. Specimens which contained less nickel than iron would be termed nickeliferous pyrite. Under this system of nomenclature, the original bravoite of Hillebrand, (1907), as well as samples high in nickel described by Henglein (1914), referred to by Doelter and Leitmeier (1926), and mentioned by Bannister (1940), would no longer qualify as bravoite but would be known as nickeliferous pyrite. It is assumed a parallel system would apply in the case of cobalt, and any member of the group with less cobalt, than iron would be cobaltian pyrite.

The usage suggested is somewhat at variance with the literature. Bravoite has been recognised in at least twelve well established localities. The work of Hillebrand, (1907), de Jong and Willems, (1927) Buddington and Bannister had established bravoite as a mineral with definate properties, isostructural with pyrite, but which contained substantial amounts of nickel. Thomson and Allen (1939), and Peacock and Smith (1944), recognised nickelian pyrite with smaller amounts of nickel. The line between the two has not been definately established, but Bannister classed material that had 36.3% Ni to 63.7% Fe, a ratio of nickel to iron of about 3 to 5 as bravoite, and

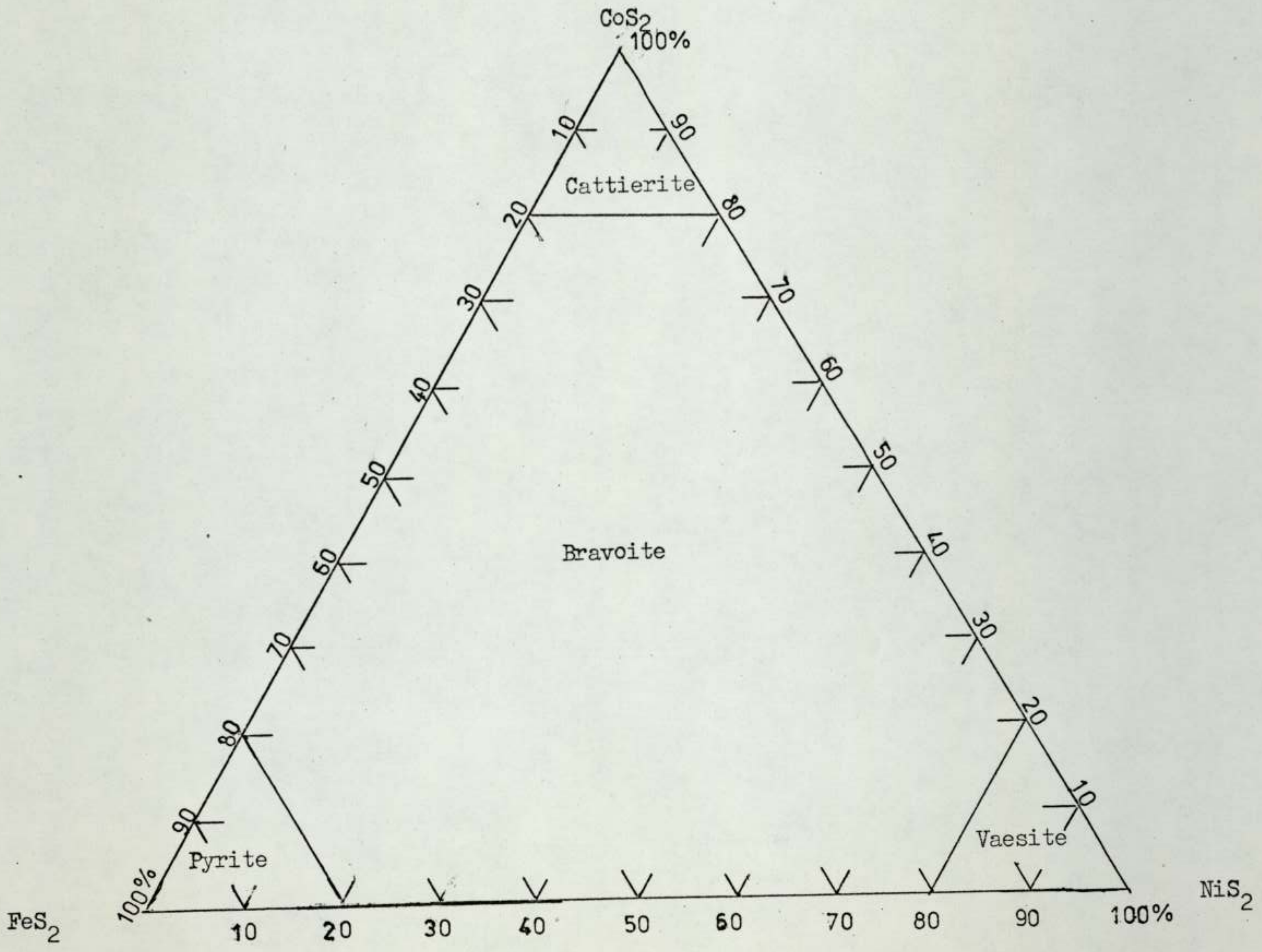


Fig. 1 FeS_2 NiS_2 CoS_2 triangular diagram. (After Kerr 1945) no objection has been expressed in considering material with a lower nickel content as bravoite. Even an excess above 20% Ni to 80%Fe would have a significance which would warrant more than adjectival description, particularly when accompanied by a definate change in lattice constant and physical properties.

The pure end members NiS_2 and CoS_2 are not known to occur in nature, but Kerr (1945) described minerals from the Belgian Congo, cattierite and vaesite, which had compositions close to the theoretical CoS_2 and NiS_2, Kerr proposed delineation of the end members at 80% Fe,Co or Ni, and left the composition of the centre of the triangular field as bravoite. See Fig. 1. The nomenclature proposed by Kerr left no place for nickeliferous (or cobaltiferous) pyrite, yet as Bannister, Vaughan (1969) and other workers had shown, a mineral intermediate between bravoite and pure pyrite having less than the 20% nickel proposed by Kerr, existed with its own characteristics and deserved a name. A satisfactory solution to the problem has not, to the author's knowledge, yet been devised.

2.2 Bravoite nomenclature employed in this research

A nomenclature based upon a knowledge of the chemical composition of a mineral derived principally through the use of the electron probe is unsatisfactory because it does not permit immediate assignment of a name. A system employing as its basis the observable optical and physical properties of the mineral is more satisfactory.

The system of nomenclature used in this reseach is based entirely on the appearance of the iron/nickel/cobalt sulphide. If the sulphide is isotropic, of high reflectivity and obviously coloured mauve, lilac, purple or brown, or zoned with these colours, with or without yellow, it is called bravoite. If the crystal is yellow with just a hint of another shade, often pink, or exhibits a zoning whose colour is distinguished from the yellow only with the greatest difficulty, it is designated nickeliferous pyrite. In the absence of any of these features, it is called pyrite. Electron microprobe analyses were consistent with this system.

No problem has arisen over the identification of nickeliferous marcasite.

CHAPTER 3

PREVIOUS RESEARCH

3.1 Recorded Associations of Bravoite and Related Sulphides

Bravoites have been found to have two main associations.

1. Magmatic
2. Low Temperature hydrothermal

3.1.1 Magmatic Associations of Bravoite

Bravoite as an alteration product of pentlandite was commonly found associated with native nickel iron alloys, (awaruite, souseite, and josephenite), in serpentinised peridotites and dunites of alpine type. Krishnarao (1964), listed localities including Switzerland where it was found, and gave a paragenesis.

Ramdohr (1969) listed localities where bravoite had been reported as an alteration product of pentlandite as Horbach, Schwarzwald; Campello Monti, Italy; Lillehammer, Evje, Rana, all in Norway; Mouat Mine, Montana, U.S.A.; Farm Vlakfontein, Magnet Heights, Mooihock, S. Africa. He also stated that bravoites that had developed from pentlandite only rarely showed distinct zoning, and occasionally exhibited an apparent but variable anisotrophy.

Michener and Yates (1944), discussed the oxidation of the primary nickel/iron sulphides, pentlandite, pyrrhotite, pyrite, chalcopyrite, and cubanite found in the ore bodies of the Sudbury, Ontario, district using weathered old drill core material. They confirmed that violarite was formed rapidly from pentlandite, and subsequently leached by further oxidation to haematite. In addition pyrrhotite altered to pyrite and marcasite, and took up nickel from the violarite leachate, and formed nickeliferous pyrite containing up to 2% nickel.

They stated that violarite was found in the pyrite marcasite ores which had replaced pyrrhotite but that its origin there was obscure. Nickeliferous pyrites and bravoites often exhibited radiating structures and hence Michener and Yates suggested this indicated these two minerals were supergene.

Unlike the findings of Heyl (1956), that in the Mississippi Valley type assemblage violarite was an oxidation product of millerite, at Sudbury, Michener and Yates found millerite replaced violarite, and they stated special conditions of oxidation prevailed leading to formation of millerite rather than limonite.

Lochhead (1955) described nickel bearing pyrite, marcasite, and bravoite, occurring in alteration haloes which extended up to 3 m either side of fractures in pentlandite $(FeNi)_9S_8$ and pyrrhotite $FeS_{1.14}$ in the Falconbridge ore deposit, Sudbury, Ontario. Because these occurrences extended to great depths, he regarded them as of hypogene rather than supergene origin. These fractures were generally filled with sphalerite, galena, marcasite, and carbonates, and he suggested they were apparantly the final phases of ore making solutions.

Andrews (1962) stated that small amounts of cobalt/nickel pyrites were found disseminated throughout the major pentlandite ore body of the Lynn Lake area, Manitoba, and Scott (1973), reported bravoite, violarite, smythite Fe_3S_4, pyrrhotite, and sphalerite, from Bird River, Manitoba, associated with argentian pentlandite, in massive sulphide deposits emplaced under the influence of regional metamorphism accompanying the main orogeny of the area.

From the same area, Thomson and Allen (1939), reported that the nickel sulphide "beyrichite", in a regionally metamorphosed norite, variously altered to a quartz diorite or a chlorite schist, from the Denison Mine, Sudbury, Ontario, was in reality a pyrite of varying nickel content, some with true pyrite colours, and either nickel free or nickel poor, other parts with a slightly violet tinge, and containing nickel in varying amounts upto 6.5wt.%. (Table 1, No. 6.) This nickeliferous pyrite is mixed very intimately with normal pyrite, and sometimes occurs as outer or inner zones in the pyrite crystals. The mixture, which is associated with quartz occurs chiefly as small aggregates or crystals in somewhat concentric arrangement with ore-free bodies of gangue, bands of ore alternating with bands of gangue. The authors stated that judging by the etch reactions it was possible there may be portions intermediate in nickel content between the two extremes. They suggest it may be a mixture of pyrite and bravoite. Their intermediate nickel content had 6½% nickel.

Krutov (1970), reviewed the special conditions which surrounded the formation of high cobalt and nickel concentrations in high temperature hydrothermal processes. He found that depending on temperature conditions, a characteristic ratio of cobalt to nickel was established, up to 1 in 4 under high temperatures, this appeared as widespread cobalt bearing pyrite. Where a high cobalt and nickel content co-existed together he believed the metals to be extracted from the host rock, for example the large copper pyrite deposit Outukumpu, Eastern Finland. He discussed the behaviour of cobalt and nickel during metamophism of previously formed pyrite deposits, from the least metamorphosed deposits (Northern Caucasus, Urals) to the most metamorphosed deposits (Rammelsberg), the cobalt content of the pyrite increased from 0.001% or 0.01% to 1% or more. Simultaneously there was an increase in cobalt/nickel ratios from 1:4 to 12:1.

Ewers and Hudson (1972) described an ortho-magmatic nickel iron sulphide mineralisation at Kambalda, Western Australia and produced data which indicated that immiscible sulphide/oxide liquids solidified at 1140°C from which pyrite was the first sub-solidus mineral to crystallise at about 400°C and grew to give bands and subhedra near the top of the massive ore, (with rejected nickel and iron diffused away) cobalt was preferentially concentrated in this pyrite and depleted from the surrounding sulphide. Pentlandite exsolving at lower temperature, however, competed favourably with late forming pyrite for available cobalt. Nickel was low in the early pyrite, but concentrated in pyrite formed at lower temperature. Thirtyone electron probe analyses revealed 0.5% to 3% cobalt but low nickel in the early formed pyrite, whereas late pyrite grains showed 0 to 1.5% cobalt and upto 3% nickel. A tendency for zonation in nickel rich pyrites was pointed out by Woodall et al (1966), grains having relatively cobalt poor and nickel rich rims. The authors found pyrrhotite contained 0.5% nickel throughout the ore zone and that some pentlandite was altered to violarite.

Blockley (1972), stated that minerals found in the Gurkha ore body, Northampton mineral field, Western Australia, were galena, pyrite, and marcasite. A specimen of marcasite and pyrite assayed 0.45% nickel and suggested the presence of pentlandite; but possibly the presence of bravoite.

3.1.2 Low Temperature Hydrothermal Associations

Ramdohr gave a selection of localities where bravoites precipitated from low temperature hydrothermal solutions are found, Mechernich, Eifel; Wissen and Grunau, Siegerland; Fredericktown Missouri; Cape Thinnes, Lancaster Co, Pa, U.S.A.; Mina Ragra, Peru; and several occurrences in the Bushveld Igneous Complex, Transvaal, S. Affica.

For the purposes of this research, low temperature hydrothermal occurrences of bravoite have been subdivided into two:

1. Mississippi Valley Type.
2. Red Bed Sandstone Type

3.1.2.1 Mississippi Valley Type

The main features of Mississippi Valley deposits were summarised by White (1968). The mineralogy of the deposits is generally simple. Galena and sphalerite are the commonest sulphides; pyrite, chalcopyrite marcasite and wurtzite are widespread but in smaller amounts, and other sulphides containing Cu, Co, Ni, Ag, and Hg occur locally (Heyl and others, 1959; Hagni and Graw 1964). Dolomite, calcite, barite, fluorite, chalcedony and quartz are the commonest gangue minerals. The ores contain J-type lead which is enriched in the radiogenic isotopes relative to nonradiogenic Pb^{204}. Gold content is very low, and silver is generally low. Many of the ore deposits are strata-bound, occurring largely in carbonate rocks of Palaeozoic age but may occur in large fissure veins. Commonly only slight structural deformation of the host rocks has occured, either before or after ore deposition; however, faults, fractures, and open folds control most of the ore deposits in detail. The ores are generally considered to have been formed at depths in the order of 300 metres to 1000 metres, and temperatures of homogenisation of fluid inclusions are systematically low - from about 70° to 180°C.

Occurrences of bravoite in Mississippi Valley type ore deposits are now described.

Bravoite occurred in a mixed Fe-Pb-Cu-Ni-Co-Zn-Sulphide ore which occurred at Fredericktown, Missouri, in the shaly and glauconitic zone between the Lamotte sandstone and the Bonneterre dolomite of the Upper Cambrian. The sulphides occurred in layers, layered disseminations and displayed several geopetal structures, and these features and certain geochemical considerations suggest a diagenetic age for the sulphides. (Amstutz, et al., 1961, Amstutz, 1959; Amstutz and El Baz, 1962).

Here bravoite was associated with marcasite, siegenite $(NiCo)_3S_4$, pyrite, chalcopyrite, galena and a little fluorite. Euhedral bravoite crystals ranged in grain size from 1 to 30 microns and contained thin violet or lavender zonal bands from 0.5u to 5u in width. Rasor (1943) suggested that the bravoite was later than the siegenite, replacing it, or more commonly, replaced the pyrite.

Heyl (1956) was the first to realise that nickel minerals occurred in comparative abundance as accessories in the Upper Mississippi Valley zinc-lead district in south west Wisconsin, north west Illinois, as well as other localities in Wisconsin, Illinois, Missouri and Indiana. In south west Wisconsin millerite was the commonest nickel mineral and it was generally associated with violarite and bravoite. Because of its normal occurrence inside vugs in the central parts of veins, Heyl suggested millerite was deposited near the end of the main period of the primary sulphides. Violarite (Ni_2FeS_4) occurred as an alteration product of millerite, pseudmorphing it; and replaced chalcopyrite with which it was intimately associated. Bravoite was also intimately associated with violarite and with 'honnesite', ($NiSO_4$) a secondary oxidation product of primary millerite. Millerite was often peripherally altered to violarite and honnesite accompanied by bravoite, and Heyl believed all the nickel minerals were probably products of oxidation and secondary enrichment of millerite.

Ramsbottom (1962) mentioned the occurrence in two veins struck at depth in the Tansley, Ashover, Derbyshire borehole, of bravoite pyrite, millerite, pyrrhotite, chalcopyrite and sphalerite, the bravoite and marcasite was associated with pyrite, the bravoite occurred in sheath-like aggregates in a thin vein. The country rocks were limestones of low D_2 or high D_1 age, Visean and were associated with the Matlock lavas.

Following Bannister's identification of bravoite at Mill Close Mine (1940), Ramsbottom's discovery in the Fallgate borehole, and Vaughan's (1969) work, Ixer (1972), found Bravoite as the earliest hydrothermal sulphide occurring in all non-sulphide phases, at Clitheroe and in a fluorspar flat at Masson, Derbyshire. He described texture, zoning, reflectivity, and modal proportions and presented 4 micro-probe analyses showing nickel content from 12% to 18% and cobalt from 0.8% to 1.2%. The crystals were 10 to 30u across, zoned and exhibited a pentagonal dodecahedral habit. From the field evidence in Derbyshire and later Clitheroe, he suggested it was a characteristic primary accessory sulphide of the low temperature lead-zinc-barite-fluorite mineralisation.

A deposit designated as probably Mississippi Valley Type is described by Ashley and Creelman (1975), from Cooleman Plains, Southern New South Wales. The orebody occurred in weakly metamorphosed Silurian limestone or dolomite as bedded replacements or veins in a collapse breccia which contained a simple mineral assemblage of dominant quartz with sphalerite, galena, carbonates, barite, fluorite, and minor chalcopyrite, nickeliferous pyrite and cobaltiferous pyrite, marcasite and tetrahedrite. The pyrite formed about 1% of the total sulphides and occurred as fine grained to medium grained anhedra which contained, from micro-probe analysis, up to 1% nickel and 3.2% cobalt, with arsenic up to 0.8% showing an inverse relationship to cobalt.

This deposit bore certain similarities to that of the Shelve, Shropshire, except that there the mineralised rock was a brecciated, slightly metamorphosed flag and shale.

3.1.2.2. 'Red Bed Sandstone' Type

A further association of bravoite is within the mineralised 'Red Bed Sandstone' type deposits.

'Red Bed Sandstone' type deposits differ from 'Red Bed Copper' deposits in being enriched in lead, barium and nickel, and depleted in selenium, vanadium and uranium.

Boyle (1971), cited the occurrence of bravoite in pyrite in the 'Red 'Bed Magnet Cove of the lead-zinc-silver-copper deposits of the Walton Cheverie area, Nova Scotia. He gave a paragenetic sequence of pyrite chalcopyrite, sphalerite and galena, associated with barite and dog-tooth spar which filled later fractures.

The textures of the bravoite and associated marcasite in this deposit were divided into five varieties.

1. Small (50 to 100µ) zoned, nickel and cobalt-rich pyrite crystals replacing sandstone.
2. Large colloform masses, apparently representing a coelescence of type 1. These appeared as interbedded layers of pyrite and marcasite, some pyrite layers being nickel/cobalt-rich, others not. The marcasite contained little or no nickel. Associated with these colloform masses were subordinate galena, sphalerite, and covellite and later infilling and cross-cutting chalcopyrite.
3. Concretionary, tubercular, and zoned masses of continguous nickel cobalt rich spheres (buckshot pyrite). The spheres averaged 2 to 5 microns in diameter. The spheres replaced siderite, and had in turn been extensively replaced by galena and chalcopyrite.
4. Very fine botryoidal masses of pyrite with nickel cobalt rich colloform zones shown by electron probe analysis to be bravoite.
5. Individual spheres ranging from 10 to 20µ in diameter. They possessed a varied outline and generally had a nickel-rich core or zone.

He suggested the globular forms of nickel cobalt pyrite found amongst plant beds in this Series might be organic framboids of bacterial origin.

He postulated the nature of mineralisation as hypogene. Connate brines ascended from the Windsor evaporites at depth and stimulated by Triassic Volcanic activity, had leached out various elements from the sandstones above, and deposited them in chemically replaceable rocks and dilatant zones along faults.

Ageykin et al (1969), described an occurrence of bravoite in the Voronezh region, 55 Km south west of Moscow. A Permian cupriferous sandstone series overlies the Precambrian crystalline basement which contained numerous basic and ultra-basic nickel bearing intrusives. The mineralised sandstone was a coarse grained inequigranular rock of a quartz/feldspar composition of which 80% was angular or half rounded quartz, 8% was feldspar and a little mica, cemented by carbonate and sulphide. The sulphides accounted for 30 to 35% by volume of the rock and were composed of bravoite and pyrite, 55 to 60%, and arsenopyrite 10 to 12%. Euhedral to subhedral bravoite crystals (50µ to 1mm), showed distinct poly-zonal texture which becomes particularly clear on etching. The chalcopyrite, in allotriomorphic aggregates (0.1 to 3mm), or thin (10µ to 10mm) veinlets, frequently replaced the pyrite and bravoite.

Ageykin maintained the distinct stratification of the mineralisation and its confinement to the basal horizon of the sandy kaolin series was evidence of a sedimentary or sedimentary infiltrational origin of the copper and nickel. He further suggested that deposits of this nature could serve as prospecting indications of deposits of the Precambrian copper-nickel sulphide ores.

Warrington (1965,)described the mineralisation of the sandstones of Alderley Edge, Cheshire. He stated that cobalt and nickel occurred in association with manganese in the form of wad, as large segregations; vein-like masses, and spots in both the Bunter and lower Keuper host rocks. Galena occurred as disseminations in the sandstone, often following current bedding and within fault breccias. The galena contained a cobalt/nickel ratio of 50:1, which is important since it is a feature of the geochemistry of ore bodies whose source was an acid igneous mass (Davidson, 1962). Such a source body could account for the abundance of arsenic present and supply the combination of ores noted at Alderley. It is concluded from the fact that since cobalt never predominates over nickel in sedimentary ore deposits (Davidson, 1962), the ratio of cobalt to nickel in galena from Alderley Edge indicated an epigenetic origin. (Mohr, 1964).

The bulk of the minerals were secondary, the primary sulphide ores being restricted to the faults. Nickel/cobalt rich pyrites have been subsequently discovered in this assemblage. (Ixer, 1974, personal communication).

3.1.3. Miscellaneous

Another mode of occurrence of bravoite was as an accessory mineral in a chalcopyrite ore body in the Palabora Carbonatite complex, Transvaal, S.A. Heinrich (1970) quoted Foster (1958) and Lombard et al (1964), who reported pentlandite, millerite, bravoite, linnaeite, violarite, covellite, tetrahedrite, sphalerite galena, pyrite, marcasite, gold, silver, uranium and baddelyite.

The occurrence of bravoite in the North Caucasus is discussed by Bocharova (1970). The ore bodies have the form of veins, lenses and stockworks, closely associated with zones of tectonic crushing in granites, metamorphosed schists, and rarely, in ultrabasic rocks transformed into highly altered carbonatised serpentinites. The mineralisation was galena and sphalerite, with subsiduary pyrites, and minor chalcopyrite, tetrahedrite, arsenopyrite, marcasite, native silver and rarely, native gold. Quartz, barite and carbonates were widespread vein materials.

At Chochukulak, nickel minerals (Chloanthite, (CoNiFe)As_3, breithauptite, NiSb and particularly bravoite) were widespread, and occurred with the pyrite and marcasite. Bocharova suggested the source of the nickel was a large serpentinite mass 10Km away, the nickel being removed in solution by hydrothermal fluids passing through the serpentinites. He postulated a case of the contamination of post magmatic hydrothermal solutions of granitic magmas with the elements of basic magmas.

An arsenic rich bravoite was described by Petruk (1971), in a cross-vein of the Keewatin lava flows, Cobalt Gowganda regions, Canada. Sulphide assemblages of the galena, pyrite, sphalerite, marcasite type occurred in cross veins between the main veins which yielded a composition equivalent to $Co_{0.62}Ni_{0.19}As_{0.15}S_{1.84}$.

Colour zoning in iron pyrites is apparently not of itself sufficient to enable a positive identification of bravoite to be made. Burkart-Bauman and Otteman (1971), reported arsenic up to 7% in pyrite in Peru, and in Tunisia which produced zoning similar to bravoite, whilst Lazar and Otteman (1973), described a Roumanian hydrothermal vein deposit which yielded a cupriferous pyrite, distinguished optically from common pyrite by brownish yellow colour and lower reflectance and was shown by electron probe analysis to contain upto 1.2% copper.

Millerite is recorded from at least four localities in the United Kingdom. Howarth (1930), reported it as tufts or radiated groups of very slender or even capillary rhombohedral crystals which occurred in cracks or concretions in clay ironstones associated with the coal measures of South Wales and reported one occurrence actually in the coal. Associated minerals were quartz, calcite, barites, dolomite, or ankerite, chalcopyrite, pyrite, galena and blende.

An unprovenanced specimen of millerite is in the British Museum, from Weardale. It is stated to be still found in the Tynebottom Limestone, but the present author has been unable to locate any. Ramsbottom, (1962), reported it from the Fallgate borehole with bravoite, and Wilson (1921,) reported it with other nickel compounds as a metasomatic replacement mineral at certain localities in Scotland.

Linnaeite, Co_3S_4 was reported by Howarth (1930), from five localities in the South Wales coal field.

La Neve Foster (1887), described a remarkable occurrence of a nickel cobalt wad at Foel Hiraddug mine, near Rhyl. The wad occurred as black lumps with haematite and limestone fragments in a red clay matrix filling a very irregular perpendicular vein. The wad contained around 30% Co_2O_3, 10% Ni_2O_3, 35% MnO_2, 15% Fe_2O_3, 10% H_2O and just under 3 tons of cobalt and 2 tons of nickel were recovered from the ore between 1878 and 1880. Iron pyrites, found as the core of a piece of haematite, on analysis yielded traces of cobalt and copper, and he presented the view that the present vein is the gossan of a lode of cobaltiferous iron pyrites.

There are many reports of cobalt and nickel from Cornwall. Dewey (1923), reports cobalt and nickel from Dolcoath Copper mine associated with uranium, bismuth and silver and from Fowey, associated with iron pyrites, nickel, antimony, tin, cadium and silver ores.

Andrews (1962), reports cobalt bloom, (erythrite $Co_3As_2O_8.8H_2O$) from near Barmouth, and nickel and cobalt oxides from Motrram St. Andrews, Cheshire, near Alderly edge, and Gunshill Copper mines, Shrewsbury.

3.2 Descriptions of Bravoite

Springer, Schachner-Korn and Long (1964), analysed natural bravoites from Mechernich, Germany, using the electron probe and from the analyses obtained showed that complete metastable solid solution between all three disulphides was highly probable.. They reviewed previous experimental work on bravoites and their experimental production of artificially zoned bravoites precipitated from aqueous solution was described. H_2S and sulphur were introduced into $FeSO_4$, $CoSO_4$ and $NiSO_4$ solutions of 0.1 moles/litre concentration, the solutions sealed in glass tubes and heated to up to 300°C for four days. The precipitated products were examined optically and in the electron probe as polished sections and found to be identical to naturally occurring zoned bravoites. From thermodynamic considerations they showed that under certain concentrations and pH levels, a very small change in a solute concentration can lead to a much more pronounced change in the composition of the crystal, leading to a zonal strucutre. They found both zoned and unzoned crystals in the precipitation products of one experiment, and suggested that the concentration changes in a solution which led to zoning seem to have occurred around certain crystals only, and were probably caused by very localised convections of liquid. They suggested that natural bravoite was formed under conditions similar to those in the experiment.

Zoned bravoites from Maubach, Germany, and Mill Close, Derbyshire, were examined by Vaughan (1969), to determine variations in colour, reflectivity and micro-hardness in relation to compositional variations. In both localities nickel and cobalt showed a sympathetic relationship in the zones, which was antipathetic to iron. Iron rich memebers were found to be harder and have a higher reflectivity than those rich in cobalt and nickel. The analyses suggested variable amounts of non-stoichiometry, and reflectivity also decreased with increase in total metals. Variations in the geometry of the zones were considered, and in some cases were considered to have been probably related to properties of the crystal surfaces. The zoning was probably the result of very local variations in conditions.

El Baz and Amstutz (1963) conducted a statistical study of bravoite zoning exhibited by bravoite crystals from Fredrickstown, Missouri. They classified them into eight zoning types, and discussed the internal regularities of the grains as well as their relationship to the surroundings, and concluded that factors other then temperature and pressure controlled such crystallisation phenomenon as zoning.

Zimmerman and Amstutz (1973), offered a condensed atlas of possible section shapes of cubes, octahedra, and pyritohedra for use in habit determinations of pyrite, bravoite, and other cubic minerals in thin and polished sections. They presented references to previous attempts to solve shape changes mathematically and stated that mathematicians have confirmed a theoretical treatment was not feasible.

Cobaltiferous pyrite in magnetite skarns from Kazakhstan was investigated by Velkiboretz and Lukyanchenko (1970). Parallel sections of pyrite crystals cut in different orientations were examined in the electron probe and the data indicated two modes of occurrence of cobalt, nickel, and arsenic in pyrite.

1. As isomorphous substitution for iron
2. As discrete inclusions of cobaltite.

The cobalt substitution was greater along 100 planes than along 111 planes, and they attributed its greater capacity for absorbing cobalt to the lesser reticular density of the 100 planes composed of regularly alternating iron and sulphur atoms as compared with the monatomic 111 planes. A rhythmic variation was detected along a normal to these planes, concentrations on 111 planes varied about a definate level, whilst on the 100 planes, traversing from the periphery to the centre, it varied about a slightly ascending straight line.

CHAPTER 4

FIELD STUDIES

4.1 Introduction

The major quantity of material collected for examination came from four regions. These were in order of abundance of material collected, Derbyshire; Alston Block and Askrigg Block, (North Pennines); and West Shropshire, (Shelve area).

Active 'metalliferous' mining in every locality with the exception of the Youlgrave Mine, Derbyshire, ceased prior to 1950. In many areas the industry had ceased before the close of the 19th century. As a consequence of this, material was collected extensively from old workings, rakes, hushes, and mine dumps. With few exceptions, material was not collected in-situ, because it was either unavailable or did not fulfil the collection criteria, namely showing signs of visible mineralisation. The use of mine dumps and other waste material introduces an element of uncertainty as to the exact source of the material, both geographically in a horizontal plane, and stratigraphically in the vertical plane. However, material collected from dumps in particular was probably quite representative of the immediate vicinity as a whole. Unfortunately it is impossible in most cases to assign a definate stratigraphic horizon to collected material because the depth of origin is unknown, and also any orientation of material with respect to the sides of a vein, or top and bottom of a flat, or the nature of the adjacent sidewalls is information which is completely unobtainable.

As the research progressed however it became apparant that lack of this information was not going to be in any way crucial to the success of the investigation. The research was directed towards determining whether there was a regional variation of bravoite so detailed location was not so important, and in the few places where it was possible to obtain data of this nature, there was no correlation between it and mode of occurrence, appearance, texture, or associated mineralogy of the bravoite crystals being found.

Many areas visited, although both from maps, published accounts and the obvious disturbed nature of the ground had been localities worked for minerals in the past, yielded no material. This accounts for the great disparity in abundances of material collected from different localities. The Mendips was the most difficult in this respect.

A brief description of each region will be given emphasising its structural and mineralogical aspects. After each description there will be a table listing the grid reference of the find spot and giving a statement of the nickel minerals found, and in the remarks column a brief description of the polished section.

The minerals listed in the remarks column as present in the section do not include galena although it is to be understood that it is present in almost every section. The oxidation products of lead, iron zinc or copper are not listed, although it is to be understood that wherever galena, pyrite, marcasite, sphalerite or chalcopyrite occur, the oxidation products, cerrusite, geothite, smithsonite, covelline and chalcocene nearly always occur. Due to much of the material collected having lain on the surface and weathered for many years, oxidation in many specimens is far advanced.

The geographical order of description of the specimens is from north to south and where applicable from west to east along the rakes and veins.

4.2 Description of the Peak District orefield, Derbyshire.

The orefield of the Southern Pennines extends from Castleton in the north down the eastern half of the North Derbyshire Carboniferous Limestone massif through Bakewell, Darley and Matlock as far south as Wirksworth. The broad geological picture is one of a series of massive well-bedded Avonian limestones of the Dibunophylum zone approaching 1000m maximum and exhibiting a bewildering variety of litho- and bio-facies, deposited on a 'Derbyshire Massif' with a suggested Llanvirnian 'basement' found at the bottom of the Eyam borehole. (Dunham, 1974). Some beds are darker and shaly, e.g. the Davisiella beds at the base of the exposed sequence, some are dolomitic, some cherty, and some are locally silicified. (Bemrose 1898). Unpublished work by Thach (1965) has demonstrated a wide zone of reef knolls, separated by channels and basin-like facies, rather than a simple marginal reef belt. To the north is a marginal reef complex around Castleton, while on the eastern flank are reefs of a rather different character including brachiopod-crinoid heaps showing quaquaversal dips, limestone breccias, coarse crinoidal limestones, and fine grained calcite mudstones and algal mounds. (Black 1954, Shirley 1959). Reef knolls enveloped by shale have proved to be favourable loci for ore deposition, (Shirley and Horsfield 1940, 1945), as Shirley has demonstrated at Mill Close Mine (1949).

The sequence is interrupted by both extrusive and intrusive igneous rocks, (Bemrose 1894, Wilcockson 1932) mainly in late D_1 and early D_2 times. Olivine basalt lavas, massive and amygdaloidal occur at two main horizons, and in several lesser ones. Associated with the lavas are tuffs and ashes, which have been subjected to widespread alteration, the ultimate product of which is a sticky clay substance forming 'wayboards', and in some horizons a mottled green rock known as toadstone. Wayboards and toadstones are almost impervious alike to ascending ore-solutions and descending water, and have exerted a very powerful contol upon the distribution of the mineral oreshoots, splitting up the massive limestones into relatively thin favourable beds (Ixer 1974).

Structurally the district as a whole is to be regarded either as a broad structural dome, or as an uplifted block limestone, with reef limestone screes and boulder beds (Simpson 1968), banked against the surrounding cliffs. Shirley (1945 and 1949) has shown that the dome is far from simple, having a broad flat axial region trending north-south near its western margin, broken by numerous faults, and having three smaller complex anticlines extending eastwards from the dome axis, the Eyam-Calver, Youlgreave, and Matlock anticlines, plicated by pitching cross folds of noth-south axial trends. Fearnsides (1933) showed that the east-west folds were already in existence during the Lower Carboniferous, and Shirley and Horsfield (1945) have shown that the master veins of the northern district run along the crests of the minor corrugations of the main structure.

Around all sides of the 'Dome' the limestone plunges under the Edale Shales, to reappear again to the east where a pitching north-south trending anticlinal ridge brings up two domal inliers of limestone at Ashover to the north and Crich to the South.

The Derbyshire massif and the Crich and Ashover inliers are traversed by innumerable mineral lodes, running within 45° of the general East-West direction practically all of them carry galena to some extent, sphalerite, a little pyrites and chalcopyrites, calcite, barytes or fluorspar. The mineral deposits are particularly rich and numerous at the northern and eastern flanks of the massif.

The deposits are classified as Rakes, Scrins, Flats and Pipes. Rakes are major fissure fillings, often extending for some kilometers, (Long Rake 11 Km.), and commonly 6m. wide. They often show horizontal slickensiding on the walls indicating final lateral fault movement. Scrins are small fissure fillings a few inches wide often occurring in swarms. Flats are horizontal ore bodies of similar length and width, while pipes are similarly horizontal but length considerably exceeds width. Both flats and pipes are replacement of limestone often with roof or floor of wayboards or toadstones.

In the rakes and scrins the minerals often show parallel banding on each wall with an occassional open vug in the centre, but a vug or cavity is much more common in the replacement deposits.

A study of Farey (1811), and Pilkington (1798) would show that fluorite is the predominant gangue mineral within a 2Km or so of the eastern boundary of the limestones, gradually giving way to barite gangue, then 2Km or so further west to calcite gangue, although in all three zones, all three gangue minerals are usually found together and this zonation is marked only by the dominance of one or the other. Wedd and Drabble (1908) suggested this zonation was largely statigraphically controlled, the fluorite being the earliest and hottest mineral was restricted to the highest beds of the limestone beneath the Edale Shales, and the restriction to the eastern margin was said to be due to the removal of the equivalent limestones by erosion further west. However, subsequent statigraphic work tends to show that these beds had in fact been removed by erosion prior to the deposition of Edale shales, and later mineralisation. Shirley and Horsfield confirmed (1945) that fluorite is more important under the anticlinal areas of the limestone, the ore solutions coming from a postulated granite magma beneath the east (Dunham 1934) and travelled up the tension fractures along the crests of the easterly pitching anticlines, in which tension fractures they subsequently crystallised. Mueller, (1954a) in his study of the distribution of fluorite varieties claimed that the north-south zones of Wedd and Drabble are partly lost in the synclines and thus confirmed Shirley and Horsfield's hypothesis concerning anticlinal control of mineralisation, and further subdivided the fluorspar zone into three distinct subzones which he claimed can be plotted with respect to each main vein and related side vein and thin stringers respectively. The subzone classification is based on colour of fluorite, and he equated colour with temperature of deposition, thus arriving at his temperature zones. The fluorite varieties he recognised are clear; colourless or yellow, containing pyrite or chalcopyrite inclusions and delimit his high temperature subzone, a medium temperature sub-zone with turbid faintly purple fluorite containing fluid inclusions, sometimes known as Bradwell or Crich spar, and a low temperature subzone recognised by fluorite with marked blue or purple colours. He ascribed the dark colours to hydrocarbons retained at lower temperatures within the fluorite, which can be driven off by the application of heat and made colourless. However, as was shown during the 1939-45 war when radium was stored in caverns containing purple fluorite, the colouration had been removed by radiation, and subsequently gradually returned, and subsequent work has shown the colouration to be a function of a lattice defect brought about by the excessive inclusion of calcium atoms in the cubic fluorite crystal lattice.

Mueller (1954b) further suggested pyrite and chalcopyrite generally are confined to the highest temperature sub-zone and drew an analogy with their distribution in Cornwall where they are usually found nearer the apparent source of the mineralising solutions. Mueller further stated he could temporally correlate fluorite and calcite crystals in different veins from similarity of shape, size, density and type of pyrite, chalcopyrite or gas bubble inclusions, and broad tendencies could be recognised throughout regions some miles across. (Mueller 1954c). However, the present investigation could detect no real evidence of colour subzones, or restriction of pyrite inclusions to one particular colour of fluorite. One explanation could be the unavailability of in-situ material, dump material being heterogeneous and inherently incapable of providing the accuracy of detail necessary to confirm Mueller's findings.

Material was collected from 69 locations in Derbyshire, and from 5 locations at Ecton, Staffordshire. Of the Derbyshire locations 55 contained bravoite or nickeliferous pyrite, 4 of which also exhibited an anomalously zoned marcasite and of the 5 from Ecton, one contained bravoite, and one a pinkish nickeliferous pyrite. Collections were made either from isolated dumps, or at intervals along the rakes. In the case of the former, the grid reference of the dump is given, in the case of the latter, the grid references of the extremities of the length of the rake collected along are given, together with the number of collections made. Purely for the purposes of this report the region has been divided into four areas of 10,000 hectares each, as shown on the key map.

Maps 1 to 4 show the boundary between the D_2 limestone and the overlying Edale Shales and the principal rakes and veins. Locations from which collected material contained bravoite or nickeliferous pyrite are shown thus, ●. Material containing no nickel is shown thus + .

Nomenclature: - 1. Bravoite and Nickeliferous Pyrite

The boundary between bravoite and nickeliferous pyrite has been assigned at 20% nickel/cobalt content. Nickel/cobalt content can only be determined by use of the electron probe. For the purposes of this research a subjective classification has been made. All crystals exhibiting pronounced colours and one or more colour zones being classified as bravoite if isotropic, or nickeliferous marcasite if distinctly anisotropic. Other iron pyrites exhibiting a very slight 'off-yellow' colour, with or without zoning were classified as nickeliferous pyrites.

2. Gangue

The term gangue is used to describe all non-sulphide minerals; fluorite, calcite, barite, quartz.

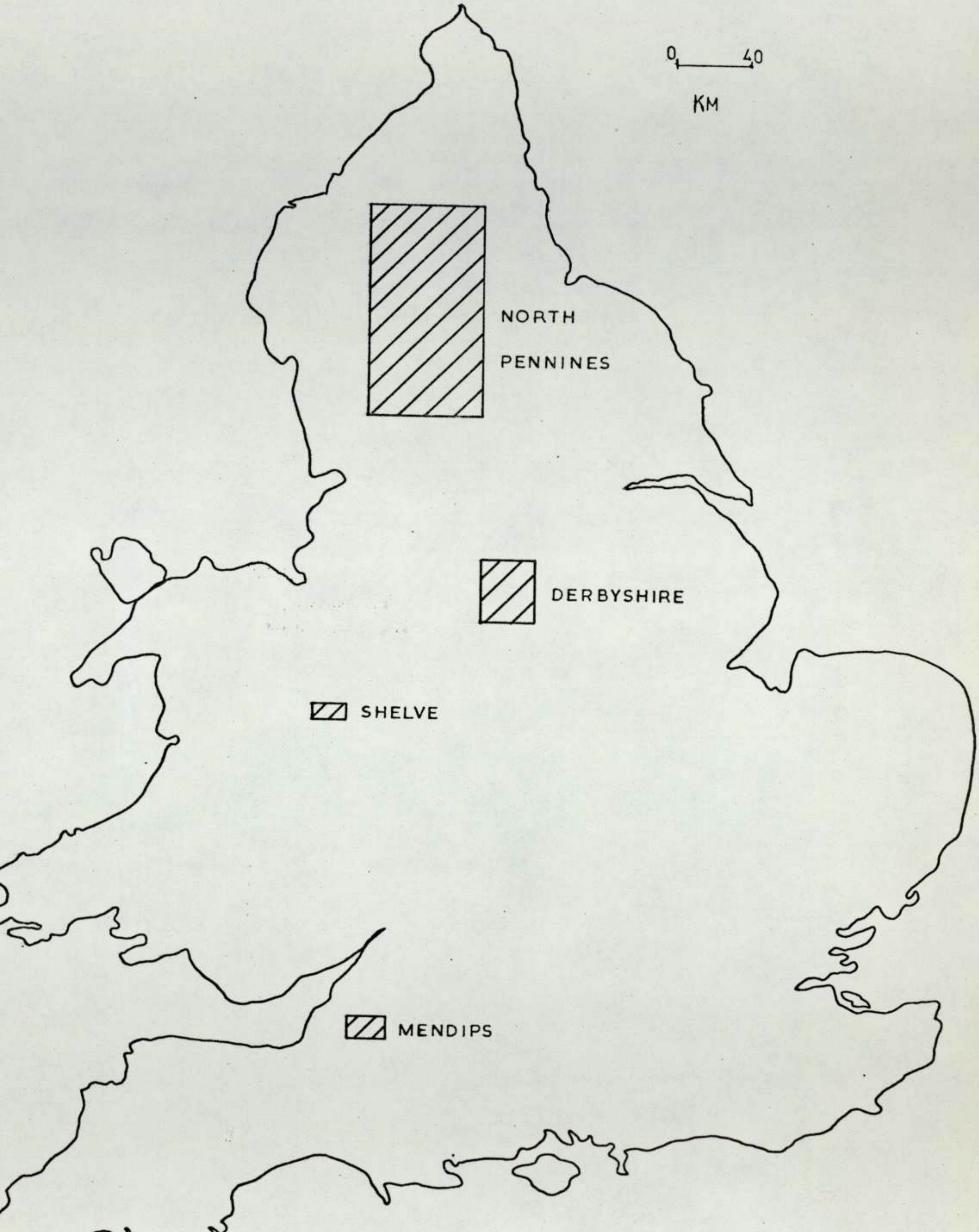


Fig. A. Sketch Map of the locations of the collecting areas.

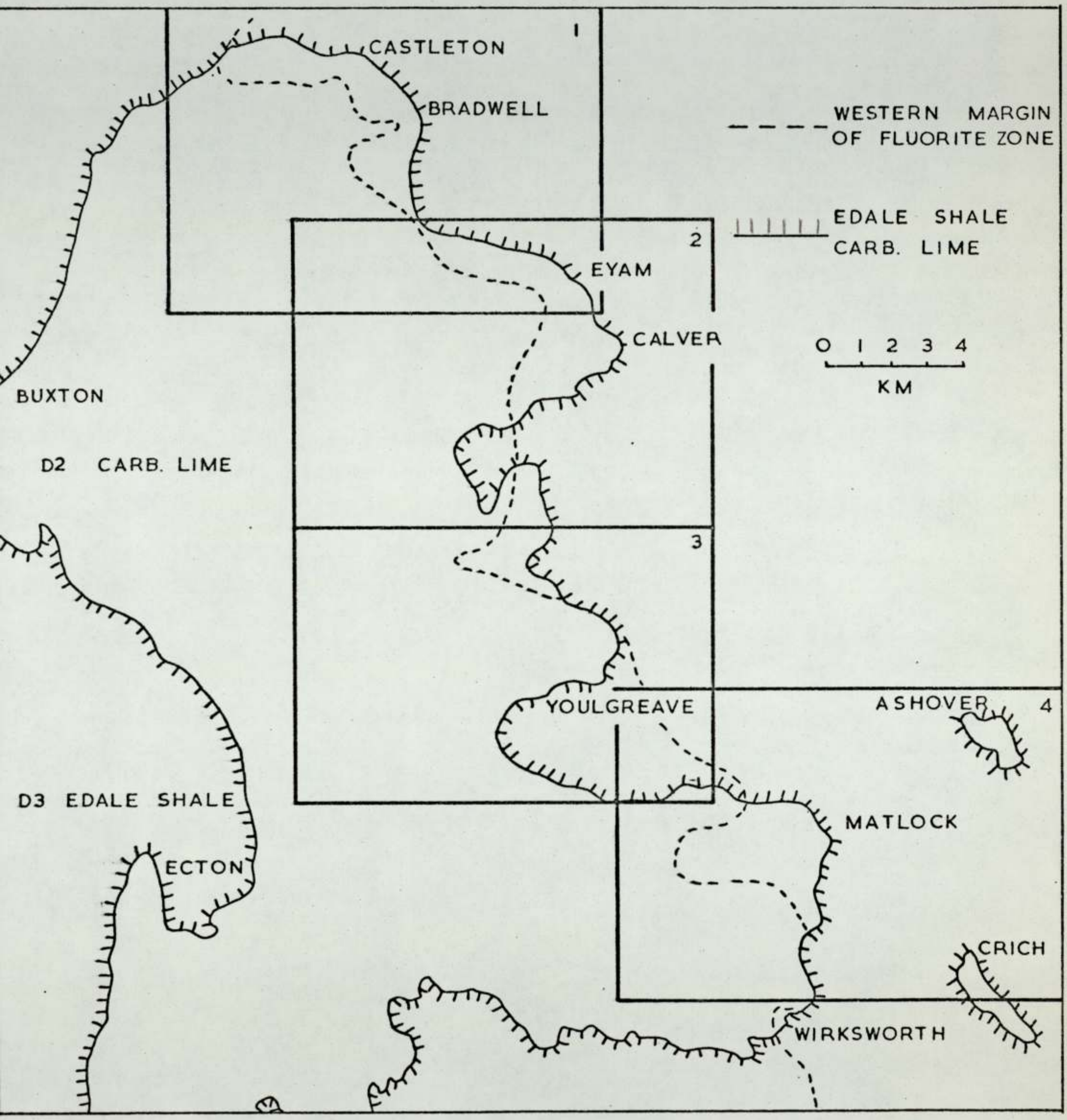


Fig. B. Sketch Map of the Derbyshire Dome showing the boundary of the limestone massif and the western margin of the fluorite zone.

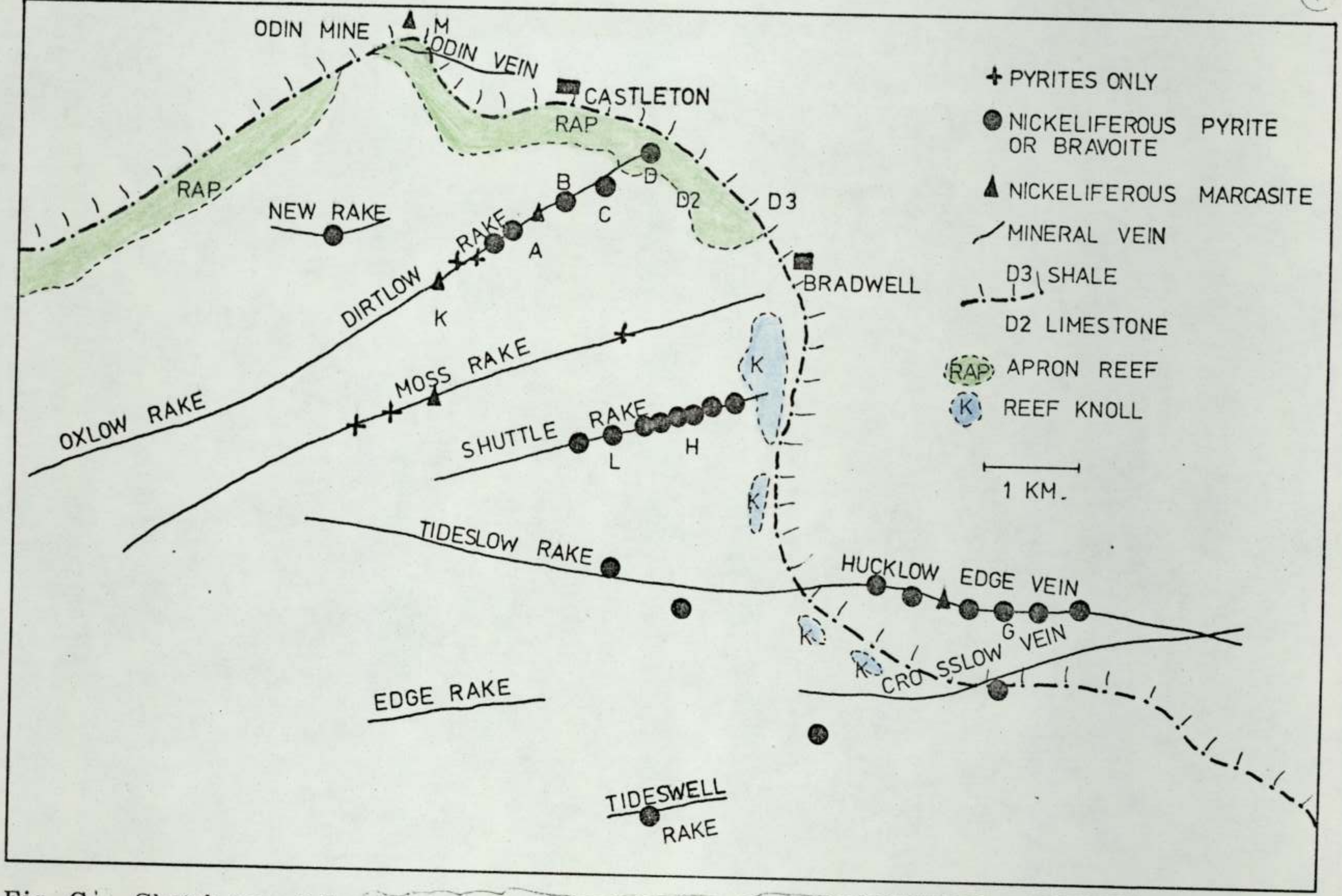


Fig. C_1 Sketch map of the Castleton Bradwell area, showing the distribution of the collecting sites.

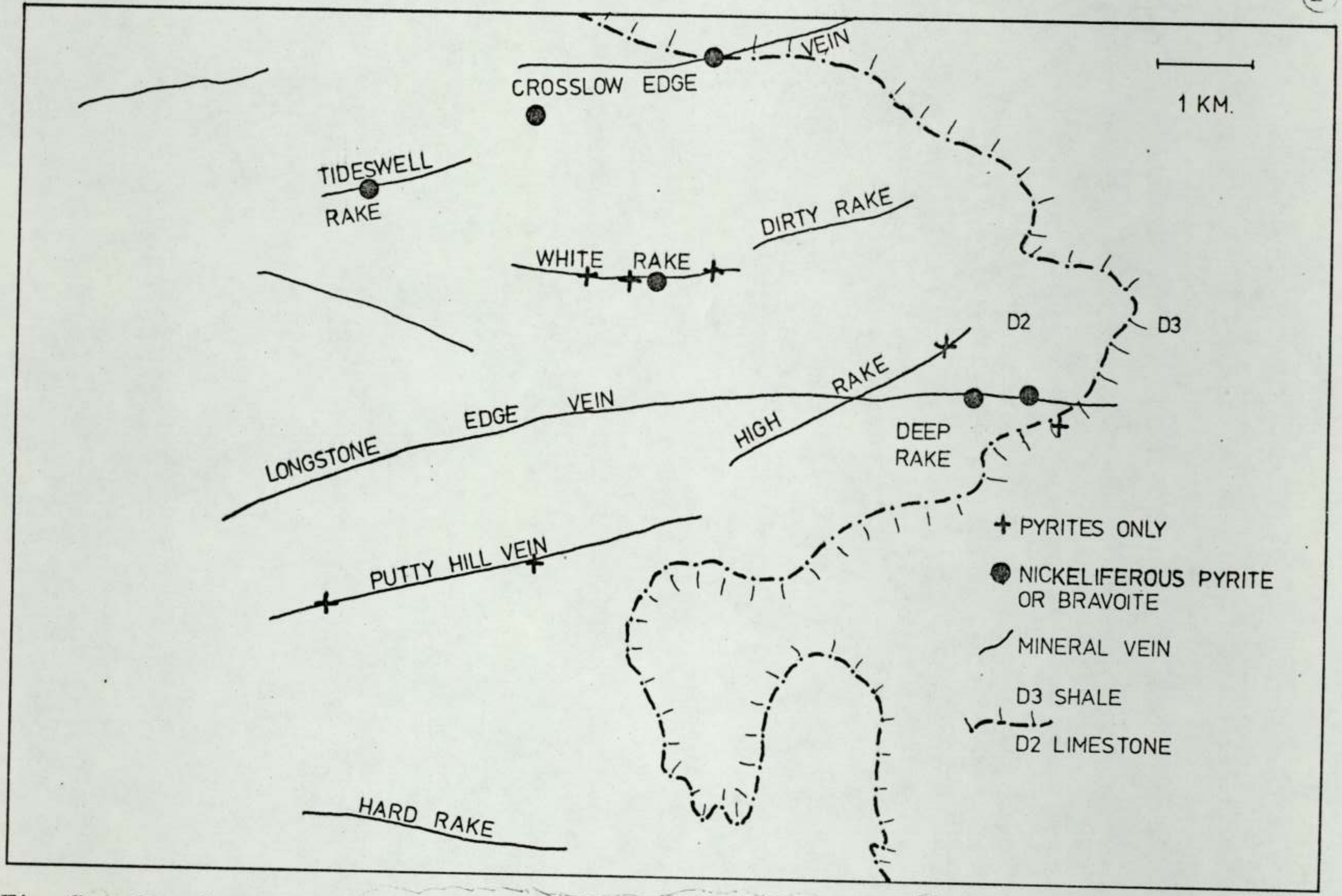


Fig. C_2 Sketch map of the Eyam Calver area showing the distribution of the collecting sites

③

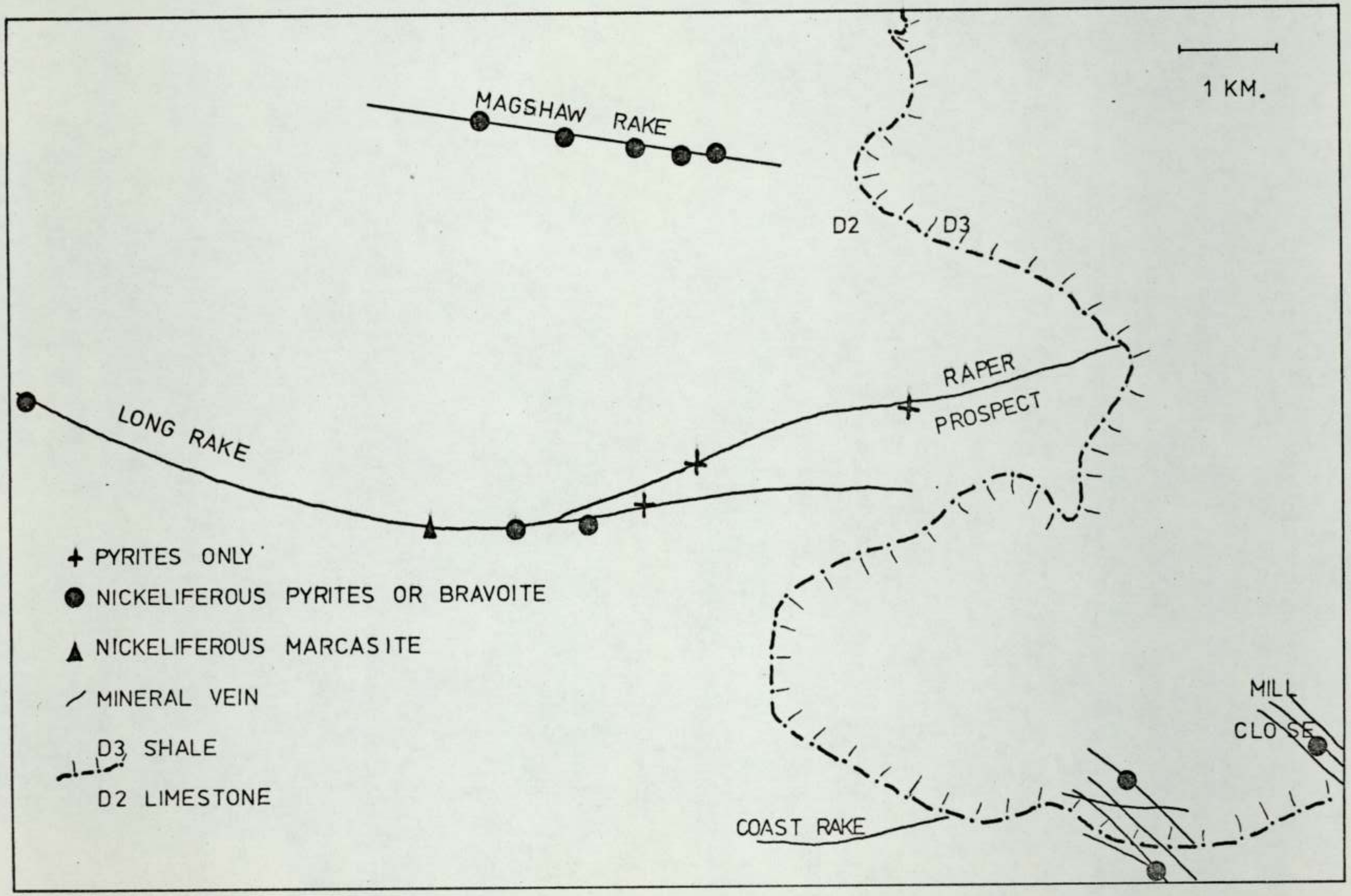


Fig. C3. Sketch map of the Youlgreave area showing the distribution of the collecting sites.

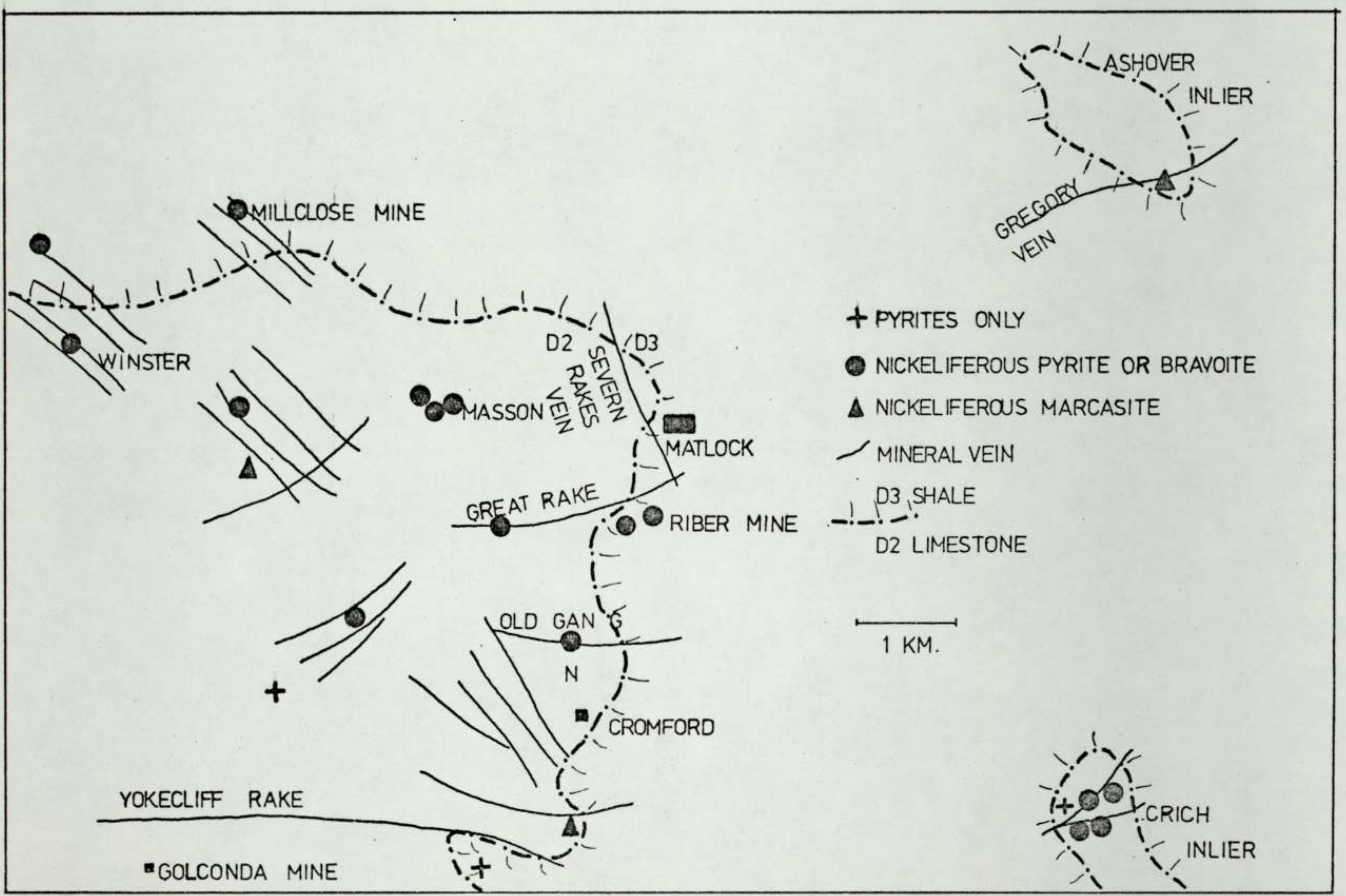


Fig. C4 - Sketch map of the Matlock Cromford area, showing the distribution of the collecting sites

A Description of the Derbyshire Specimens

	Name	Ref.	Style	Nickel Species	Remarks.
1	Odin Mine	135837	Void infill	Zoned and unzoned bravoite	Common, unbanded, 50μ, 10μ euhedral to subhedral. Rarely associated with chalcopyrite and bornite.
				Ni. Pyrite	Pink, some faintly zoned. 20μ
				Ni. Marcasite	Associated with some bravoites.
					Gangue, calcite quartz, barytes.
2	New Rake	128816	Void infill	Zoned bravoite	Common, unbanded, 10μ, rarely clustered. Subhedral to euhedral.
					Faint brown. Chalcopyrite, rare.
					Calcite, fluorite.
3	Dirtlow Rake (1)	137813	Replacement	Zoned brown pyrite	Common, banded, 10μ triangular parallel edge fluor crystals.
					Associated with 10μ galenas.
				Zoned Ni. marcasite	Rare
					Assemblage in massive flourite.

A Description of the Derbyshire Specimens Continued

Name	Ref	Style	Nickel Species	Remarks
3 Dirtlow Rake (2)	140815	Void infill	Nil	Few chalcopyrite, subhedral galena, covelline, 5μ pyrites, calcite, subsiduary fluorite, barytes.
(3)	142816	Void infill	Nil	1μ pyrites common in calcite, with chalcopyrite, 5μ galena around calcite scalenohedra, banded. Subsiduary fluorite.
(4)	144817	Void infill	Zoned bravoite	Common, banded, 10μ inclusions in alternating bands of calcite and fluor.
(5)	148819	Void infill	unzoned bravoite	Rare, unbanded, 20μ, euhedral, as inclusions in barytes. Few marcasites.
(6)	149820	Void infill	Zoned and unzoned bravoite,	Common unbanded, 15μ, euhedral, inclusions in fluorite, rarely in barytes. Associated with pyrites.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
3 Dirtlow Rake (6) Cont...	149820	Void infill	Zoned marcasite	Rare, 30μ, surrounding anhedral bravoite, as inclusions in fluorite Gangue, blue, sugary fluorite.
(7)	151821	Void infill	Zoned and unzoned bravoite	Common, clustered, brown, purple 10-50μ. Inclusions in calcite and barytes. Associated with pyrites and marcasite. Calcite scalenohedral.
(8)	155822	Void infill	Zoned and unzoned bravoite	Very common, clustered brown, lilac some bizoned, 10-25μ. inclusions in calcite and fluorite. Associated with marcasite.
(9)	158825	Void infill	Zoned and unzoned bravoite	Common, clustered, brown, purple, 10-25μ, inclusions in fluorite and calcite scalenohedra.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
4 Moss Rake (1)	130795	Void infill	Nil	Few unbanded pyrites in calcite.
(2)	133706	Void infill	Nil	As Moss Rake (1) with rare cerrusite.
(3)	138798	Void infill	Zoned bravoites	Rare, banded and clustered 10u, along calcite crystal boundaries.
			Zoned marcasite	Rare, surrounding bravoite in pyrite 120µ. Marcasite crystal zoned in one region side only.
(4)	166805	Void infill	Nil	As Moss Rake (1).
5 Shuttle Rake (1)	152793	Void infill	Zoned bravoites	Common, banded and unbanded, 20µ Alternating bands of galena bravoite/ pyrite, and fluorite. Gangue, calcite and fluorite.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (2)	155795	Replacement See Remarks	Zoned bravoites	Common, unbanded, 20μ. euhedral and anhedral, alterations to goethite common except where inclusions are in fluorite. Associated with pyrite, rare chalcopyrite. 98% fluor, rare calcite and barytes. Relict transparent circular structures 50μ dia. of uncertain origin.
(3)	160796	Replacement	Zoned bravoites	Rare unbanded, 10μ euhedral, associated with rare euhedral 20μ chalcopyrite. Gangue fluorite replacing calcite.
(4)	162797	Undetermined	Zoned bravoites	Common, unbanded 20μ euhedral associated with pyrite, marcasite.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (4) Cont..	162797	Undetermined	Zoned pyrites	Rare, 5μ, pinkish gangue, calcite, fluorite. Calcite replacing fluorite?
(5)	165798	Replacement	Zoned bravoite	Common, unbanded, 3μ, very pale, some with pyrite centres. Bravoites mainly in fluorite. Relict crinoid ossicles, and transparent circular structures of uncertain origin, rarely showing incipient pyritisation.
(6)	166798	Undetermined	Zoned pyrite	Common, unbanded, 20μ, faint brown zoning, associated with normal pyrite and marcasite. Commonly inclusions in scalenohedral calcite. Gangue, calcite, fluorite, little barytes.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
5 Shuttle Rake (7a)	167799	Void infill	Zoned bravoites	Common, unbanded, 30µ, hexagonal habit. Zoning complicated, esp. as inclusions in fluorite.
			Ni pyrite, zoned	Very rare, very pale brown, 2µ, euhedral inclusions in large (late?) calcites. Gangue, calcite, fluorite.
(7b)	"	Void infill	Zoned bravoite	Common, unbanded 30µ, brown. pentagonal habit, very irregular zoning with multiple re-entrant angles in euhedral crystals occur. Associated with pyrites, marcasite. Gangue, Calcite scalenohedra with rare fluorites on faces.
(8a)	168800	Void infill	Zoned bravoite	Common, banded, purple, 12µ, euhedral to subhedral inclusions in calcite. gangue, fluorite replacing calcite cross-cut by later fluorite.

A Decription of Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
5	Shuttle Rake (8b)	168800	Replacement?	Unzoned bravoite	Rare, unbanded, purple, 5μ euhedral. Associated with sphalerite, and rarely chalcopyrite. Gangue, calcite/fluorite bands.
6	Tideslow Rake (1)	156782	Undetermined	Zoned bravoite	Common, banded, 20μ euhedral, Inclusions in galena. Gangue calcite, rare fluorite.
7	Nr. Tideslow Rake	164776	Undetermined	Unzoned bravoite	Rare, unbanded pale brown 20μ euhedral, inclusions in fluorite. Lines of inclusions along bravoite crystal faces Gangue, fluorite with 25-50% replacement by euhedral quartz 20μ.
8	Tideswell	162756	Undetermined	Zoned bravoite	Rare, unbanded, brown 10μ pentagonal inclusion in fluorite. Associated with pyrite. Gangue calcite, being replaced by fluorite.

A Description of the Derbyshire Specimens Continued

Name	Ref	Style	Nickel Species	Remarks.
9 Hucklow Edge Vein (1)	186779	Void infill	Zoned bravoite	Very rare, unbanded, 5µ euhedral inclusions in scalenohedral calcite.
(2)	189778	Void infill	Zoned bravoite	Rare, unbanded purple 5µ euhedral, and common subhedral lilac 20µ, inclusions in fluorite. Associated with pyrite. Gangue, calcite, purple fluorite, barites, quartz. Rare dolomite. Semi-translucent single or multiple bodied structures 5-20µ dia. in fluorite.
(3)	192777	Void infill	Zoned and unzoned bravoite.	Common, banded, and unbanded 40µ, euhedral. Generally as inclusions in fluorite. Associated with pyrite and marcasite.
			Ni pyrite	Rare, pink, 5µ.

A description of the Derbyshire specimens Contined

Name	Ref.	Style	Nickel Species	Remarks
9 Hucklow Edge Vein (3) Cont.	192777	Void infill	Ni Marcasite.	Rare, zoned, infrequently associated with framboidal pyrite. Gangue, 90% fluorite, 10% calcite. All sulphides in fluorite.
(4)	196776	Void infill	Zoned bravoite	Common banded, brown, 20μ associated with pyrite, marcasite, sphalerite. Alternating bands of calcite, fluorite galena, subsiduary barites.
10 Crosslow Vein	196770	Void infill	Zoned bravoite	Rare 20μ and common, banded, purple 6μ subhedral to euhedral, associated with covelline, pyrite, marcasite, in narrow band between galena.
			Ni pyrite	Rare pink.
11 1.6 Km South of Gt. Hucklow	178765	Void infill	Zoned bravoite	Rare unbanded, 15μ euhedral associated with pyrites, marcasite, sphalerite. Gangue fluorite, calcite, minor barite.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
	MAP				
12	White Rake (1)	184748	Void infill	Nil	Massive calcite, pyrites, 3µ along fractures.
	(2)	189748	Void infill	Nil	Massive calcite, pyrites marcasite 300µ, along fractures in calcite.
	(3)	192748	Void infill	Zoned bravoite	Rare, unbanded, 20µ euhedral associated with pyrite as inclusions in calcite and fluorite in calcite/fluorite breccia.
	(4)	198749	Void infill	Nil	Rare pyrites 10µ euhedral in fluorite/calcite breccia recemented with barites
13	High Rake	222743	Replacement?	Nil	Marcasite 2µ enclosed in pyrite, gangue 80% fluorite, 18% calcite, 2% quartz. Many semi-transparent structures in calcite, rarely mineralised by framboidal pyrite.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks.
14	Deep Rake (1)	225735	Void infill seen in situ	Zoned and unzoned bravoites	Common banded, 50µ euhedral and 5µ euhedral inclusions some with pyrite centres in alternating fluorite/galena/calcite bands associated with covelline. Common unbanded 10µ bravoites in calcite scalenohedra.
	(2)	229735	Void infill	Zoned and unzoned bravoites	Common, banded, violet streaked, 50µ, euhedral, habit change in crystals common. Inclusions in fluorite. Associated with pyrites, chalcopyrites Gangue 100% fluorite.
15	White Coe Mine	233734	Void infill	Nil	Calcite cleavage flake. Pyrite, marcasite, chalcopyrite. (3 specimens examined, nil result).
16	Putty Hill Vein (1)	178718	Void infill?	Nil	Fluorite with unbanded chalcopyrite, pyrite and marcasite in clusters. Chalcopyrite rarely in galena. Fluorite exhibits sugary texture.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
16	Putty Hill Vein (2)	158713	Void infill	Nil	Similar to Putty Hill vein (1) overleaf.
17	Magpie Mine (1)	173681	Void infill	Zoned bravoite	Common banded purple 150μ euhedral part goethitised inclusions in calcite. Associated with pyrite, marcasite sphalerite. Alternating bands of calcite pyrite/bravoite, galena, Gangue 100% calcite.
	(2)	"	Void infill	Zoned bravoite	As (1) above. Pyrite wedges in bravoite preferentially goethitised.
	(3)	"	Void infill	Zoned bravoite	As (1) above. Host rock limestone.
	(4)	"	Replacement	Zoned bravoite	Rare unbanded, 10μ, associated with sphalerite and framboidal pyrite, some framboids coelescing. Gangue, re-crystallised micrite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
18 Magshaw Rake (1)	183680	Undetermined	Zoned and unzoned	Common, unbanded, lilac 10μ pentagonal showing habit change in pyrite Associated with pyrite as inclusions in barites. Gangue fluorite, barytes barytes replacing fluorite. All sulphides in barytes.
(2)	189678	Void infill	Unzoned bravoite	Rare, unbanded, pale, 15μ on galena/ fluorite boundary, rarely in galena. Alternating bands of fluorite and galena.
(3)	193677	Void infill	Zoned and unzoned bravoite	Common, unbanded, multi-coloured, multi-zoned 60μ inclusions in fluorite. Associated with pyrite, goethite, Goethitised bravoite darker blue than goethitised pyrite. Gangue fluorite and calcite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks.
18 Magshaw Rake (4)	19677	Void infill	Zoned and unzoned bravoite	Rare, banded, 10μ associated with marcasite and pyrite as alternating bands in fluorite gangue.
19 Long Rake (1)	127653	Replacement	Unzoned bravoite	Very rare, unbanded, lilac 5μ, in pyrite. Gangue fluorite, with replaced relict coral containing bravoite. Cherty limestone replacement.
(2a)	167640	Undetermined	Zoned bravoite	Common banded, 20μ euhedral, associated with pyrite, marcasite. Chalcopyrite.
			Ni marcasite.	Very rare, 2μ, showing optical continuity with bravoite. Gangue, calcite.
(2b)	"	Void infill?	Nil	2μ-50μ pyrite, rare quartz inclusions, and euhedral to subhedral quartz gangue containing pyrite inclusions, Milky neomorphic spar.

A. Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks.
19 Long Rake (3)	176640	Void infill?	Ni pyrite	Rare, unzoned, pink 50μ associated with pyrite and marcasite, in calcite scalenohedra intersected by later quartz vein of subhedral crystals.
(4)	183640	Void infill?	Unzoned bravoite	Rare, brown, 10μ anhedral associated with chalcopyrite, pyrite, marcasite, in calcite scalenohedra.
Youlgrave Mine on Long Rake (5)	188643	Void infill?	Nil	Fluorite inclusions in galena in calcite scalenohedra.
Long Rake (6)	195645	Void infill	Nil	Pyrite 0.8μ rare associated with 30μ galena in massive calcite.
20 Raper fluorspa Opencast (1)	216652	Replacement	Nil	Massive fluorite with chert (hand specimen) Rare pyrite 10μ.
(2)	"	Replacement	Nil	Sugary fluorite, goethite.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
21 Portaway Mine	234614	Void infill	Zoned and unzoned Bravoite	Common repetitive banding purple 5μ-30μ, euhedral to subhedral, associated with alternating bands of pyrite and marcasite with rare chalcopyrite as inclusions in calcite flake.
			Ni pyrite	Rare pink pyrite, 10μ
			Ni marcasite?	Rare marcasites show traces of zoning. Five sections all very similar.
22 Near Winster	Unknown not in situ	Void infill	Zoned and unzoned	Common banded and unbanded, 5μ-150μ euhedral to subhedral, multi-habit associted with pyrite and marcasite and rare chalcopyrite.
			Ni pyrite	Pink pyrite, adjacent to bravoites.
			Ni marcasite	Rare, generally partially or completely enclosing bravoite/pyrite. All as inclusions in calcite flake. Four sections, all very similar.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
23 Shaft at Mill Close Mine (a)	258617	Replacement	Nil	Pyrite, 10μ-100μ euhedral to subhedral as inclusions in calcite, and a vermiform incrustations around relict titanomagnetite reticulated structures in calcite. Rare pyrrhotite, haematite, rutile (after ilmenite). Rare fluorite and barytes. Later pyrite in fractures. A replaced lava.
(b)	"	Void infill	Zoned and unzoned bravoite	Rare, banded, 15μ associated with alternating bands of chalcopyrite and minor pyrite with rare marcasite as inclusions in calcite flake. Four specimens all similar.
24 Slack Mine	258597	Undetermined Void infill?	Zoned and unzoned bravoite	Common, banded, lilac and purple, below 10μ and between 50μ-75μ euhedral to anhedral, rarely interdigitating with pyrite, associated with rare chalcopyrite, along calcite crystal faces. Gangue 100% calcite.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
25	Oxclose Mine (a)	275599	Replacement	Zoned bravoite	Common, unbanded, purple, 10μ-40μ zoning concentric, rarely radial. Associated with pyrite, marcasite, as inclusions in fluorite. Gangue 80% fluorite, 20% calcite Sulphides mainly in fluorite.
	(b)	"	Void infill	Zoned bravoite	Rare, unbanded, 20μ associated with pyrite and chalcopyrite in calcite flake.
26	Jughole (a)	279598	Replacement	Zoned bravoite	Rare unbanded, 20μ associated with pyrite. marcasite. Gangue, calcite, dolomite, fluorite.
	(b)	"	Void infill	Zoned and unzoned bravoite	Common, euhedral unbanded 10μ, associated with pyrite and marcasite as inclusions in calcite flake.
27	Masson	284592	Replacement	Zoned and unzoned bravoite	Rare unbanded, brown, 20μ associated with pyrite in fluorite gangue.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks.
28	Bonsall Moor	258592	Undetermined	Zoned bravoite	Rare, unbanded, brown, 4µ associated with pyrite in calcite with minor fluorite, and quartz porphryblasts.
				Ni marcasite	Rare, 5µ, faint zoning.
29	Low Mine (a)	283586	Void infill	Zoned bravoite	Common unbanded, 10µ purple associated with pyrite, marcasite and chalcopyrite 5µ and rarely 40µ, in fluorite gangue.
				Ni pyrite?	Rare pinkish unzoned pyrite species in fluorite.
	(b)	"	Void infill	Zoned and unzoned bravoite	Common, banded, 30µ euhedra to anhedral, associted with alternating bands of galenz and fluorite/calcite. Minor Chalcopyrite adjacent to galena.
				Ni pyrite?	Pink (?) pyrite, 30µ.

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
30	Riber Mine	299588	Void infill	Zoned bravoite	Rare, unbanded, euhedral and anhedral 25µ associated with pyrite, marcasite, sphalerite, rarely enclosed by sphalerite, in massive, fractured calcite infilled with quartz.
31	Tip Nr Riber Mine (a)	296584	Void infill	Zoned and unzoned bravoite	Rare, unbanded, 5µ-100µ inclusions in calcite, rarely replacing cerrusite Associated with pyrite and chalcopyrite.
				Ni pyrite, unzoned	Rare, unbanded, pale pink 8µ-20µ. Gangue calcite, fluorite, rare euhedral quartz.
	(b)	"	Void infill	Zoned bravoite	Common, unbanded, brown, 5-10µ, euhedral interdigitating with pyrite, commonly ringing galena, associated with chalcopyrite in a fluorite/calcite matrix.
32	Slaley	268576	Undetermined replacement?	Nil	Rare marcasite in brecciated fluorite, fluorite being replaced by calcite, later,

A Description of the Derbyshire Specimens Continued

	Name	Ref.	Style	Nickel Species	Remarks
	Slaley Cont.				marcasite-bearing quartz cross-cutting both earlier phases.
33	Old Gang Vein	291574	Replacement?	Unzoned bravoite	Rare, unbanded brown, 20μ interdigitating with pyrite, Gangue, recrystallised micrite, minor fluorite.
34	Near Cromford	292558	Void infill	Unzoned bravoite	Rare, unbanded, 5μ euhedral associated with sphalerite pyrite, marcasite, and barite replacing minor fluorite.
				Ni. marcasite ?	Anomalous pink, low bi refringence, very rare.
35	Middleton	282552	Replacement	Nil	Marcasite common, 50μ altering to goethite Rare chalcopyrite, covelline. Matrix, recrystallised limestone with barites replacing shell fragments and crinoid ossicles.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
36 Ashover (1)	351621	Undetermined	Zoned and unzoned bravoite	Common, banded, lilac, 50µ euhedral, inclusions in fluorite.
			Ni marcasite zoned.	Rare, associated with bravoite. Gangue fluorite, minor barites.
(2)	"	Replacement	Nil	Pyrites, marcasite, galena, malachite, cuprite, covelline, recrystallised micrite.
37 Crich (1)	343559	Void infill	Zoned and unzoned bravoite	Common, grey/brown, unzoned in fluorite, lilac, zoned in barites, altered to goethite in barites only. Alternating bands of barite, fluorite, galena, fluorite replacing galena?
(2)	345560	Void infill	Zoned bravoite	Common, pale lilac, unbanded, 10µ anhedral associted with 150µ pyrite and sphalerite in 100% calcite matrix.

A Description of the Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
37 Crich (3)	340558	Replacement	Nil	Common 150-300µ euhedral pyrite, galena. covelline, gangue, recrystallised limestone, fluorite replacing fossil debris, minor barites laths.
(4)	342556	Void infill	Zoned bravoite	Common, unbanded, 40µ, euhedral, inclusions in barite and fluorite. Bravoite in barites much goethitised. Associated with pyrite. Gangue, alternating bands of barite and fluorite.
(5)	344556	Undetermined	Zoned bravoites	Very common, 80µ euhedral inclusions in fluorite and barite. Associated with chalcopyrite, covelline, pyrite, Gangue black fluorite, interpenetrated by barites laths. Bravoite much altered to goethite in barites.

A Description of Derbyshire Specimens Continued

Name	Ref.	Style	Nickel Species	Remarks
38 Ecton (1)	095577	Void infill	Zoned bravoite	Rare, unbanded, 10µ anhedral inclusions in calcite associated with chalcopyrite. pyrite, marcasite and sphalarite.
(2)	096585	Replacement?	Nil	Pyrite, chalcopyrite, galena, sphalerite, covelline, chalcocene, in calcite with rare euhedral quartz, and pyrite framboids.
Ecton (3)	"	replacement?	Nil	As (2) above, but including barites.
(4)	"	replacement?	Nil	Pyrite, chalcopyrite, marcasite, sphalerite in dolomite gangue.
(5)	"	replacement	Ni pyrite	Rare, faintly zoned pyrite, pink, or different habit to normal associated pyrite. Marcasite, chalcopyrite, galena, sphalerite. Gangue; alternating bands of creamy and brown dolomite with rare euhedral quartz.

4.3 Description of the Northern Pennine orefield.

The Northern Pennine orefield is divided structurally into two rigid blocks, the Alston block to the north and the Askrigg block to the south underlain by Devonian granites, (Dunham 1974), which are separated by the Stainmore syncline. To the north the region is bounded by the Northumbrian trough, and to the west and south by the Pennine, Dent and Craven fault systems. To the east, the mineralised Lower Carboniferous of the stable blocks plunges beneath the Carboniferous and Permian rock higher in the succession. The Carboniferous deposits over the rigid blocks are thin and may be regarded as having accumulated in a shelf area, those of the Alston block being primarily of typically Yoredalian facies of the Lower Carboniferous, and those of the Askrigg block having a tendency towards showing rhythmic sedimentation in the higher horizons, but dominated by the D_1 and S_2 Great Scar Limestone at the base of the succession.

The major quartz dolerite igneous intrusion of the Whin Sill is present in the Alston block, and is believed to be the source of silica and iron necessary for the silicification and ankeritisation of much of the limestone. In places the Whin is altered to the "White Whin", a rock composed of secondary carbonates, clay minerals, anatase, residual quartz and apatite, (Wager, 1929; Smythe, 1930). formed by the removal of iron, magnesium, silica, and soda, and addition of potash and carbonates. The fluids responsible for this metasomatism are considered to represent the first phase of mineralisation, introducing ankerite, chalybite and silica to the limestone, the second stage of mineralisation introduced sulphides, fluorite, barite and carbonates, and a late phase is characterised by the deposition of calcite.

In the North Pennine orefield, ore occurs either in mineralised fissures seldom deviating more than 20° from the vertical, or as metasomatic flats, owing their form to replacement of flat-lying favourable beds of limestone. The orefield is remarkable for the perfect conjugate pattern of vein fissures it exhibits, these representing mineralised faults. Generally faults having a displacement greater than 12 metres are un-mineralised, being filled and rendered unsuitable by shale gouge dragged in, but those less than this width in hard limestones, dolerite, and sandstones that remained open to the mineralising fluids are ore-bearing, with the greatest concentrations of mineralisation in and near the Great Limestone at the bottom of the Upper Limestone Group. In general, veins in the limestone are wider that those in the sandstone due to widening during mineralisation by solution and metasomatism. (Dunham 1949).

The minerals of the Askrigg block deposits include fluorite, galena, sphalerite, quartz, chalybite, ankerite barite and calcite, the distribution of fluorite and barite follows a crude zoning pattern as shown on map Fig. D. The innermost fluorite zone centred around St. John's Chapel, and Weardale, yields only minor quantities of sulphides, except for a unique occurrence of payable chalcopyrite. Quartz is generally most abundant in the innermost parts of the fluorite zone. Towards the periphery of the fluorite zone galena becomes important, with sphalerite appearing in places. In certain areas, a zone whose predominant mineral is barite follows next, but in other areas intermediate zones where the predominant minerals are galena, or galena and sphalerite with or without witherite are significant. (Dunham 1934, 1937.) Within the fluorite zone, the purple or green fluorite gives way to amber as the edge of the zone is approached, and, unlike Derbyshire, where the gangue mineral zoning describes only the predominant gangue mineral, visible barite is absent in the fluorite zone, and similarly, fluorite is not found in the barite zone.

The typical veins of the area exhibit a banded texture, paralleling the vein walls. The bands normally consist of pure or nearly pure minerals, with crystal faces developed on that side of the band nearest the centre of the vein, indicating that the veins were filled from the walls inwards. Bands of matrix material, fluorite, quartz or barite are generally continuous but the sulphide bands may be broken. Post-mineralisation movements are shown by slickensliding accompanied by narrow belts of brecciated vein material, but are seldom if ever accompanied or followed by the deposition of new primary minerals. The veins exhibit many repetition of bands, followed by several minor phases of reopening. Under these circumstances no general "order of deposition" of minerals can be acceptable. Dunham (1934), has however showed that marcasite and chalcopyrite were generally "early" sulphides, and that the crystallisation of fluorite was completed before the deposition of barite in the few instances where these minerals are associated in the field.

The Great Sulphur Vein, more properly described as a lode, is unique among the veins of the orefield. Its total length is 15 Km as shown on map Fig D. Its greatest width is 350 metres decreasing downwards to 33 metres where seen in the valley bottoms, and from structural evidence, it is known to post-date the Whin Sill. (Thompson 1933). The dominant mineral introduced is quartz, mainly present as a replacement of limestone, shale and sandstone within the lode, but making a few shoots of massive vein quartz which stand out as ribs. In the higher regions it is almost completely unmineralised but at the lowest exposed horizon, that of the Tynebottom Limestone there is what may be presumed to be a continuous zone of sulphides of tabular form containing pyrrhotite, pyrite and marcasite with in places a little chalcopyrite. A sequence of replacement is seen, pyrite replacing earlier pyrrhotite, marcasite replacing both minerals. Polished sections reveal that the tabular form of the sulphides is due to replacement of small slabs of argillaceous limestone derived from above which is considered to have collapsed during the metasomatism of the lower more calcitic beds. Structural arguments have been advanced to show that the Great Sulphur Vein is of a younger age that the remainder of the Pennine Veins, (Dunham 1934), yet it both shifts and is shifted by Sir John's Vein, (a normal mineralised vein) so the problem of its age remains open for the present.

The Askrigg block, consisting of Arkengarthdale, Swaledale, Wharfdale, Wensleydale and Midderdale is patchily mineralised. In Swaledale, Arkengarthdale and Wensleydale the rocks are of the rhythmic Yoredale facies, which thin towards the south at the same time the sandstones and shales decrease in significance with a marked increase in thickness of limestones until at Grassington a predominantly limestone sequence represents the D_2 subzone, and at Greenhow, the Great Scar limestone, (D_1 and S_2), or its lateral equivalent prevails. The southern margin of the mineral field lies in the vicinity of the Craven fault system, which also marks the strucutral change from 'block' conditions (Hudson 1924), to the basin of Bowland Shale and thick Millstone Grit sedimentation.

The limestones of the southern part of the Askrigg block are noted for the abundant and luxuriant growth of corals and crinoids, (Rayner 1946), probably induced by their favourable position in the shallow and clear waters immediately bordering the basin. (Ramsbottom, 1974).

The mineralisation is of veins in fissures, with the rare 'flat' and 'pipe' in the Greenhow area. The gangue minerals are fluorite, calcite, quartz and barytes, with galena, and fluorite occurring in strictly localised occurrences as shown on the map. Having regard to the well-defined central fluorite zone in the Alston Block (Dunham 1934), these areas may be considered to be adjacent to feeding centres. The most productive galena deposits occur in or marginal to these areas, as in the Alston Block.

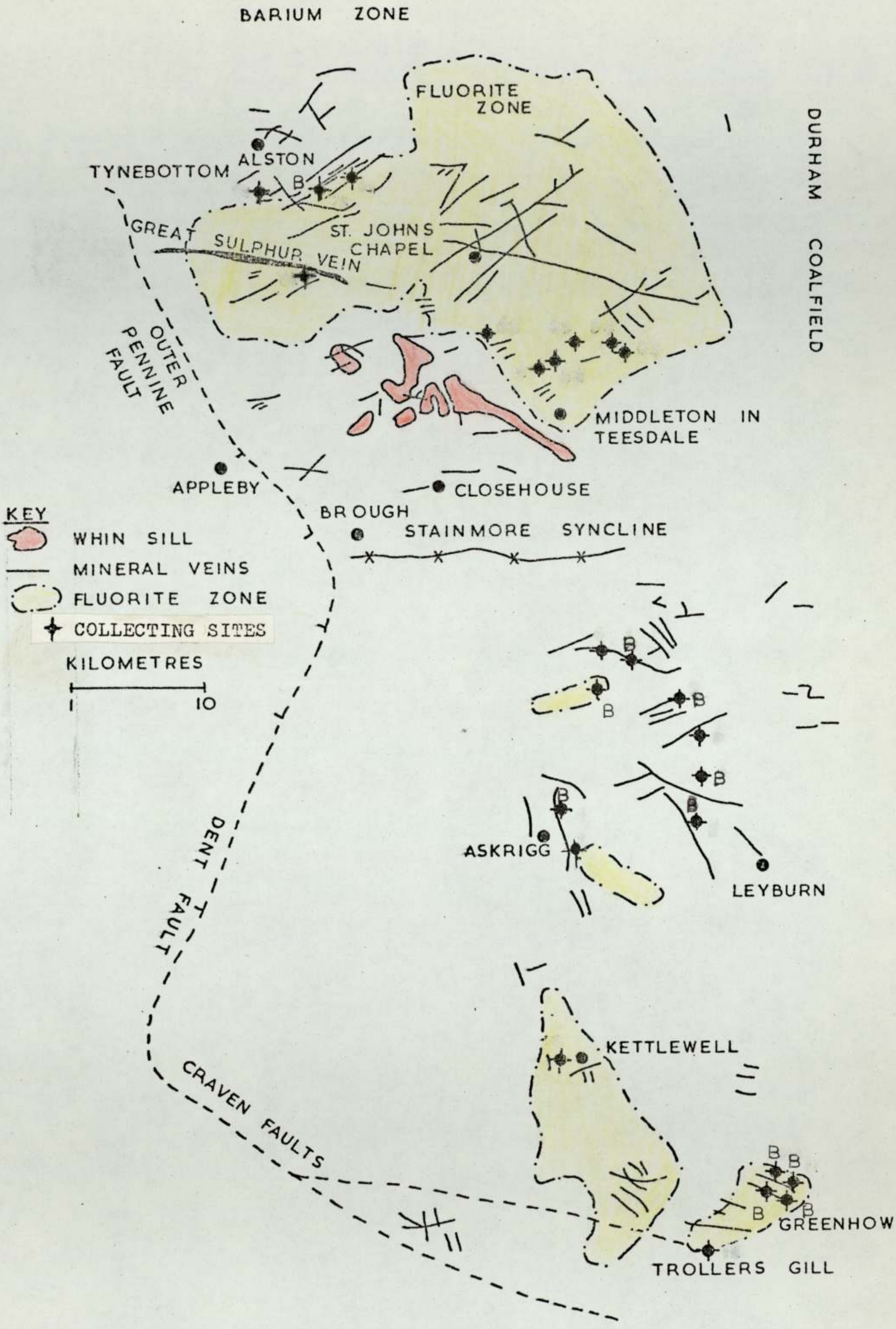


Fig. D. Sketch map of the Northern Pennines area showing the distribution of the collecting sites. B. indicates Bravoite.

A Description of the North Pennine Specimens. A. Askrigg Block.

Name	Ref.	Style	Nickel Species	Remarks
1 Swaledale				
Warton Hall	955905	Replacement	Nil	Pyrite, two generations, euhedral crystals of coelescing framboids in micrite, and later, large non framboidal pyrite in vein-filling calcite. Smithsonite. Gangue, recrystallised limestone, relict crinoids, rare euhedral quartz.
2 Redmire Scar	059931	Void infill	Zoned bravoite	Common, banded, brown, 50µ associated with pyrite, marcasite, sphalerite, as inclusions in barites, rarely in fluorite. Alternating bands of fluorite barites, galena. Bravoite frequently follows barite/fluorite boundaries.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
3	Summerlodge Moor (a)	946944	Replacement	Unzoned bravoite	Rare, unbanded, pale brown smudgy 10μ, anhedral, associated with very rare pyrite and marcasite. Gangue, brecciated dolomite.
	Summerlodge Moor (b)	946944	Replacement	Ni. pyrite	Rare, very pale lilac, pyrite in calcite. Gangue, calcite re-cemented limestone breccia.
4	High Faggergill	989062	Undetermined	Nil	Massive marcasite bands replaced by hematite. Marcasite rarely radical.
5	Langthwaite (a)	980030	Undetermined	Zoned and unzoned bravoite	Common unzoned unbanded lilac 15μ euhedral inclusions in barites, rarely in fluorite then zoned. Very pale lilac, 3μ in galena. Associated with rare chalcopyrite, pyrite, anglesite. Gangue, barites laths in fluorite.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
5	Langthwaite (b)	980030	Undetermined	Unzoned bravoite	Extremely rare brown, unbanded, 5µ in barites. Alternating bands galena/barites. Galena framboid. Gangue 100% barites.
6	Copperthwaite Mine	063005	Undetermined	Zoned bravoite	Common unbanded brown 50µ euhedral, inclusions in barites, associated with pyrites, marcasite.
				Ni. marcasite	Rare marcasites show possible zoning. Gangue; fluorite and barites.
7	Hurst	045023	Undetermined	Zoned bravoite	Common, unbanded, brown, 15µ, subhedral, as inclusions in fluorite. Rare bravoite in fluorite in galena. Gangue, barites and fluorite.
8	Greenhow Hill (a)	108640	Undetermined	Unzoned bravoite	Rare, lilac, unbanded, 5µ inclusions in fluorite associated with pyrites in barites/fluorite gangue.

A Description of the North Pennine Specimens Continued.

Name	Ref.	Style	Nickel Species	Remarks
8 Greenhow Hill (b)	108640	Undetermined	Unzoned bravoite	Rare, brown, unbanded, 5μ inclusions in fluorite, associated with 20μ euhedral pyrite in brecciated flourite with later fluorite cementing.
Greenhow Hill (c)	108636	Undetermined	Unzoned bravoite	Rare pale lilac, unbanded, 5μ associated with 100μ pyrites and rare marcasites,in barites with subordinate fluorite gangue.
Greenhow Hill (d)	108636	Undetermined	Zoned and unzoned bravoite	Rare, pale lilac, 10μ, unbanded, associated with pyrite and marcasite, as inclusions in barite gangue.
Greenhow Hill (e)	108636	Replacement	Nil	Pyrite, common, euhedral, 5μ associated with rare anhedral chalcopyrite, 5μ, in a calcite matrix with fossil debris and quartz porphryblasts.

A Description of the North Pennine Specimens Continued.

	Name	Ref.	Style	Nickel Species	Remarks
8	Greenhow Hill (f)	108636	Replacement	Nil	Rare, 2μ pyrites, euhedral associated with galena 100μ, in calcite gangue.
9	Trollers Gill	066621	Undetermined	Nil	Rare 5μ pyrites in fluorite gangue.

A Description of the North Pennine Specimens, B.Alston Block.

Name	Ref.	Style	Nickel Species	Remarks
Nent and South Tyne.				
1 Nenthead (a)	790436	Void infill and replacement	Zoned bravoite	Rare, unbanded, brown, 5μ inclusions in quartz around limestone fragments. Associated with 100μ chalcopyrite. Gangue, quartz, ankerite,chalcedony.
Nenthead (b)	790436	Undetermined Replacement	Ni. pyrite	Common, unbanded, zoning concentric, purple, very faint and fine, 10μ, euhedral, inclusions in quartz. Associated with chalcopyrite, pyrite, in quartz gangue with minor barites.
Nenthead	790436	Void infill	Nil	Pyrite, 10μ euhedral,chalcopyrite, galena, sphalerite around chalcopyrite. Quartz inclusions in sulphides common. Gangue, quartz, chalcedony barites, around limestone breccia. Later quartz

A Description of the North Pennine Specimens, B. Continued.

Name	Ref.	Style	Nickel Species	Remarks
				replacing galena.
2 Great Sulphur Vein (a)	739381	Replacement	Nil	Chalcopyrite, euhedral; chalcocene, covelline, in quartz matrix.
(b)	739381	Replacement	Ni. pyrite	Pyrite, 1cm., with marcasite inclusion, galena with pyrite inclusion. Rare pyrite, 10µ with possible very faint zoning. Gangue, quartz.
3 Garrigill (a)		Replacement	Nil	Arsenopyrite with minor euhedral pyrite 10µ, gangue ankerite, calcite quartz.
(b)		Replacement	Nil	As (a) above.
(c)		Replacement	Nil	Chalcopyrite, pyrite, euhedral; gangue, replacing ankerite.

A Description of the North Pennine Specimens, B. Continued.

	Name	Ref.	Style	Nickel Species	Remarks
	Teesdale.				
4	Newbiggin Common	903314	Undetermined	Nil	Sphalerite, galena, goethite in fluorite matrix.
	Lodgesike-Manorgill Vein 6.5Km		Mineralised shatterbelt with replacement.		
5	Coldberry	942290	Void infill	Nil	Galena, graphite, pyrite of two generations, framboidal in limestone breccia pieces; late in quartz matrix. Gangue; ankeritic limestone breccia, quartz.
6	Lodgesike Mine	955293	Void infill	Nil	Chalcopyrite, 40µ euhedral; sphalerite, galena, in shattered quartz matrix around siliceous breccia containing framboidal pyrite and 5µ marcasite.

A Description of the North Pennine Specimens, B. Continued

Name	Ref.	Style	Nickel Species	Remarks
7 Eggleshope Mine (1)	977307	Void infill	Nil	Pyrite, euhedral 120µ; chalcopyrite euhedral 100µ. Galena, containing and contains chalcopyrite. Gangue, quartz, cemented siliceous breccia.
(2)	997308	Void infill	Nil	Coelescing framboidal pyrite in ankerite breccia, cemented by sphalerite-bearing quartz.
(3)	013308	Void infill	Nil	Framboidal pyrite in shale breccia cemented by quartz bearing pyrite, sphalerite and galena.

4.4 Description of the Central Mendip lead-zinc orefield.

The Central Mendip area is included in the Wells Sheet (280) of the 1" to the mile Geological Survey Maps. (New Series).

The geology consists of two main elements, a relatively complex basement of upper Palaeozoic rocks, and a strongly unconformable cover of gently folded lower Mesozoic rocks. (Welch 1929).

The ore-bearing rocks are the limestone facies of the Carboniferous Limestone Series and the massive facies of the Dolomitic Conglomerate (Keuper in age). The limestones are described by Green (1958) and Green and Welch (1965), and are of the order of 800m thick.

The Dolomitic Conglomerate is typically a breccia or conglomerate largely composed of fragments of Carboniferous Limestone with some scattered Upper Palaeozoic sandstone and quartzite. The matrix varies from a marl in the finer grained varieties to a calcareous rather angular gravel in the coarsest varieties. The Conglomerate has a variable thickness and has been proved to over 120m.

The main structures in the Palaeozoic rocks, described by Welch (1929), are three en-echelon periclines aligned east-west, and contemporary faults and thrusts. Folding had ceased by Mesozoic times, and a landscape of great relief was buried by the Dolomitic Conglomerate and subsequently Keuper Marl. (See Map Fig. F)

The controlling factor in ore deposition was local structure rather than lithology. The whole of the limestone and conglomerate are mineralised, especially adjacent to the faults and on the flanks of the periclines, which are in places overturned.

Examination of the debris thrown out from old workings shows the dominant gangue mineral is calcite, usually coarsely crystalline and milky white or red and yellow stained. It is sometimes banded, sometimes veined with barite. Fluorspar is present as very rare traces. Schnellman and Wilson (1947), have suggested the spatial distribution of gangue minerals corresponds to a rough temperature zoning, in order of decreasing temperature, fluorite, barite, calcite, and it is noteworthy that in the Mendips, the strongest mineralised zone contains abundant barite, whilst peripheral to this, barite is unknown in the calcite.

The galena is widespread, both as specks and small crystals scattered in the calcite and barite, and as occasional nodules of many kilograms (Green 1958). Trace quantities of sphalerite are widespread, the main ore of zinc is calamine (smithsonite $ZnCO_3$). Much very siliceous 'brown haematite' is present, whether it is much later or an oxidation product of pyrites contemporary with the other sulphide mineralisation, is unknown. Kingsbury (1941), gives a detailed account of mineral localities on the Mendip Hills, many of these were visited, but in the greatest majority agricultural and natural processes have completely covered and rendered non-locatable the sites he records. It was with the greatest difficulty that any mineralisation was found; all mining activities having ceased at the beginning of the century, and no re-working having taken place subsequently to expose the material. Calcite pieces were fairly widespread in ploughed fields, and especially so in one recently shown to be the site of Roman smelting operations, but none revealed any trace of metalliferous mineralisation. Because of the problems of finding suitable material the number of samples studied is small.

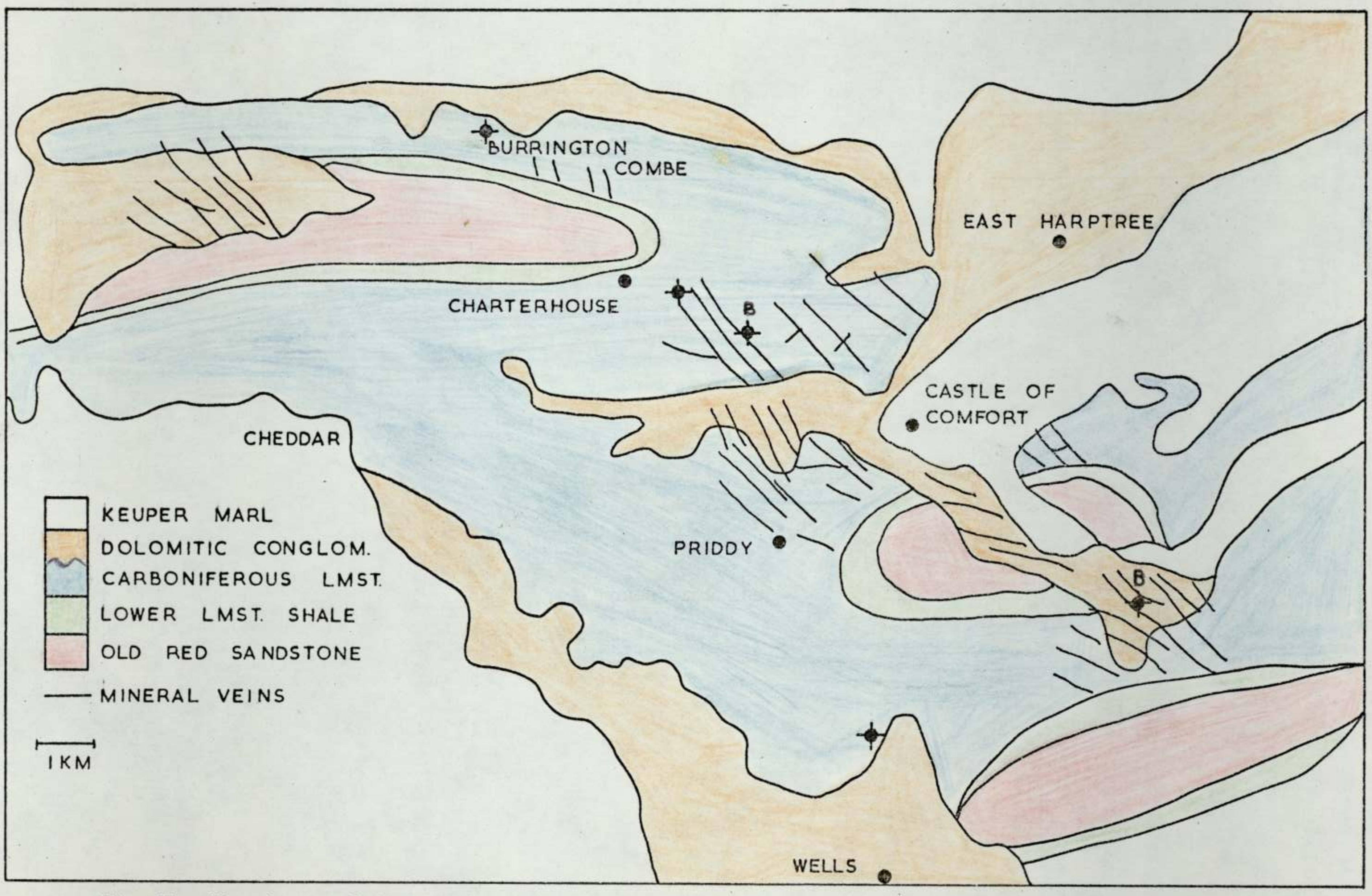


Fig. F. Sketch map of the Mendips, showing the chief mineralised areas and distribution of the collecting sites. Bravoite marked B.

A Description of the Mendip Specimens.

Name	Ref.	Style	Nickel Species	Remarks
Charterhouse	504555	Void infill	Nil	Rare anhedral pyrite, 75% goethitised, associated with cerrusite; gangue, calcite, much brecciated and weathered.
Haydon Grange	518548	Replacement	Unzoned bravoite	Rare, unbanded, 3µ, euhedral lilac, associated with 3µ pyrite in a recrystallised brecciated limestone with secondary calcite matrix.
Green Ore	560505	Undetermined	Unzoned bravoite	Extremely rare, brown, 4µ euhedral, enclosed by 10µ euhedral pyrite, associated with framboidal pyrites, occasionally having darker inner zone. Gangue calcite.
1.6 Km. E. of Wookey Hole	548482	Void infill	Nil	Very rare, pyrite, 3µ euhedral in calcite gangue.

4.5 Description of the Shelve-Habberley mining region, West Shropshire.

The ore-field lies roughly within a radius of 10Km around Shelve village, 22Km south-west of Shrewsbury, but is confined almost exclusively to the Mytton Beds of the Arenig Series, Ordovician. (Geol. Surv. sheet 152, new series). In this area the sequence of Ordovician rocks seems to be nearly complete (Whittard 1958). except for the absence of the Ashgill series. The Mytton Stage commences with the Stiperstones quartzite, a very hard, siliceous, in part conglomeratic sandstone. The Mytton Beds, which follow, consist of hard flags and shales of which all the spoil heaps of the lead mines are composed. These are overlain by the Hope Shales, the base of the Llanvirn Series, and succeeded by the Stapeley Volcanics, an inter-bedded series of tuffs, breccias, lavas, and shales. In general the strike is to the north-north-east, with Mytton Flags cropping out either side of the Ritton Castle syncline, in which the unmineralised Hope Shales and Stapeley Volcanics appear at the surface. To the east the mineralised area is bounded by the Stiperstones Quartzite, forming the very prominent ridge and crags of the Stiperstones. To the west the beds plunge underneath, as successively higher Series of the Ordovician come in.. A transgressive sill of dolerite is present in the area. The mineralisation is confined to regions in the most competent rock shattered by a series of parallel east-north-easterly trending and north westerly trending faults. In the shaly strata, where the softer rock has been comminuted and reduced to a pug, filling the fault fracture, the mineralising solutions have been unable to penetrate, and the beds are barren.

The mineralisation occurs as galena, sphalerite, and rarely pyrite, in a gangue of crushed country rock with quartz, calcite, barytes, and occasional fluorspar. Although the veins show no direct connection with the igneous intrusions, they may be related to a concealed mass of granite.

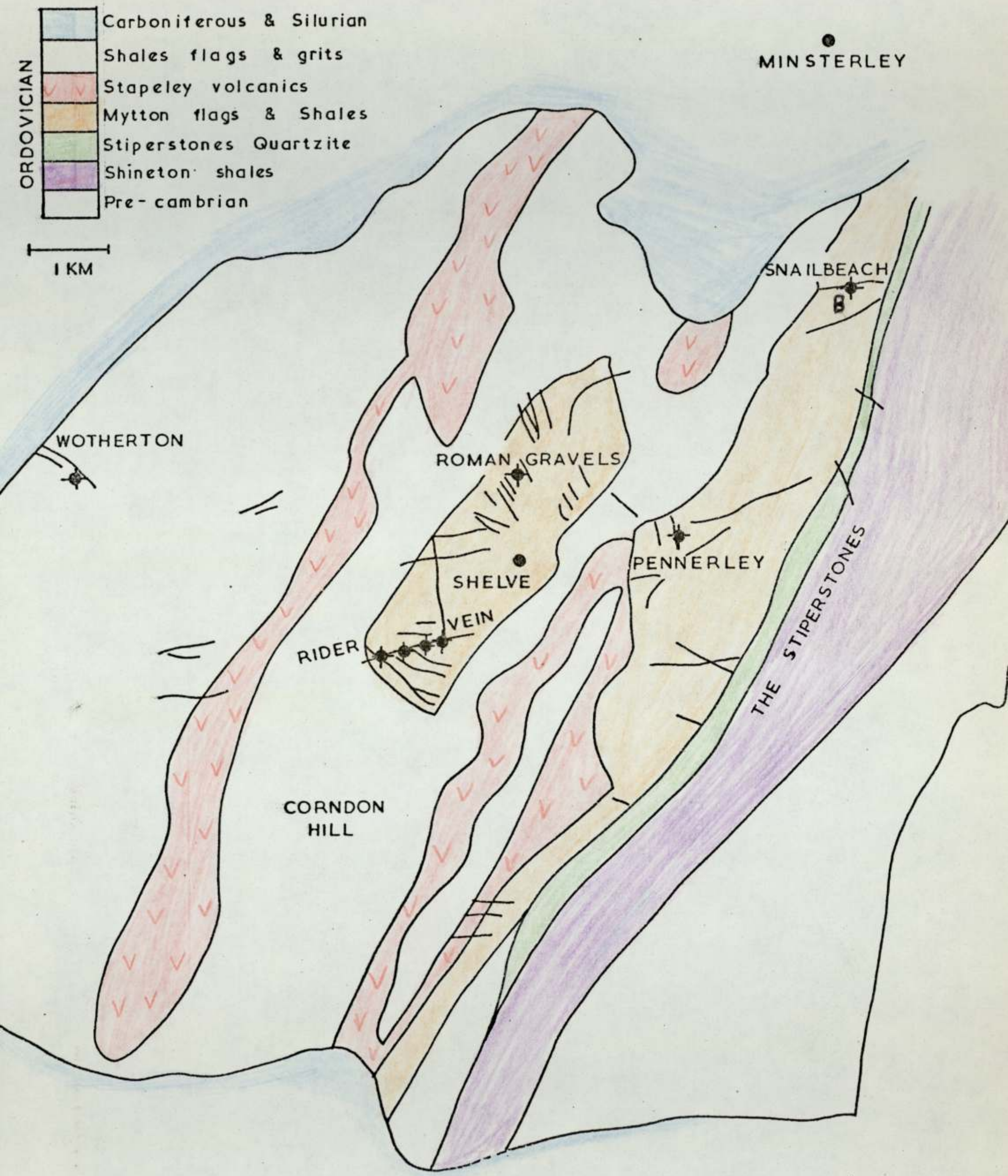


Fig. E. Sketch map of the Shelve, Shropshire, area, showing the chief mineral veins and distribution of the collecting sites. B. indicates Bravoite.

A Description of the Shelve-Habberley Specimens.

Name	Ref.	Style	Nickel Species	Remarks
Snailbeach Mine	374023	Void infill	Unzoned Bravoite	Rare, unbanded 5μ, brown, as inclusions in sphalerite, associated with chalcopyrite in a calcite gangue being replaced by quartz.
Roman Gravels	335002	Replacement	Ni. pyrite	Rare, pale pink pyrite, 5μ, associated with pyrite, pyrrhotite, graphite, rutile, Hematite, Sphalerite, anatase.
Pennerley Mine	355995	Undetermined	Nil	Pyrite, chalcopyrite, graphite, sphalerite, pyrrhotite, gangue; quartz.
Whitegrit	319979	Undetermined	Nil	As above, with ruby blende.

PHOTOGRAPHS OF POLISHED SECTIONS

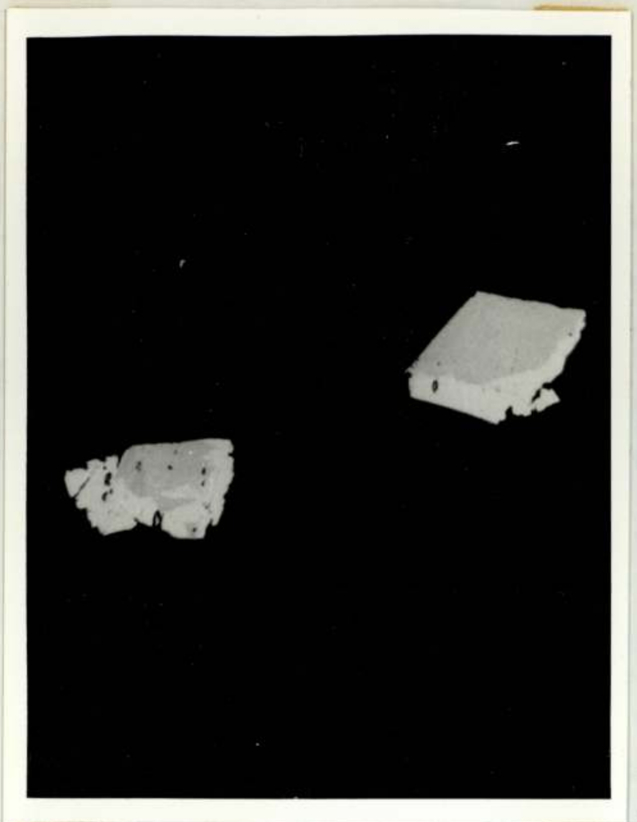
All the photographs are of specimens found in Derbyshire unless otherwise stated. The columns headed 'Location' and 'Number' refer to the description tables.

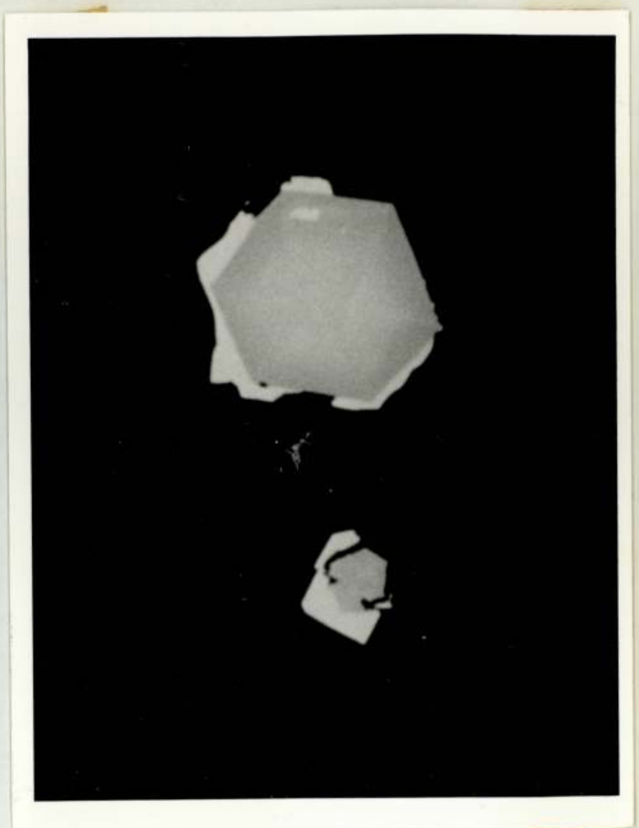
Plate No.	Photo. No.	Location	Number
1	1	5 Shuttle Rake	7b
	2	14 Deep Rake	2
	3	25 Oxclose Mine	(a)
	4	37 Crich	1
2	1	9 Hucklow Edge	3
	2	5 Shuttle Rake	7b
	3	9 Hucklow Edge	2
	4	37 Crich	2
3	1	1 Odin Mine	
	2	5 Shuttle Rake	2
	3	9 Hucklow Edge	2
	4	2 New Rake	
4	1	14 Deep Rake	2
	2	2 Redmire Scar (Askrigg)	
	3	9 Hucklow Edge	3
	4	9 Hucklow Edge	3
5	1	14 Deep Rake	2
	2	1 Odin Mine	
	3	7 Hurst (Askrigg)	
6	1	22 Near Winster	
	2	22 Near Winster	
	3	9 Hucklow Edge	3
	4	9 Hucklow Edge	3

Plate No.	Photo. No.	Location	Number
7	1	9 Hucklow Edge	3
	2	9 Hucklow Edge	3
	3	22 Near Winster	
	4	22 Near Winster	
8	1	22 Near Winster	
	2	22 Near Winster	
9	1	3 Garrigill (Alston)	(a)
	2	3 Garrigill (Alston)	(a)
	3	3 Garrigill (Alston)	(a)
	4	3 Garrigill (Alston)	(a)

PLATE 1

No. 1 U.L.	Two brown bravoites in calcite with pyrite rims on three sides only. Zoning in right hand grain very irregular. X 350.
No. 2 U.R.	Euhedral lilac bravoites showing faint concentric and radial zoning, partially rimmed with pyrite. X 750.
No. 3 L.L.	Euhedral lilac bravoite in fluorite partially rimmed with pyrite. Characteristic pentagonal habit with concentric and radial zoning. X350.
No. 4 L.R.	A double bravoite crystal showing concentric zoning, with a dark nickel-rich centre adjacent to a pale pyritic centre. X400.





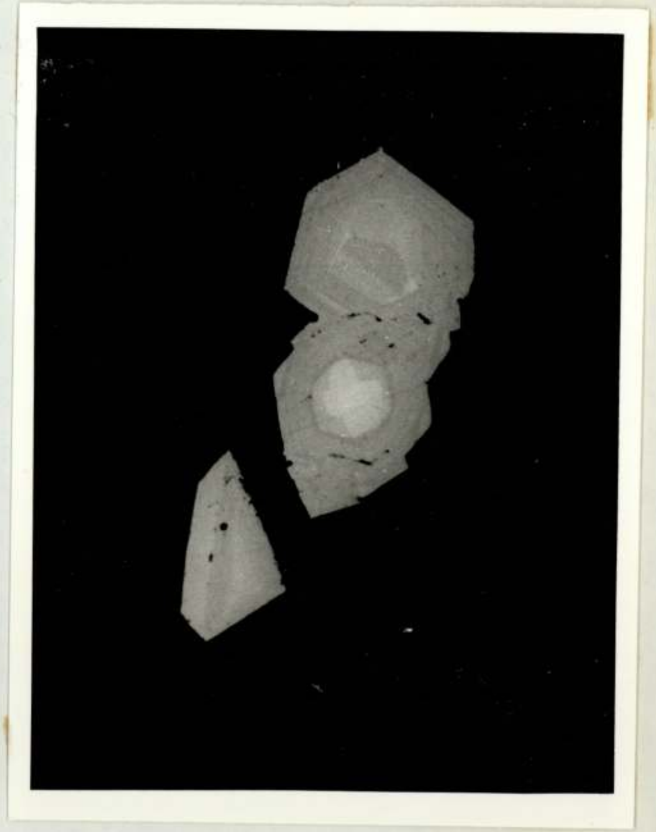
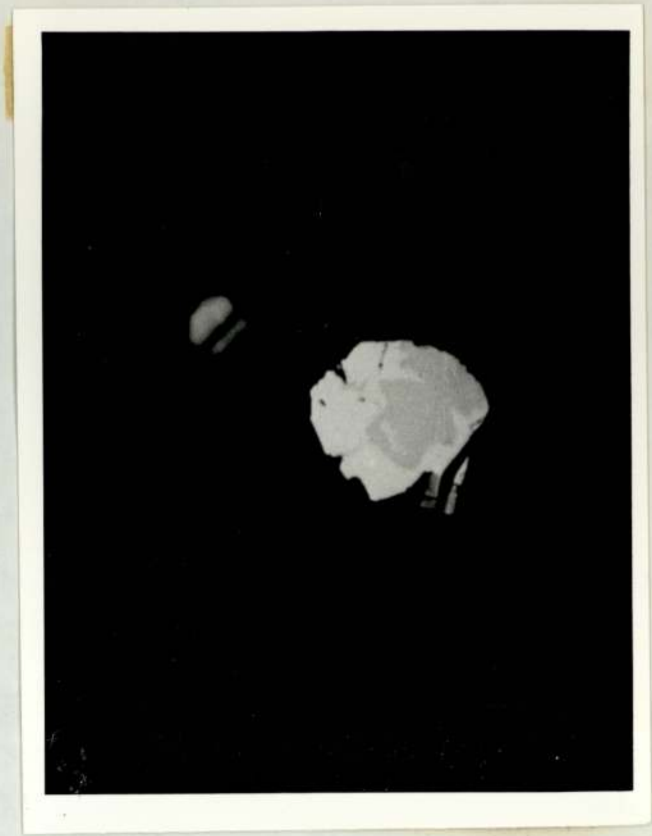
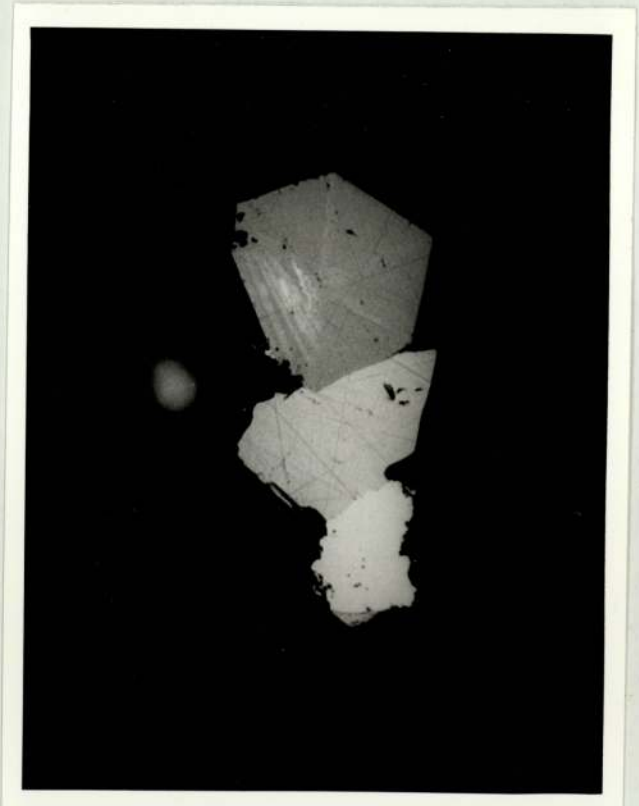


PLATE 2

No. 1 U.L.	Elaborately zoned bravoite in fluorite showing faint concentric zoning and below, a well defined sub-parallel zoning with a superimposed fine structure and 'cross zoning'. X250. Compare with 3 below.
No. 2 U.R.	Elaborately zoned bravoite partially surrounded by pyrite, in fluorite. X700.
No. 3 L.L.	Subhedral chalcopyrite separating anhedral pyrite from very euhedral bravoite. Bravoite shows pale streaks sub-parallel to long face. X250. Compare with No. 1 above.
No. 4 L.R.	Lilac bravoite in fluorite, partially enclosed by a 1 to 2u rim of pyrite, with an irregular pyritic zone in centre. X700.





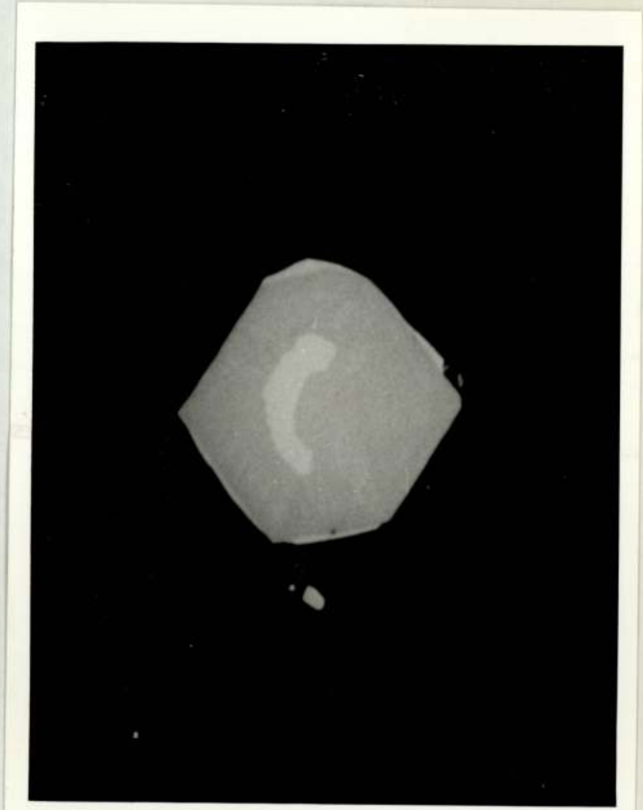


PLATE 3

No. 1 U.L.	Scalenohedral pentagonal bravoite with faint concentric zoning, and nickel rich rim in nickeliferous pyrite. Outer zones of bravoite being preferentially replaced by goethite. Quartz gangue. X500.
No. 2 U.R.	Concentrically zoned subhedral bravoite with nickel rich centre and pyrite rim, in calcite. X1000.
No. 3 L.L.	Double zoned purple bravoite surrounded by pyrite on three sides. The bravoite crystal is growing on the face of a fluorite crystal. X750
No. 4 L.R.	Bravoite in fluorite showing three main subhedral zones. The central euhedral hexagonal darker zone contains 1μ wide fine zoning structure. X500.

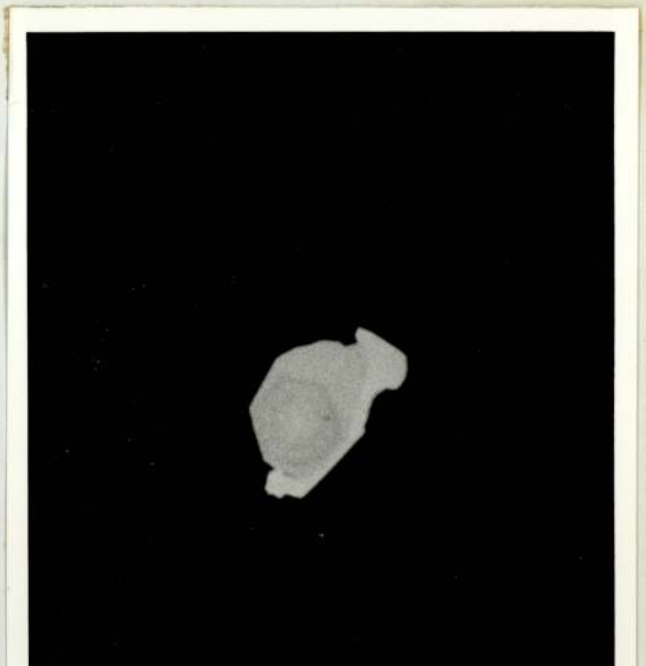
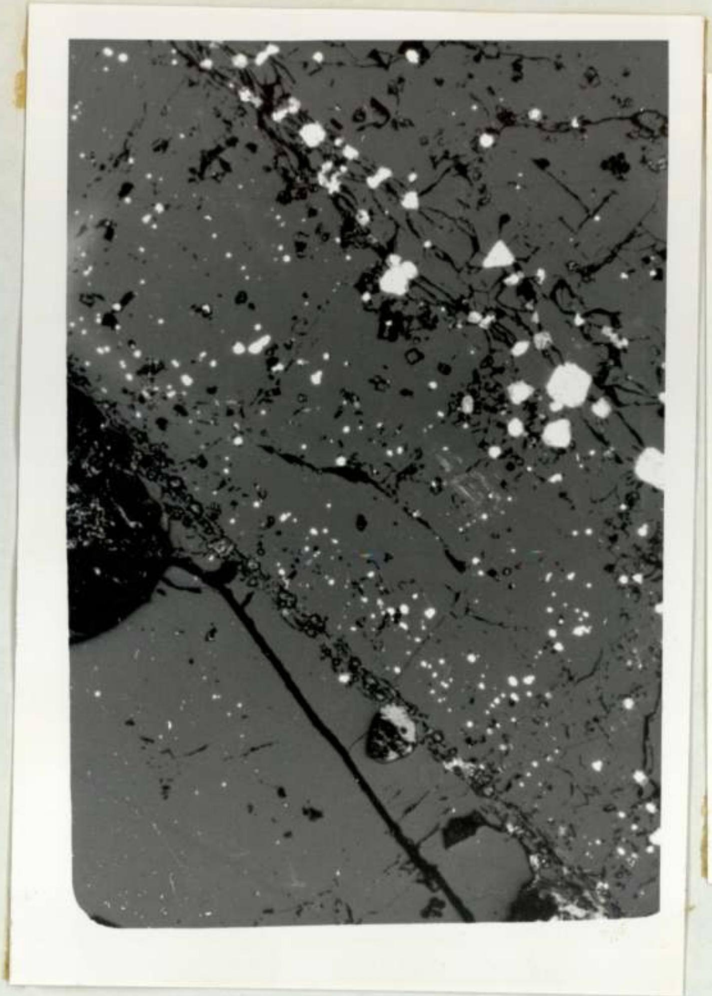


PLATE 4

No. 1 U.L.	Two bands of bravoite crystals in fluorite, and some scattered inclusions. These are generally small and unaltered, but the larger bravoite crystals on the fluorite crystal faces are being replaced by goethite in some instances. X50.
No. 2 U.R.	Bands of bravoite crystals following barites-fluorite junction. The bravoites are confined to the barites. Large pyrite crystal on left. X30.
No. 3 L.L.	Assemblage of bravoite, pyrite and marcasite in fluorite. Bravoite dark grey and streaky grey; marcasite pale grey; fluorite black. X250
No. 4 L.R.	As lower left. X250



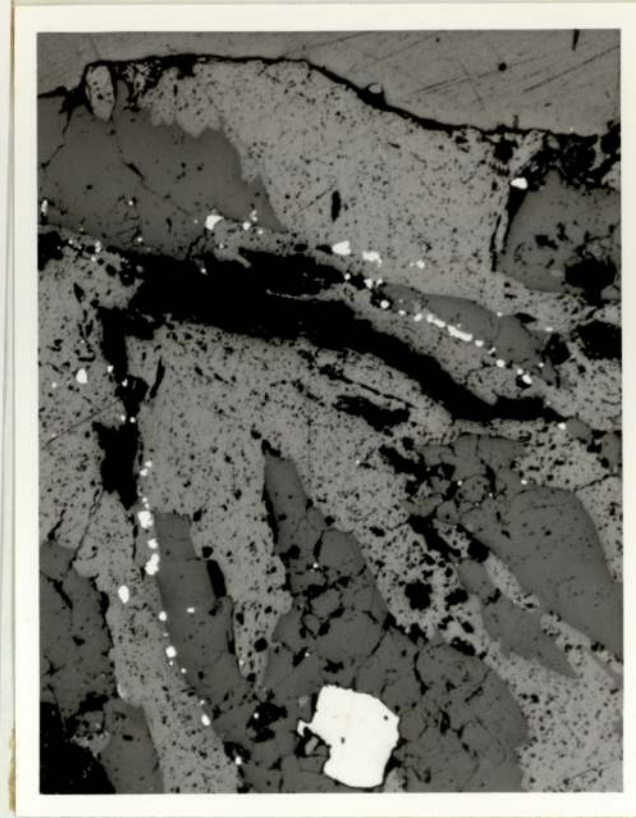


PLATE 5

No. 1 U.L.	Zoned goethite pseudomorphing bravoite on fluorite crystal faces. Small unaltered bravoite in centre of fluorite crystal as inclusion. X250
No. 2 U.R.	Pyrite white, chalcopyrite pale grey, bornite dark grey. Marcasite grain below. From Odin Mine, Derbyshire. X100.
No. 3 L.L.	Bravoite in fluorite being replaced at centre and radially by goethite. X300.

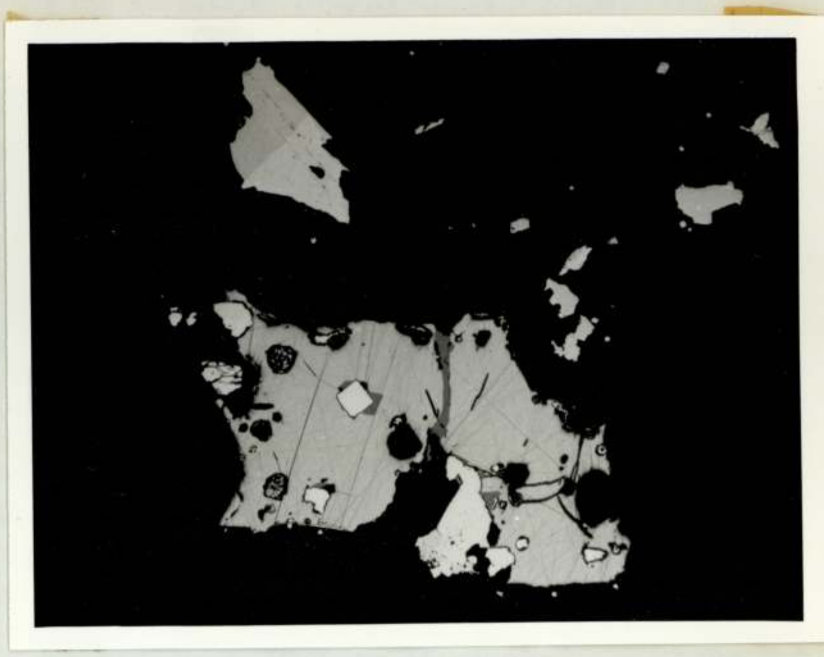
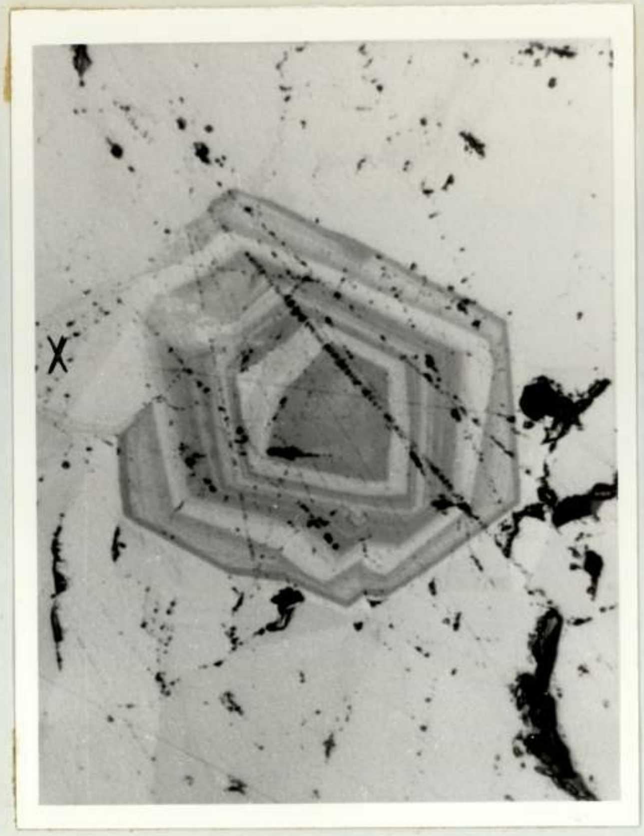


PLATE 6

No. 1 U.L.	Nickeliferous marcasite. Fine multizoned bravoite in marcasite in calcite flake. Note continuation of bravoite zoning into marcasite on left. Polars uncrossed. X300.
No. 2 U.R.	As left. Polars crossed. Note anisotropy at left where bravoite zoning continues into marcasite. X200.
No. 3 L.L.	Nickeliferous marcasite. Bravoite crystals separated by marcasite. The upper bravoite has a fainter outer zone, with intermittant pyrite boundary, and a dark inner zone. The continuation of the darker inner zone is seen as a relatively darker band crossing the marcasite and joining up with the adjacent bravoite. Polars uncrossed. X250.
No. 4 L.R.	As lower left. Polars partially crossed. Note the marcasite and the dark band joining the bravoites cut by the marcasite crystal boundary. X250.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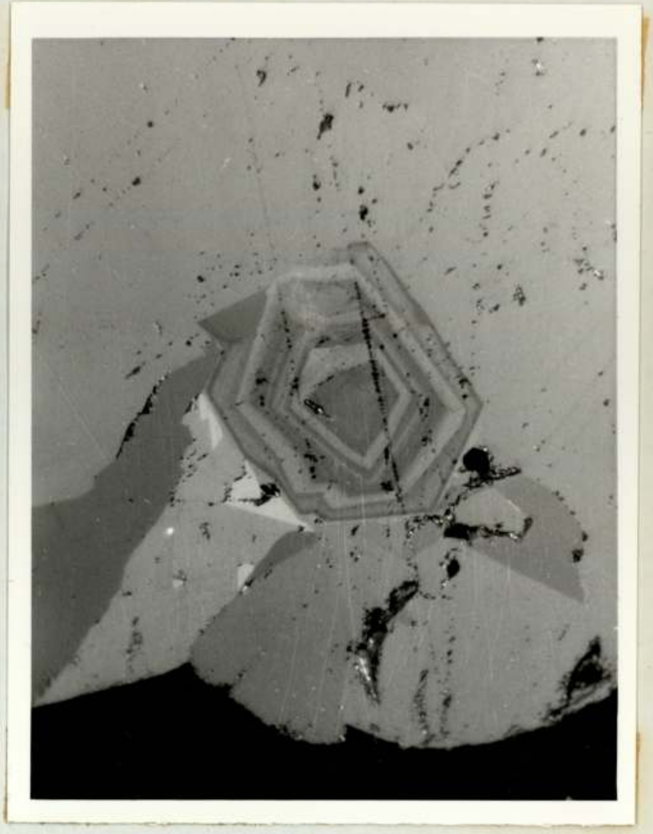
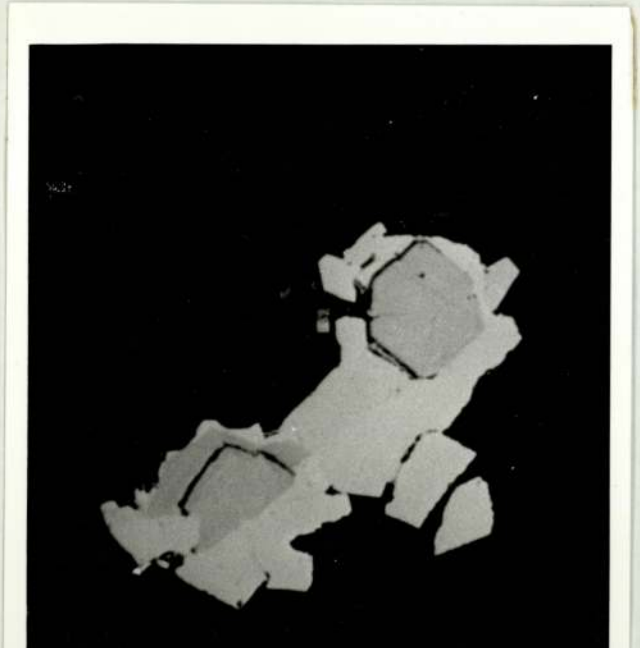




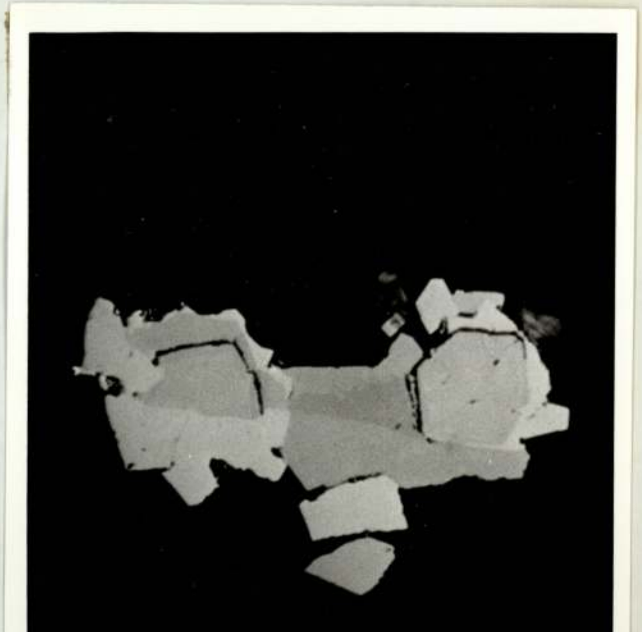


PLATE 7

No. 1 U.L.	Zoned marcasite. Marcasite showing bravoite-type colour zoning. This is purple, and not pleochroism. Polars uncrossed. X300
No. 2 U.R.	As above, polars crossed. Zoning remains, but anisotropy changes it to a deep purple. X300
No. 3 L.R.	Multizoned bravoite surrounded by marcasite and pyrite. Polars half crossed. X250.
No. 4 L.L.	Multizoned bravoite in pyrite. Gangue, calcite flake. Bravoite colours, from top; pale lilac, centre and lower, brown, separated by dark lilac, V shaped zone. X500.

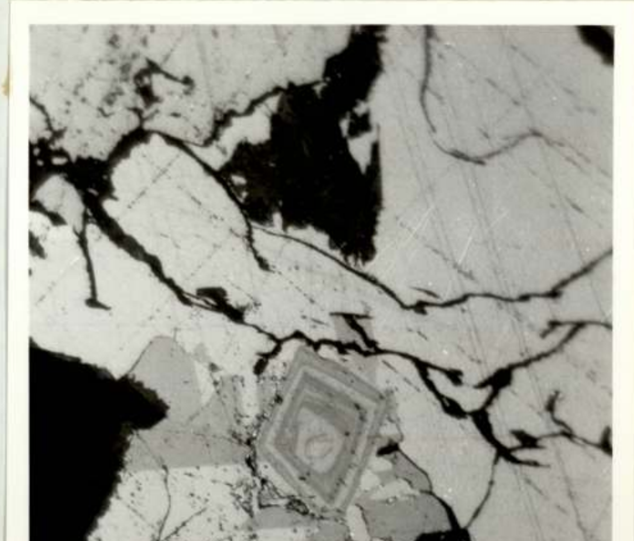
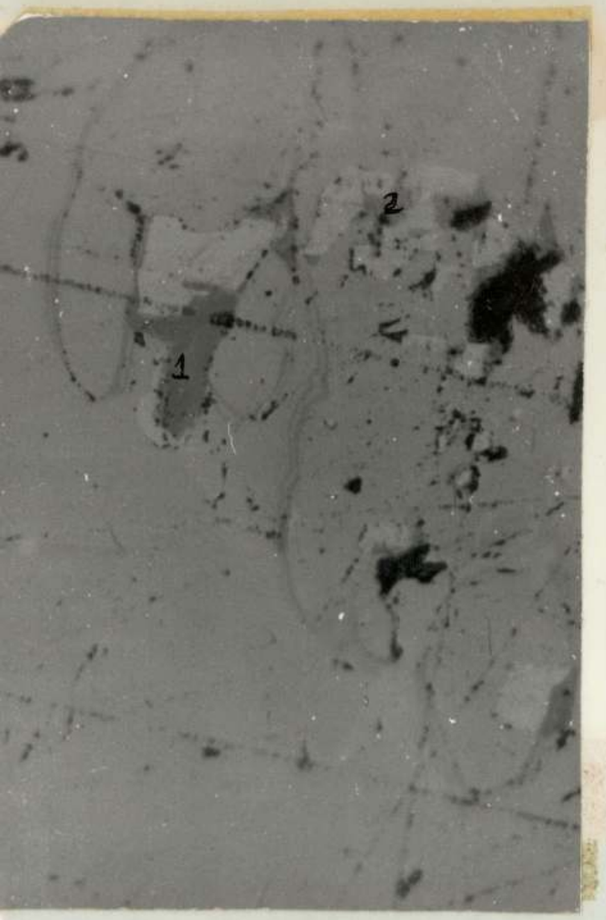


PLATE 8

No. 1 U.L.	Nickeliferous marcasite. Deep purple bravoites in marcasite with sinuous purple band cutting marcasite crystal boundaries. Dark grey; bravoite, Pale grey; marcasite, light grey; pyrite. Polars uncrossed. See Fig. 3. X500.
No. 2 U.R.	As left, polars partially crossed. Marcasite anisotropy seen, with coloured bands cutting across it. X500.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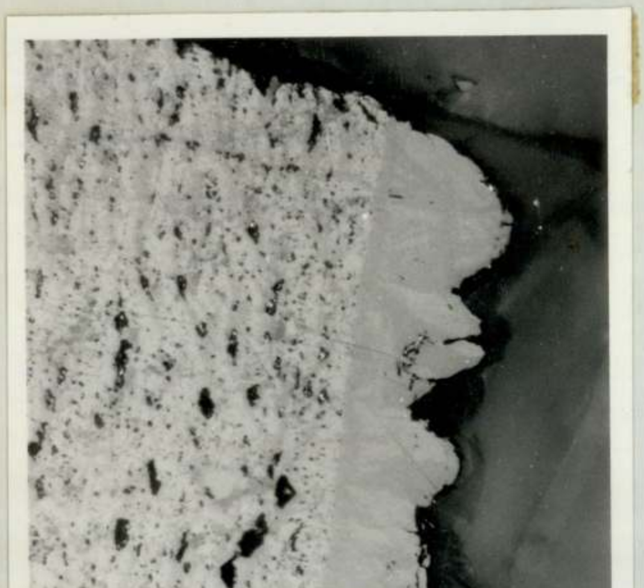


PLATE 9

No.1 U.L.	Much fractured arsenopyrite in quartz. Tynebottom Limestone. X25
No. 2 U.R.	As left, showing anisotropic rim of different phase. X100.
No. 3 L.L.	As above, showing various unidentified phases. X250.
No. 4 L.R.	As above, polars crossed. X300

CHAPTER 5

DISCUSSION OF RESULTS.

5.1 Classification.

The nickel species observered were classified as

1. Bravoite
2. Nickeliferous pyrite
3. Nickeliferous marcasite.

5.1.1. Bravoite.

Colour brown, violet, mauve, lilac, grey.

The colours varied both as indicated above, and in depth or saturation, from a faint tinge to moderately and rarely very, deep. The determination of the colours was very subjective except in the case of the rare deep hues.

Zoning Zoned or unzoned. An extremely common form of zoning was the bizoned pentagonal form which consisted of an inner coloured core surrounded on four sides with a narrow rim of yellow pyrite, groups of similar crystals often arranged in semi-parallel bands, and had a certain orientation of the zoning. This is discussed later. (Fig 2).

Zone widths varied from less than 0.5µ to almost the complete width of the crystal. Zone boundaries were generally sharp, rarely diffuse. Rare instances of a zonal boundary gradually disappearing by gradual convergence of the colours either side to one common colour are known.

Zones were generally regular, often exhibiting some coarse symmetry. (Plates 1,2,3) Completely irregular zoning patterns were rare, but ranged from interdigitation to those which approximated in appearance to a myrmekitic intergrowth.

A regular variation of zone width linked with a similar regular variation of zone colour often occured. This led to an appearance of a coarse symmetry about some point in the crystal.
Pl.2.1 illustrates a unique cross-hatched pattern.
Superimposed on a course zoning pattern was commonly a finer pattern, which consisted of subtle variations within the zone of the dominant zone colour. The widths of this fine zoning extended down to the limit of resolution of the microscope.

Isotropy	Isotropic, rarely slightly anistropic.
Twinning	Not apparant.

5.1.2 Nickeliferous Pyrite

Colour	Faint pinkish superimposed on yellow pyrite.
Zoning	Not present, or very faint.
Isotropy	Generally isotropic, rarely showing faint anisotropy.
Twinning	Not apparant.

5.1.3 Nickeliferous Marcasite Plate 6.

Colour	Similar to bravoites, less intense, less variation in one crystal.
Zoning	Usually zoned or 'streaky', zones or 'streaks' which cut across crystal or twin boundaries.
Isotropy	Strong anisotropy.
Twinning	Often present.

5.2 Detailed description of Bravoite.

5.2.1 Bravoite distribution.

Bravoite was found throughout all the geographical locations where the study was made. There was no-where any detectable difference in colour, shape, zoning pattern or mode of occurrence. Regional variations that were found in the distribution are shown below:

Locality	Collection sites	Number with			Percentage of sites with bravoite	Specimens made	Number with bravoite
		Br	Py	Mc			
Derbyshire	79	56	14	10	71	93	70
Askrigg Block	10	7	1?	1?	70	16	10
Alston Block	10	1	2	–	10	14	1
Shelve, Salop	4	1	1	–	25	4	1
Mendips	4	2	–	–	50	4	2

5.2.2 Bravoite associations - other sulphide minerals.

% of all specimens containing	Pyrite	Chalcopyrite	Marcasite
	86	30	50
% of all bravoite - bearing specimens containing	97	37	38

These figures show that bravoite had a very strong tendency to be associated with pyrite and chalcopyrite, and less so with marcasite. A possible reason for copper to show a preference for co-precipitation with nickel as the sulphide is that the chemical and physical conditions required by both were similar for the precipitation of chalcopyrite and bravoite, respectively; and were not so favourable for the precipitation of marcasite. An interesting point arises as to why the nickel/iron sulphide favoured precipitation from numerous nuclei from many small crystals, and the copper/iron sulphide favoured fewer nucleation sites but produced much larger crystals.

Insufficient samples were studied from regions other than Derbyshire to be able to construct a similar analysis concerning relative mineral occurrences.

5.2.3 Bravoite associations - gangue minerals.

Bravoite was found in all three common "gangue" minerals; fluorite, calcite and barytes. Rare occurrences in quartz were also noted. Where a banding of gangue occurred, bravoite had a tendency to be located at or just adjacent to the contact zone between the gangues. Where the admixture of gangues was heterogenous especially as between fluorite and calcite, no preferential host could be determined. However in a mixture of fluorite and barites, the barite appeared to be the more favourable host. No reason is offered for this. See Plate 4, No. 2.

5.2.4 Textural Relationship.

1. Banding. See Plate 4, No. 1.

In many polished sections, a marked banding of bravoite was observed in the gangue mineral. This was particularly apparent in fluorite and scalenohedral and rhombohedral calcite. Parallel and sub-parallel bravoite bands were commonly of the order of 10 to 20 microns wide, composed of 5 micron bravoite crystals which exhibited diverse crystal forms. Each band had characteristically its own modal size of crystal, although there was considerable scatter about the mode with the distribution being skewed towards the smaller sizes. The crystals were either found predominantly on the gangue mineral crystal faces, or predominantly as inclusions inside the gangue mineral.

2. Bravoite and Pyrite.

The relationship of the pyrite to the bravoite varied from one of being a completely enclosing mineral, to merely rimming the bravoite on one face only. As an enclosing phase, the widths of rim on all faces commonly varied, not only in relation to the width on adjacent faces, but also along each face. A very common relationship was that of a pentagonal bravoite, generally not exceeding 10 microns, having a pyrite rim well developed on four faces, but missing on the fifth face. A statistical analysis of the angular direction of the normal to the faces of the bravoite that was nickel free was carried out, the angle subtended by the normal through the bravoite produced was measured with respect to some arbitrary direction as reference on the polished section. A bimodal distribution was commonly found, having maxima less than 90° apart particularly when the crystals were growing in a fluorite gangue. Since a crystal will grow in a direction normal to the substrate on which it commences growth, assuming unimpeded flow of ions in solution to all exposed faces, the directions of the measured normals will in fact be the direction of growth, and since the pyrite follows the bravoite spatially, it is therefore later than the bravoite in the paragenetic sequence. See fig 2 .

3. Bravoite and other sulphides.

Other sulphide minerals, galena, sphalerite, and chalcopyrite are seldom hosts for bravoite, There is further, a special and marked association between bravoite and marcasite which will be discussed in a later chapter. Notwithstanding the rarity of bravoite as inclusions in galena, sphalerite or chalcopyrite, there is exhibited a marked tendency for bravoite to be located in bands adjacent to galena separating it from the associated gangue mineral. Although the evidence is by no means free of ambiguity,

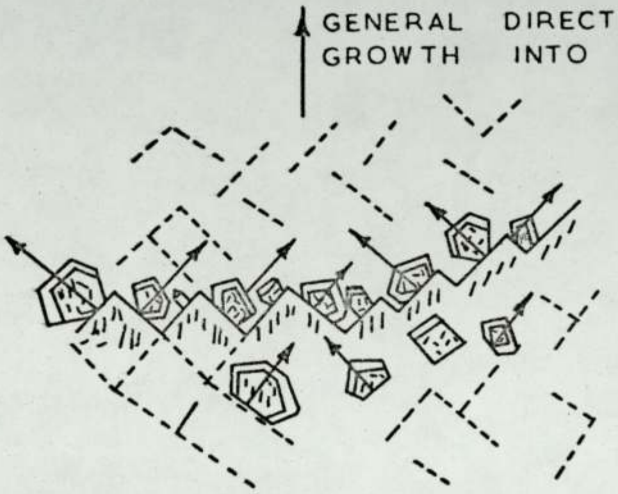


Fig. 2 . Sketch showing the arrangement of bravoite in pyrite growing on fluorspar crystal faces, indicating the direction of growth. The bravoite is shaded inside the pyrite.

there is a tendency for bravoite to be associated with minor purple fluorite showing contact colouration adjacent to galena, in an otherwise colourless fluorite field.

5.2.5 Physical Properties.

1. Size

Bravoite crystals range in size from a minimum diameter of 2 microns to a maximum of 150 microns, the commonest size would appear to be about 10 to 20 microns. There appeared to be no correlation between size and colour, nor between size and crystal habit. The smaller crystal is commonly more euhedral than the larger, because adjacent crystal growth is less likely to interfere.

2. Colour.

Bravoites range in colour from grey, lilac, violet, mauve, to brown, or any intermediate hue of varying saturation. They can be of one colour, two, or many, and if not monochromatic, the colours form zones, either continuous or discontinuous, concentric or radial, or both. In one crystal successive colour zones or groups of zones commonly show a change of outline for example, from pentagonal dodecahedral to cubic. Similarly, colours, successive order of colours, width and arrangement of colours and zones commonly changes radically from crystal to crystal within a few microns. An attempt was made to classify the colours exhibted by bravoite crystals using the Munsell Colour Charts, but it was found impossible to obtain reproducible results. This is believed to be due to the combined effect of the relatively dark background and the oil immersion lens on the extremely small crystals, compared with the size and illumination of the colour chart.

3. Zoning.

The great variation in zonal patterns displayed has been shown by El Baz (1963), to be incapable of mathematical analysis; the variation in the geometric shape of the successive zones was originally believed to reflect a change in crystal habit brought about by the change in composition also indicated by the change in colouration, but considerations of crystal geometry of the pyritohedral class of the cubic system in which bravoite crystallises show that the pentagonal dodecahedron, the common form it exhibits, will give figures of three, four, five and six sides in cross section, depending on how many faces are cut by the section and when this form is combined with the octahedron, can give figures of eight sides. Thus there appears to be no need to postulate a change in habit with composition, (Vaughan 1969).

Zones in bravoite crystals are very often irregular, occasionally discontinuous or cut by radial boundaries, seldom curved, and commonly exhibit an ultra-fine discrete, or some-times a gradational, zoning within the courser zoning pattern as described earlier. This internal, superimposed assymetric zoning within a given zone can be explained by invoking a differential supply of nickel or cobalt (or copper) ions to each crystal face.

4. Reflectivity.

Reflectivity measurements using a Reichert reflex microspectrophotometer were attempted on various of the nickel species, but because of their small size, no reproducible results were obtained. This confirmed the finding of other workers who have stated that the optimum size for reflectivity measurements is 100µ, and accuracy is greatly reduced at sizes below 40µ.

5. Hardness.

Again because of the small size of the bravoite crystals no Vickers hardness tests were carried out. Using optical methods, some bravoite zones showed a positive relief against pyrite, others negative.

5.2.6 Bravoite Alteration Products. Plate 5, Nos. 1 and 3.

Bravoite was commonly seen to be altering to goethite. In many cases the goethite pseudomorphs the bravoite zoning. Goethite after pyrite shows no regular structure. Often in one section no unoxidised pyrite or bravoite remained, but the former presence of bravoite was revealed by the goethite pseudomorphs. There was some evidence to suggest that goethite after bravoite is of a deeper red or blue than geothite after pyrite which was often pale blue or grey.

Bravoites as inclusions in fluorite, and to a lesser degree as inclusions in calcite, altered to goethite far more rarely than bravoite lying along fluorite or calcite crystal boundaries. This would reflect the relative ease of ingress of water along crystal boundaries rather than crystal cleavage planes or fractures. The difference between degree of oxidation of bravoite in calcite of those lying along the crystal boundaries and those found as inclusions was not so marked as in the case of fluorite, this probably reflects the greater solubility of calcite leading to wider and longer solution channels into the crystal up which the water can travel, and oxidise the bravoitic and pyritic inclusions.

5.3 Nickeliferous Marcasite

A mineral species believed to be nickeliferous marcasite was discovered at 10 different randomly distributed locations in Derbyshire and at one possible location in the Alston Block. Two types were found. In one, Pl.6, No1, a deep lilac bravoite 15µ by 8µ, very euhedral, surrounded on two sides by normal pyrite varying from 5µ to 10µ in width is situated in a large marcasite field, the boundary on one side of the pyrite crystal forming a continuation of the adjacent marcasite on the left. Plate 8, No. 1, plane polarised light, shows the bravoite in the lighter coloured pyrite, with smaller scattered bravoites and associated pyrites to the right, set in grey marcasite. See Fig 4 . A series of lilac lobes, in places double or triple bounded, having vague crystal outlines cut across the marcasite field and in general emanate from or terminate in the deep lilac bravoites. The fine double or triple bands defining the lobes are 1µ wide, in places widening out to 3µ. Pl 8 No 2 (crossed nicols), brings out the marcasite boundaries which in places cut directly across the lilac lobes, and in one place becomes contiguous with them. Electron micro-probe studies showed the lilac bravoite to have up to 57.44% nickel and no cobalt, whilst the lilac band had between 13.37 & 13.72% nickel. The uncoloured regions across which the band lay had 0.24% Nickel. The second type of nickeliferous marcasite appeared under plain polarised light to be a normal zoned bravoite, euhedral, with well marked colour zoning, but which exhibited a pleochroism on rotating the stage, superimposed

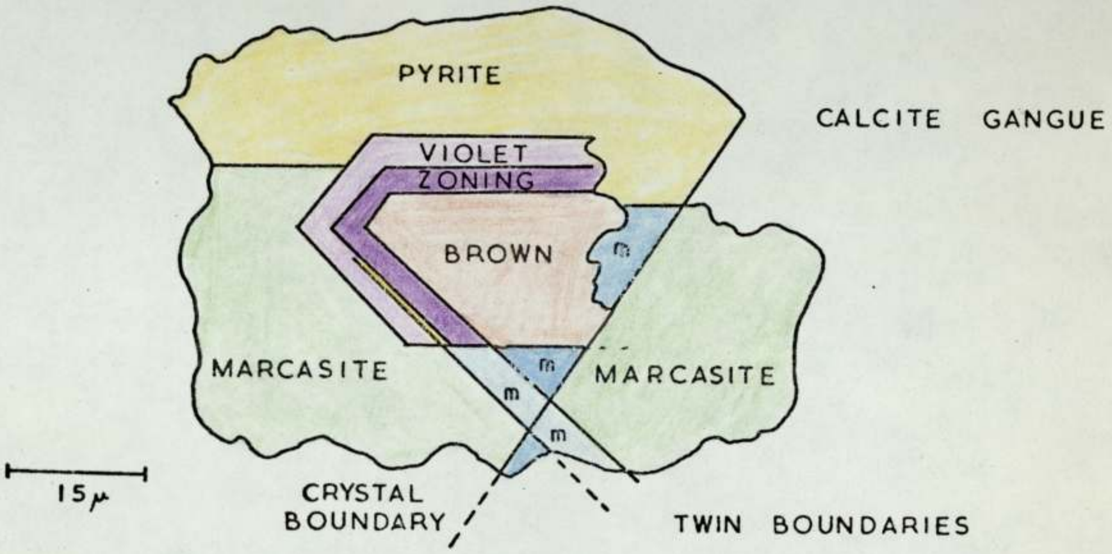


Fig. 3. A typical nickeliferous marcasite showing twin boundaries as an extension of a coloured zone of the included bravoite. Seen under crossed nicols.

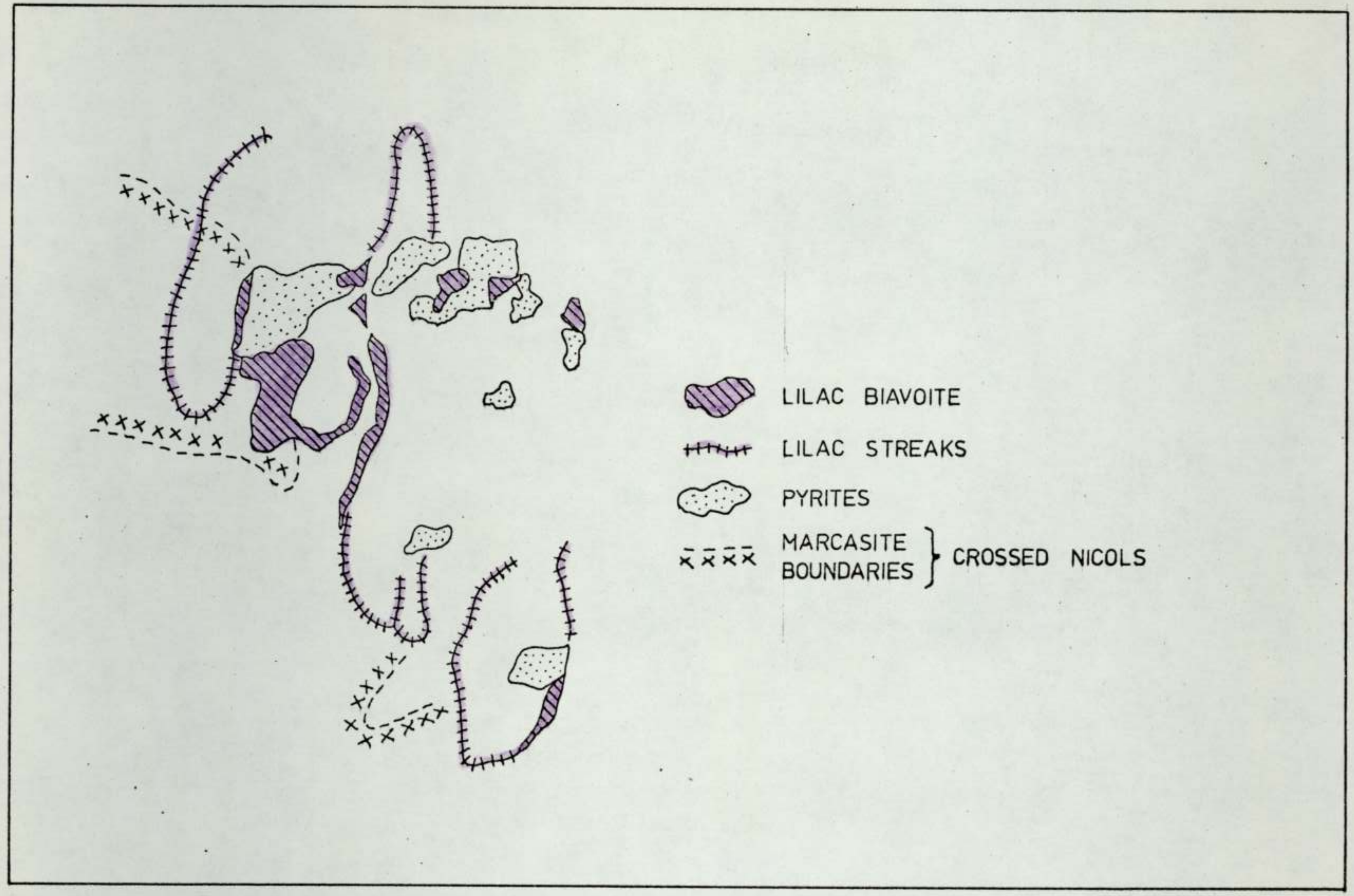


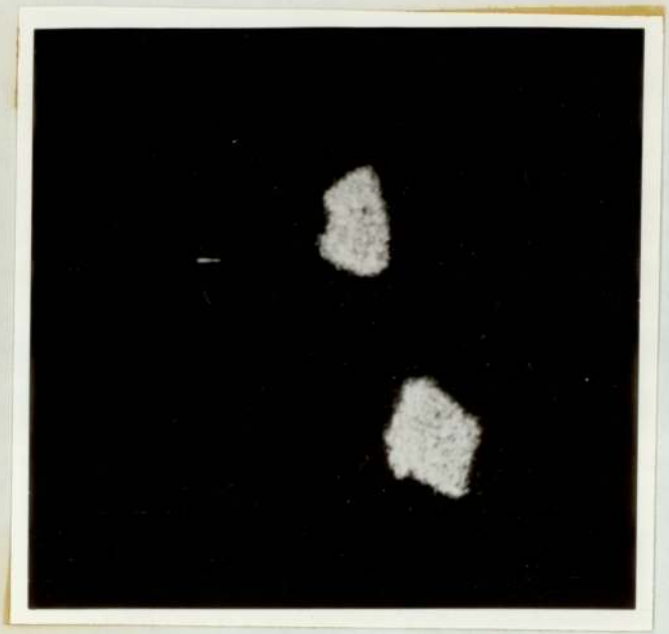
Fig. 4. A nickeliferous marcasite, as in Plate 8 Photo 2 , showing the lilac nickel rich streaks crossing the marcasite boundaries when seen under crossed nicols.

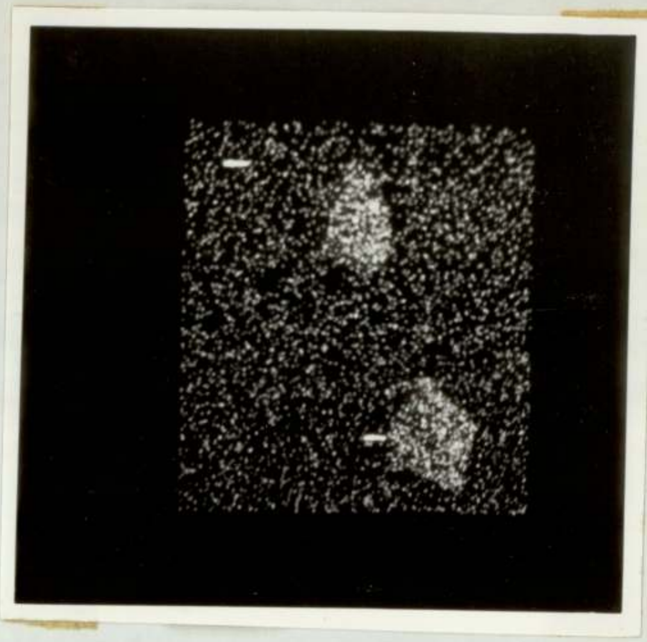
on the colour zoning. With crossed nicols, strong anisotropy with contrast across a twin plane appeared, whilst the colour banding still could be seen. Other examples of this type had a marcasite twin or crystal boundary as an extension of a colour zone boundary of an included bravoite. See Fig 3 and Plate 6, Nos. 3 and 4, and Plate 7, Nos. 1 and 2.

There is slight evidence that these nickeliferous marcasites show their best development in large, void-infilling, rhombohedral calcite.

The first described marcasite, (Plate 8) is most remarkable. A possible explanation is that the whole complex of crystals were originally a group of zoned bravoites of a normal type, but subsequently the (unstable) zoned bravoites established equilibrium by exsolving the greater part of the nickel which migrated to the now nickel-rich areas with a minor portion migrating to the previous bravoite boundaries. Either simultaneously, or later, parts of the newly formed nickel-free pyrite converted to the marcasite structure, but leaving within them nickel pseudomorphs or relict structures of the old bravoites. See Plate 13, No. 4 electron probe nickel picture.

Pl 6,1 shows a large, 80μ zoned bravoite where one part of the rim appears to have lost its nickel and gone over to marcasite. In this vicinity other parts of adjacent zones appear to be 'decaying' also.





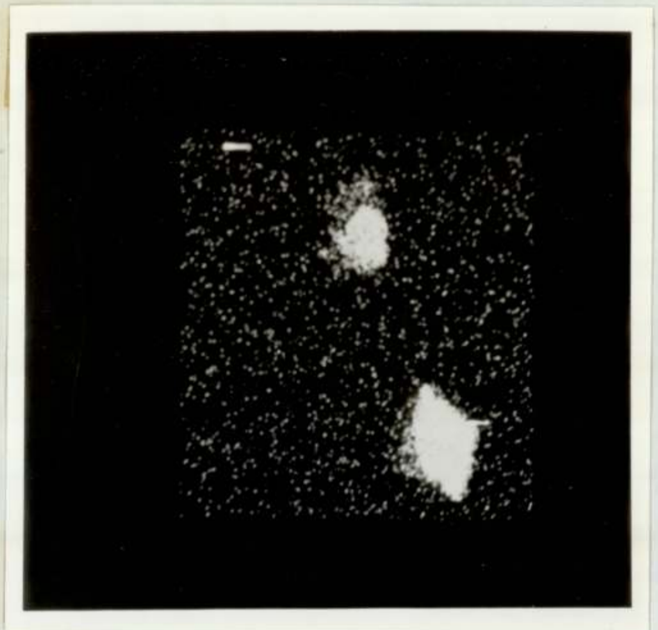
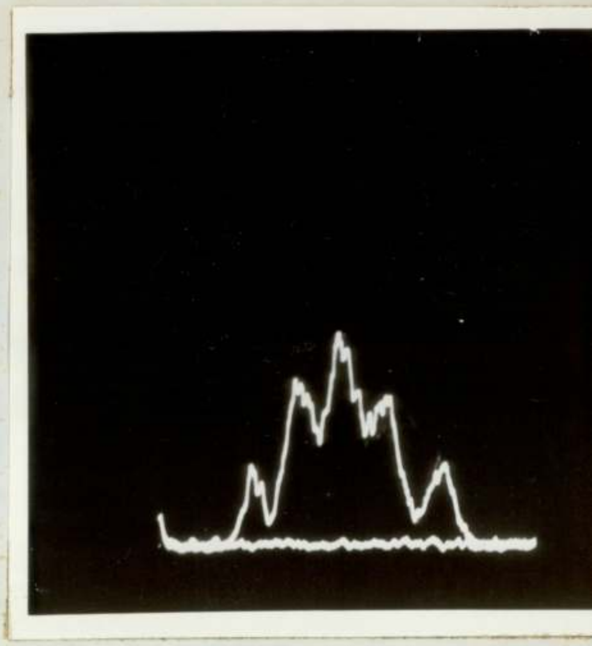
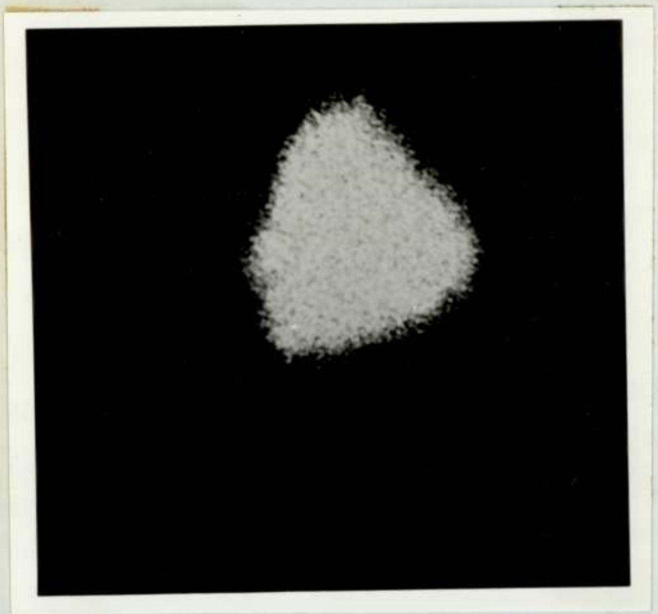


PLATE 10

No. 1 U.L.	Nickel X-Ray picture of specimen in Plate 1, No. 1.
No. 2 U.R.	Cobalt X-Ray picture.
No. 3 L.L.	Iron X-Ray picture.
No. 4 L.R.	Nickel X-Ray picture of specimen E in table 2. E_1 is the central area, E_2 is the left hand boundary, rather diffuse.





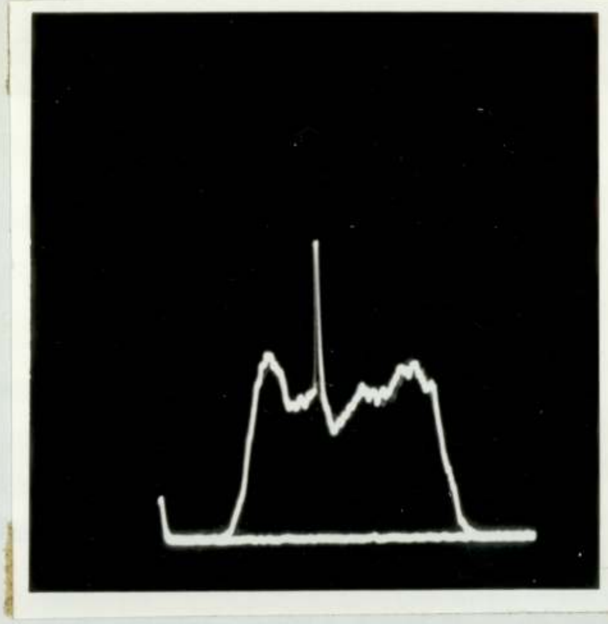
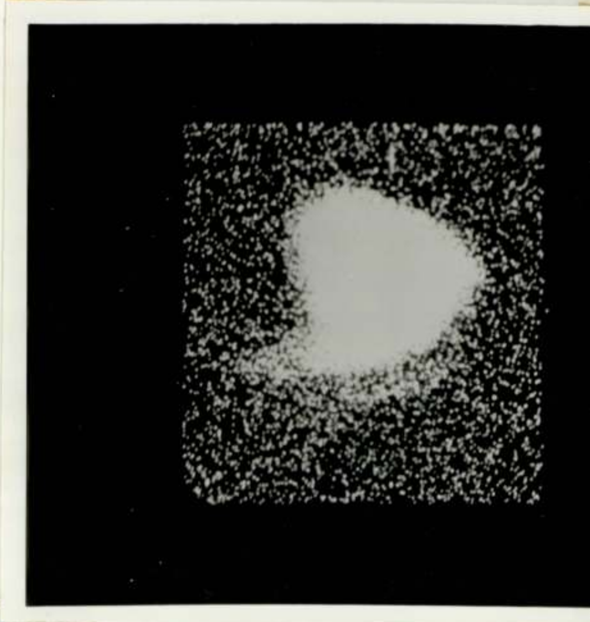
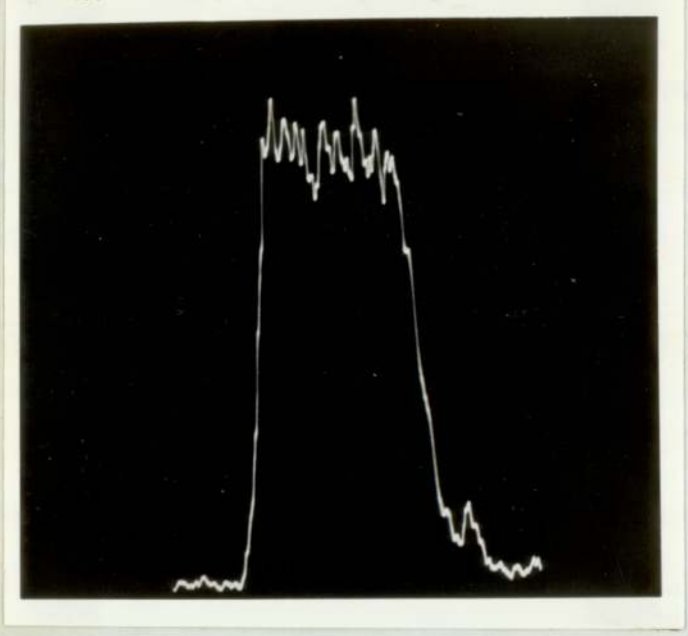
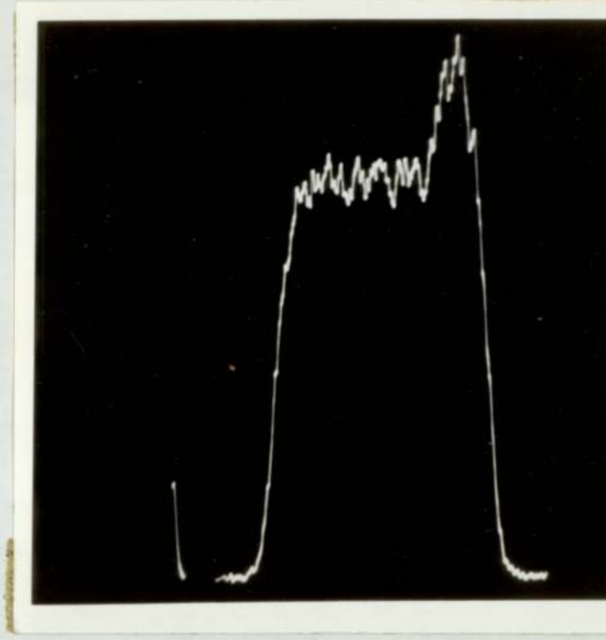


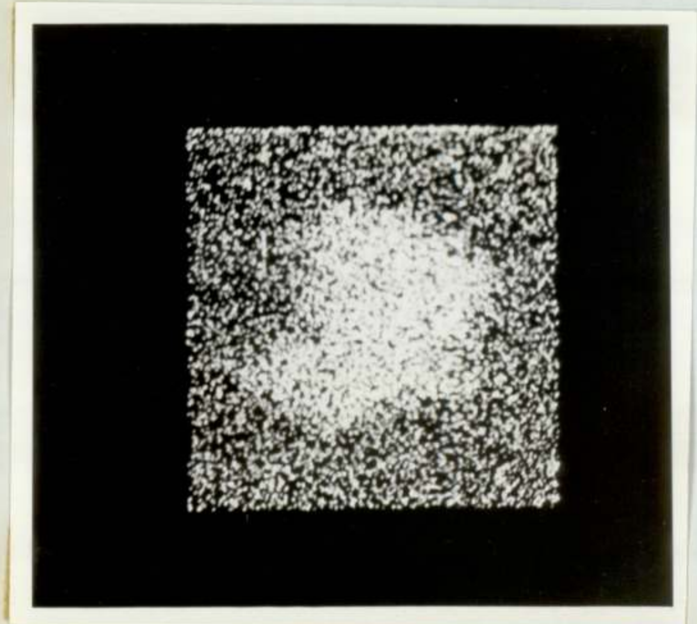
PLATE 11

No. 1 U.L.	Nickel X-Ray picture of specimen in plate 3, No. 2.
No. 2 U.R.	Nickel X-Ray trace. .
No. 3 L.L.	Iron X-Ray picture.
No. 4 L.R.	Iron X-Ray trace.









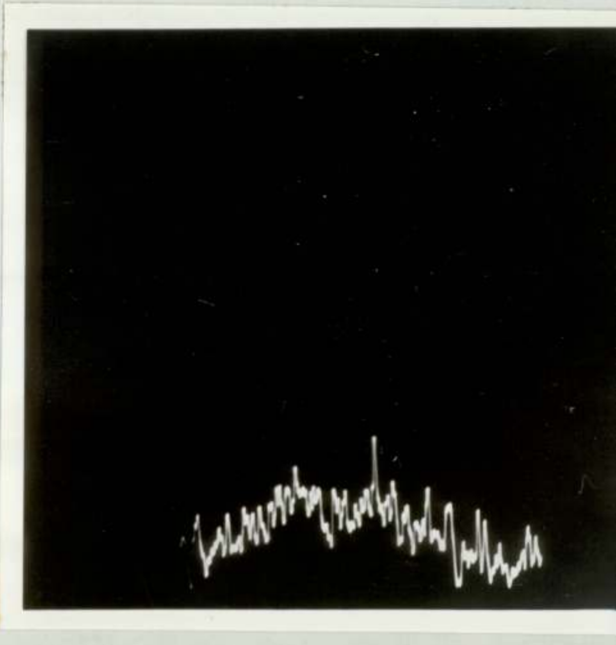
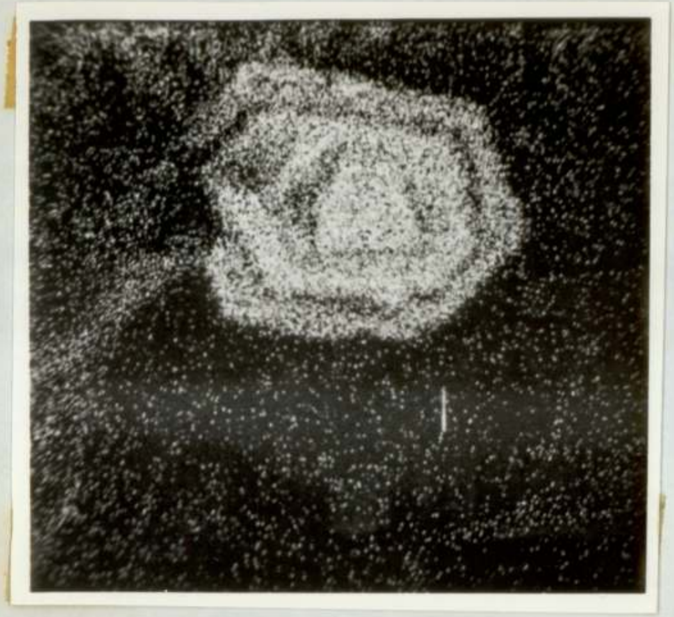
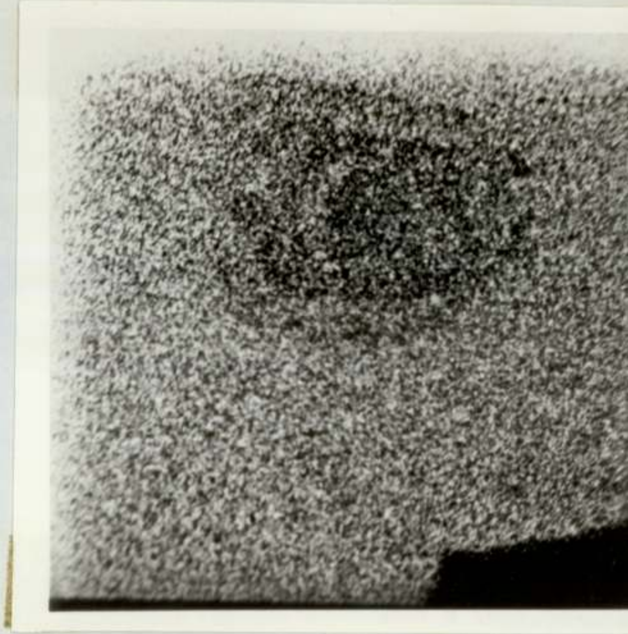
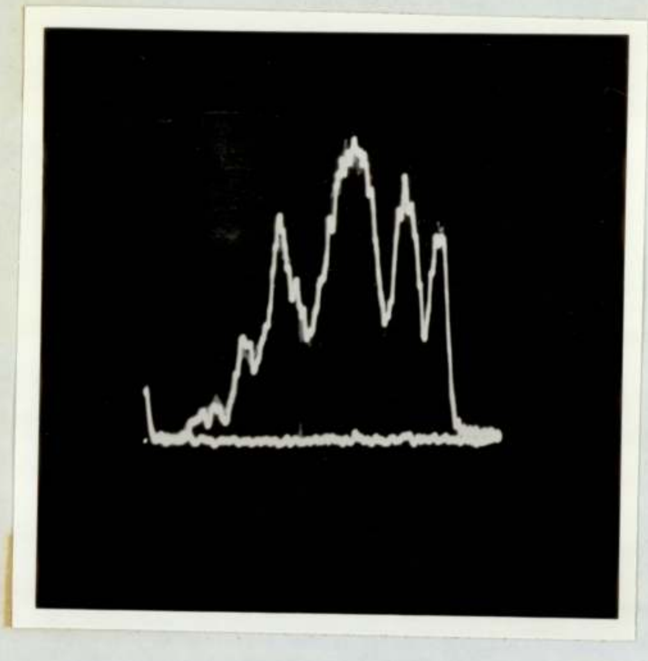


PLATE 12

No. 1 U.L.	Bravoite having partial rim of pyrite. Trains of inclusions of unknown type. X2000.
No. 2 U.R.	Nickel X-Rays electron picture. Note lesser concentration along lower boundary, but slight increase at extreme edge.
No. 3 C.L.	Nickel X-Ray trace.
No. 4 C.R.	Iron X-Ray trace. Note greater iron where nickel decreases along pyrite boundary.
No. 5 L.L.	Cobalt X-Ray picture. No variation in cobalt can be detected.
No. 6 L.R.	Cobalt X-Ray trace. Concentration appears to increase towards the centre, but the crystal is so small and the concentration so low, that background effect is noticeable.







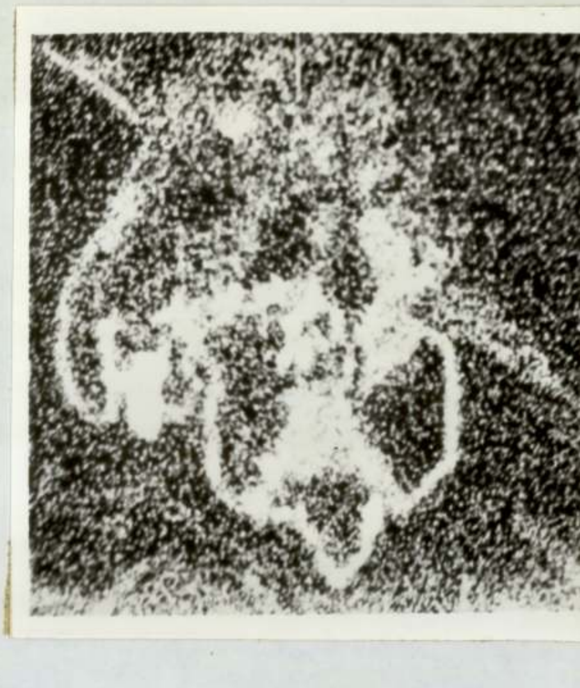
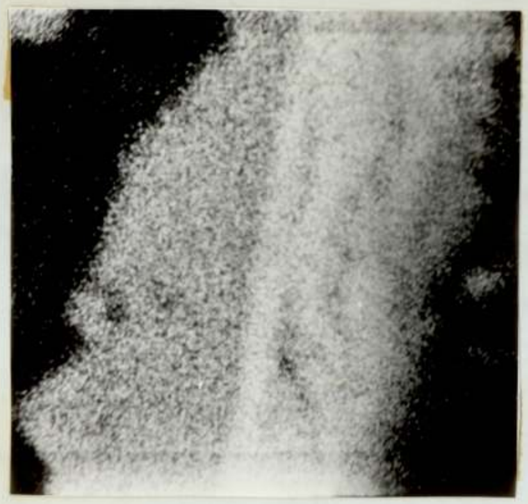
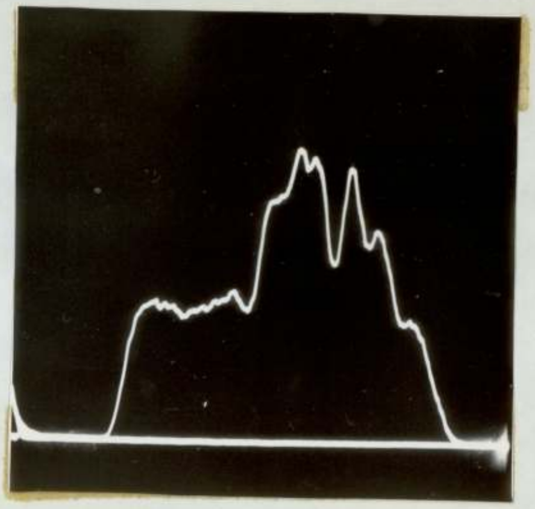
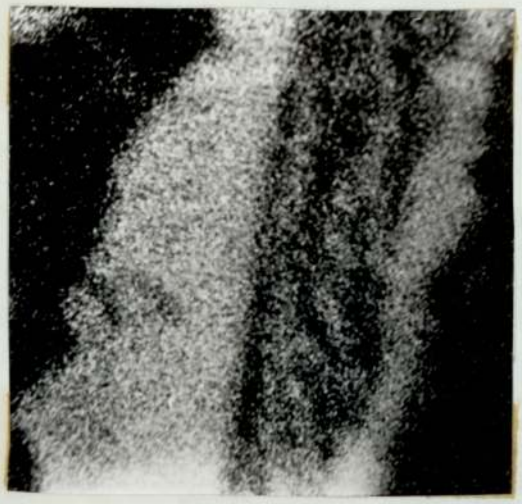


PLATE 13

No. 1 U.L.	Nickel X-Ray picture of specimen in Plate 6, Nos. 1 and 2. Notice break in outer nickel zone, with a diffuse region of nickel of lower concentration situated in the marcasite. X250.
No. 2 U.R.	Iron X-Ray picture. X250
No. 3 L.R.	Nickel X-Ray trace from right to left across the specimen.
No. 4 L.R.	Nickel X-Ray picture of specimen in Plate 8, showing sinuous nickel rich band. X250.







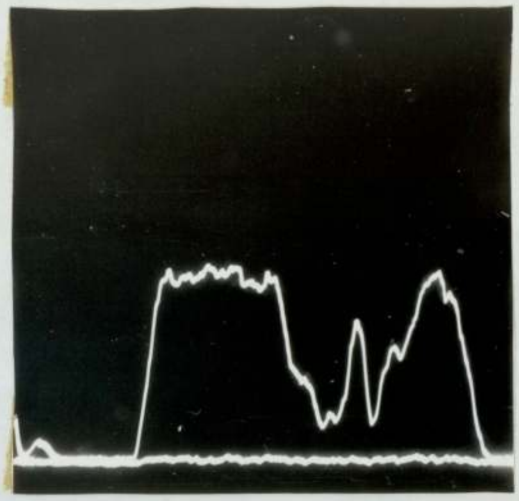
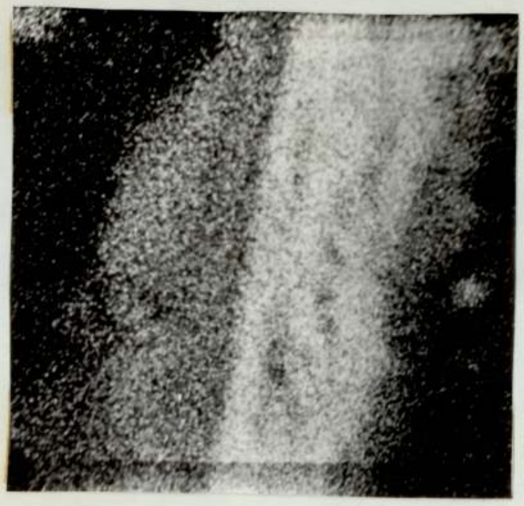
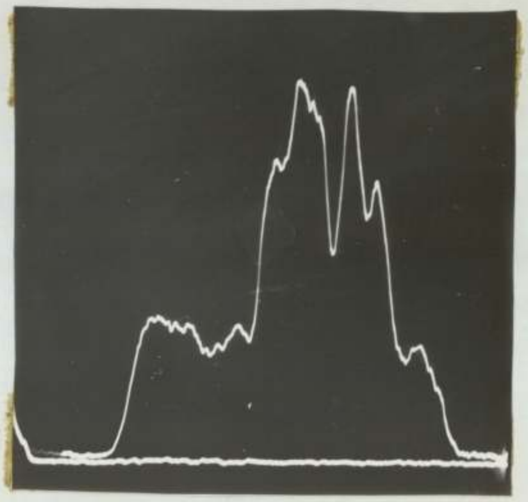


PLATE 14

No. 1 U.L.	Sulphur X-Ray picture of specimen similar to that in Plate 9, No. 2. Note central region, and boundary regions.
No. 2 U.R.	Sulphur X-Ray trace.
No. 3 L.L.	Arsenic X-Ray picture
No. 4 L.R.	Arsenic trace.





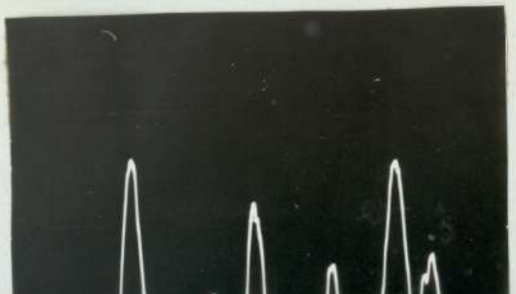
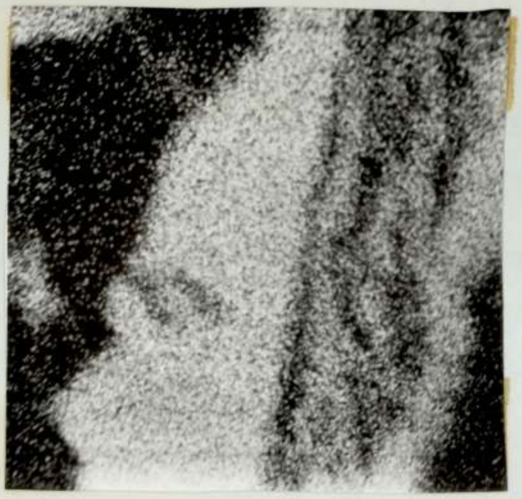


PLATE 15

No. 1 U.L.	Iron X-Ray picture of specimen similar to that in Plate 9, No. 2.
No. 2 U.R.	Iron X-Ray trace.
No. 3 L.L.	Nickel X-Ray picture.
No. 4 L.R.	Nickel X-Ray trace.



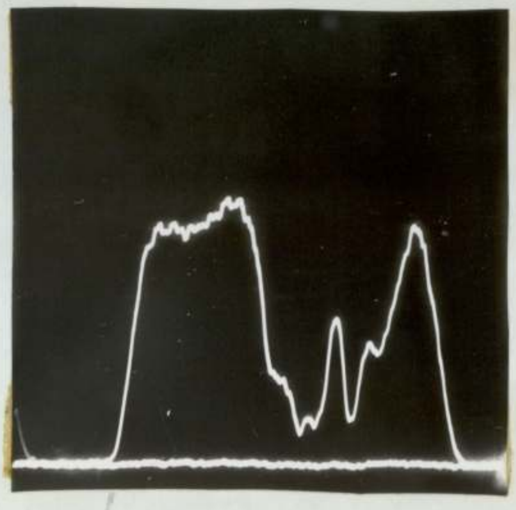


PLATE 16

No. 1 U.L.	Cobalt X-Ray picture of specimen similar to that in Plate 9, No. 3.
No. 2 U.R.	Cobalt X-Ray trace

CHAPTER 6

ELECTRON MICROPROBE

6.1 Introduction

A Cambridge Mk V electron probe microanalyser was used to analyse material from fifteen sites in Derbyshire, one site in the Mendips, and one site in the Alston Block, North Pennines.

27 quantitative and 25 qualitative measurements were made by the author using a voltage of 15Kv and specimen current of 100 mA for the first 29 analyses and a tube voltage of 20 Kv and a specimen current of 100 mA for the remaining 23 analyses. The standards used were metallurgical ones consisting of the pure elements for iron, copper, nickel, cobalt and arsenic, and zinc sulphide for sulphur.

Many of the specimens analysed were less than 10µ across, and they included zones narrower still. In these circumstances, the actual depth of crystal in to which the electron beam penetrated was very small and in fact may be less than the actual depth to which the beam penetrated. This occasions errors in the results since the intensity of X-rays generated is reduced, but cannot be allowed for in the calculations.

Results lying in the range 96.5% to 103.5% were used and are tabulated under three headings,

Nickeliferous pyrites and bravoites	Table 2
Nickeliferous marcasites	Table 3
Arsenical nickel/cobalt/iron sulphides from Tynebottom limestone	Table 4

The results in Tables 2 and 3 were recalculated to 100% and plotted on triangular diagrams firstly as plots of composition be weight of sulphur, iron and nickel/cobalt, Figs 5 and 8, and then as plots of composition by molecular proportions of FeS_2, NiS_2, and CoS_2, with a greatly exaggerated scale in the CoS_2 direction. The analyses quoted by Bannister Table 1 are also plotted for reference on Fig. 6.

The percentage of sulphur recorded was in the majority of cases rather higher than that reported by previous workers on these iron/nickel/cobalt sulphides. This is believed to be due to the use of a zinc sulphide standard rather than the more usual iron pyrites one. The relative proportions of iron, cobalt and nickel are unaffected.

Table 2 Ni Pyrites and Bravoite

Designation	S%	Fe%	Ni%	Co%	Total	Notes
B	55.99	53.162	12.266	-	101.424	Pale Brown
C	55.61	29.575	11.400	0.206	96.800	Pale Brown
D	51.85	35.252	10.071	-	97.173	Very Pale Lilac
E_1 Plate 11 No. 4.	57.19	20.397	24.827	0.092	102.510	Centre Brown
E_2	56.90	35.384	9.659	-	101.952	Edge Purple
E'_1	57.09	24.173	20.408	0.046	101.722	Centre Brown
E'_2	56.44	35.941	7.604	0.011	99.997	Edge Purple
G	55.85	31.983	10.607	0.286	98.726	Centre
K_1	51.72	29.729	14.588	0.905	96.951	Inner Brown
K_2	48.91	34.523	12.127	0.451	96.020	Outer Brown
L_1	51.19	32.359	13.012	-	96.585	PurpleCentre Zone
L_2	51.13	38.098	8.538	-	97.770	Purple Outer Zone
L_3	54.12	35.949	5.994	-	96.072	Purple Middle Zone

ELECTRON MICRO-PROBE ANALYSES

Collection sites of specimens probed are given below.

Table 2 Nickeliferous pyrites and Bravoite

Specimen designation	Location
B	Dirtlow Rake 7
C	Dirtlow Rake 8
D	Dirtlow Rake 9
E	Near Winster
G	Near Winster
K	Dirtlow Rake 1
L	Shuttle Rake 2

Table 3 Nickeliferous Marcasite

Specimen designation	
A	Dirtlow Rake 1
F	Near Winster
F'	Near Winster

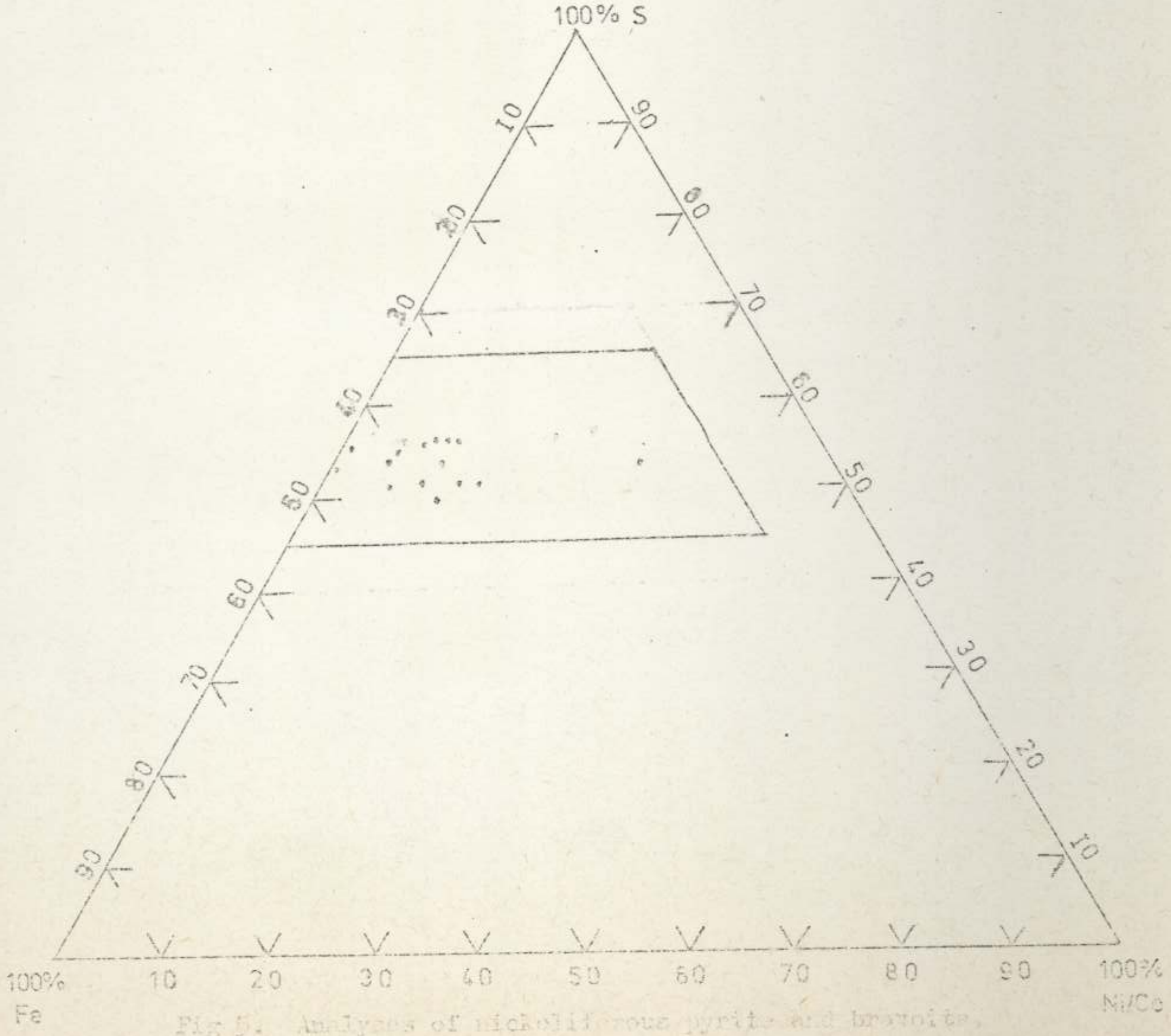


Fig 5. Analyses of nickeliferous pyrite and bravoite.

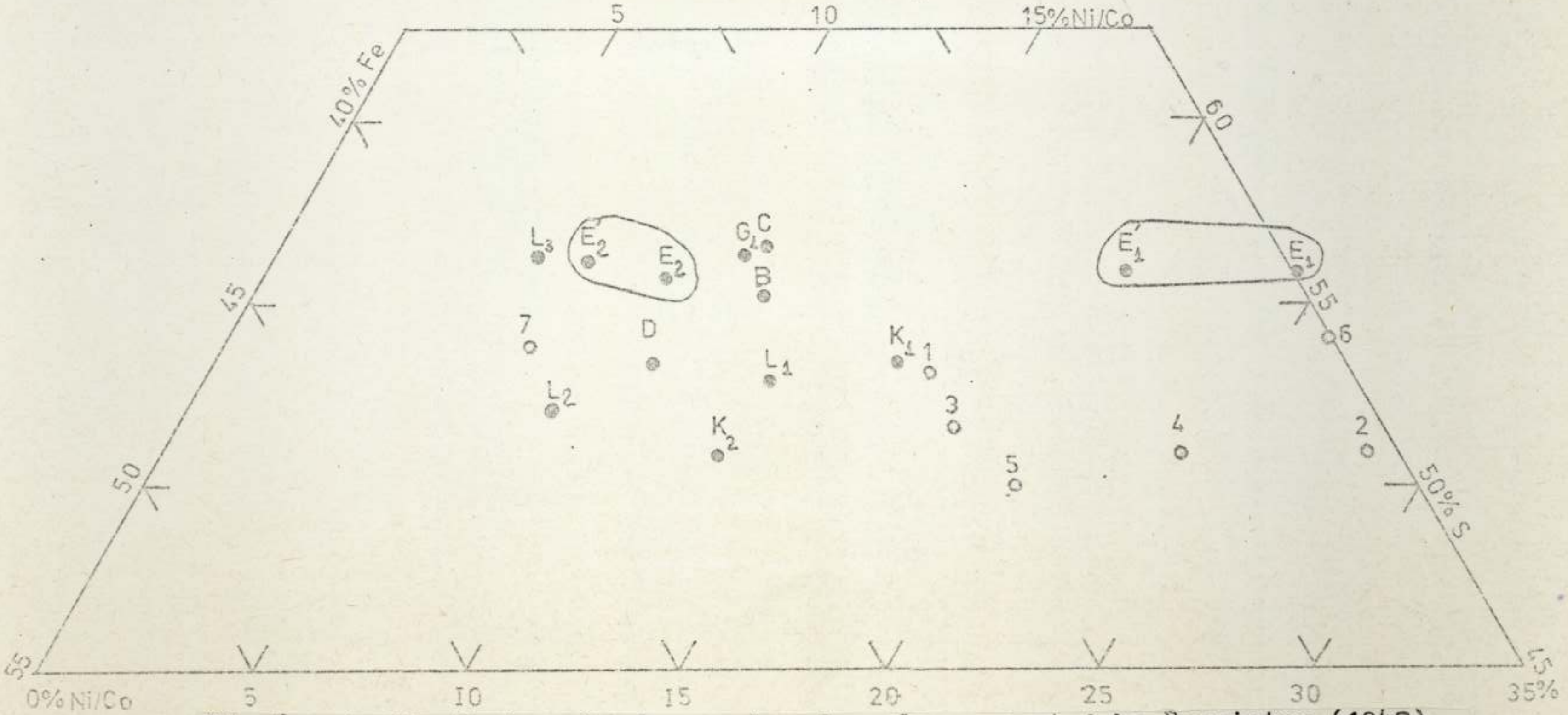


Fig 6. As Fig 5 also showing numbered analyses quoted by Bannister (1940).

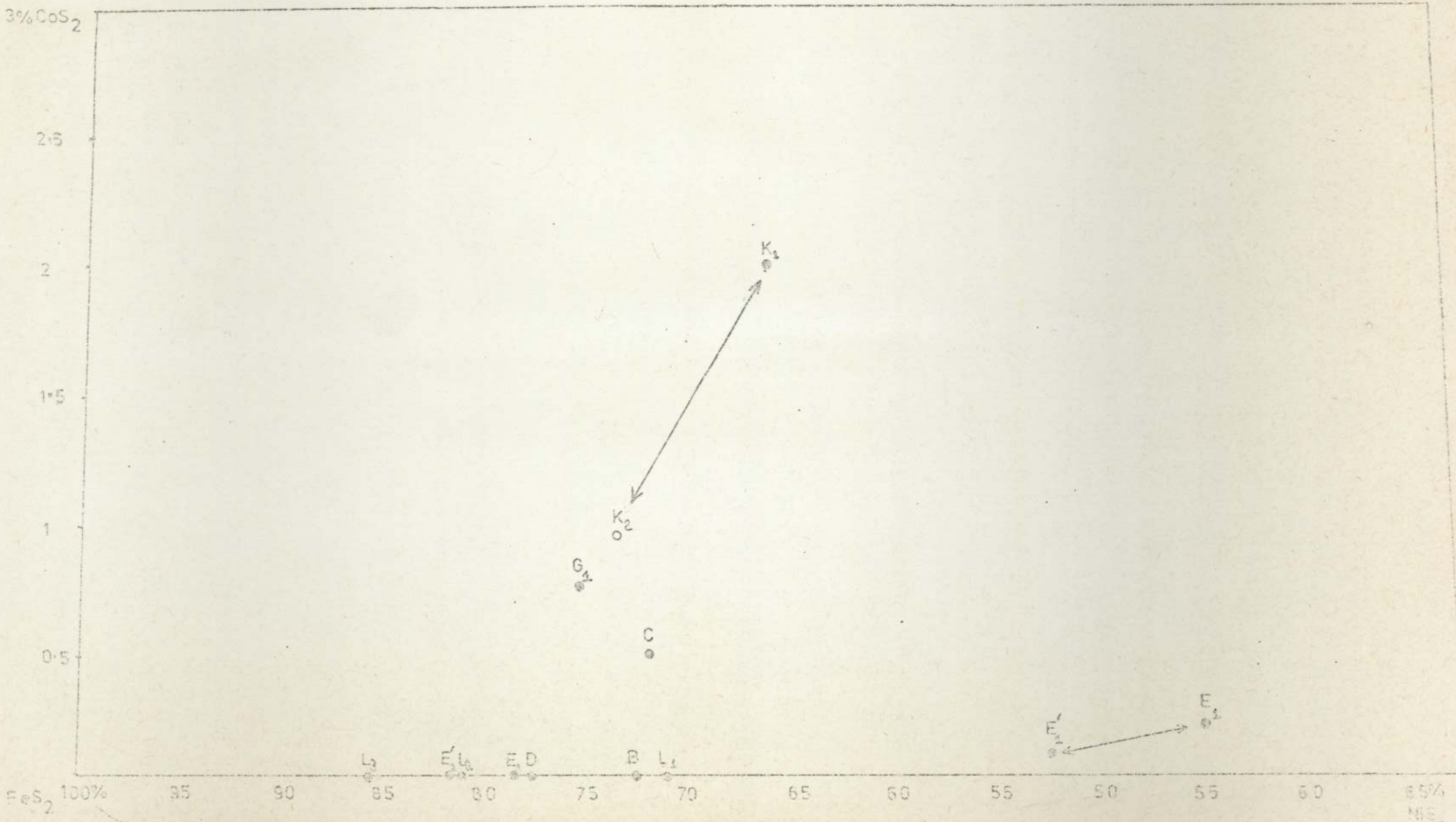


Fig 7. Analyses of nickeliferous pyrite and bravoite as nickel, iron, and cobalt sulphides.

6.2 Nickeliferous Pyrite and Bravoite

Analytical results are presented in Table 2 for 8 crystals obtained from seven different localities in Derbyshire. Fig 5 shows the general field occupied by these results. The modal value for nickel/cobalt concentrations was around 12%, with a maximum value of 24.9%, the modal value for cobalt alone being around 0.15%.

Results for specimens B, C, D, G, were single valued, these being very small, either non-zoned, very faintly zoned, or zoning so close together as to be outside the resolving capabilities of the electron probe.

Results for specimens E_1, E_2, E'_1, E'_2, K, L, were multi-valued, being values for different colour zones in each specimen. In the case of specimen E two crystals on the one polished section were probed, designated E and E' respectively. The maximum nickel/cobalt values are plotted on Fig 6 and lie relatively close to each other at around 23%. The correlation between the minimum values of the E crystals, at around 8%, is also shown on Fig 6.

The colours of the crystals and included zones cannot be correlated with composition except for a general tendency towards a lower reflectance as the percentage of iron decreases. Table 2 illustrated that nickel/cobalt concentrations above about 12% produced a tendency towards brown, becoming darker with decrease in iron.

The specimen pictured in Plate 3, No. 2, and the associated nickel X-Ray picture, Plate 11, No. 1, illustrates the correlation between reflectance and nickel concentration.

The correlation between maximum nickel concentration shown by two sets of adjacent crystals, E and E', are evidence to support Vaughan (1969) who stated that zoning is probably the result of very local variations in conditions.

Fig 7 illustrates the general increase in cobalt found to occur with an increase in nickel.

6.3 Nickeliferous Marcasite

Analytical results are presented in Table 3 for 3 crystals from 2 different localities in Derbyshire. Fig 8. shows the general field occupied by these results, which fall into two well-defined areas, that had modal values of nickel/cobalt concentrations of 4% and 26% respectively. Fig. 9 plots the nickel/cobalt values.

Specimen A was classed as a marcasite because it exhibited marked pleochroism cutting across the colour zone boundaries. Specimens F and F' occurred in massive calcite within 3000µ of each other. Crystal F is illustrated in Plate 6, Nos. 1 and 2, and F' in Plate 8.

Plate 6.1 shows the nickel-rich streak seen faintly and marked X in a violently anisotropic region as shown by the photographs taken with polars crossed and uncrossed respectively.

Specimen F'; Plate 8, Nos. 1 and 2, polars crossed and uncrossed respectively, shows a coloured banding cutting the anisotropic boundaries, and which showed on the nickel X-ray picture Plate 13, 4; the coloured streak contained 5.98% nickel and no cobalt, and the violet regions marked 2 on plate 8, 6.385% nickel and no cobalt. The dark coloured central part marked 1 on Plate 8, No. 1, has an approximate nickel content of 29% corresponding with the 28.8% nickel of the central zone of crystal F.

The Nickel X-ray photograph Plate 13 No. 4, appears to show nickel delineating crystal boundaries. The author is hesitant to suggest this depicts some form of migration of nickel from an excessively rich nickel core towards the boundary, assuming a nickel concentration of 29% is unstable.

Table 3 Nickeliferous Marcasite

Designation	S%	Fe%	Ni%	Co%	Total	Notes
A	53.29	43.010	1.574	-	97.876	Faint Zoning
F_5	54.92	43.964	0.450	-	99.343	
F_2	51.79	20.628	25.285	Trace	97.716	Brown
F_3	53.78	36.948	6.471	Trace	97.217	
F_6	51.75	14.744	28.881	1.244	96.623	
F'_1	53.68	40.165	6.385	-	100.232	Centre Deep Violet
F'_2	53.37	38.776	5.984	-	98.135	Coloured Streak
F'_3	51.67	47.069	0.133	-	98.860	Uncoloured Region

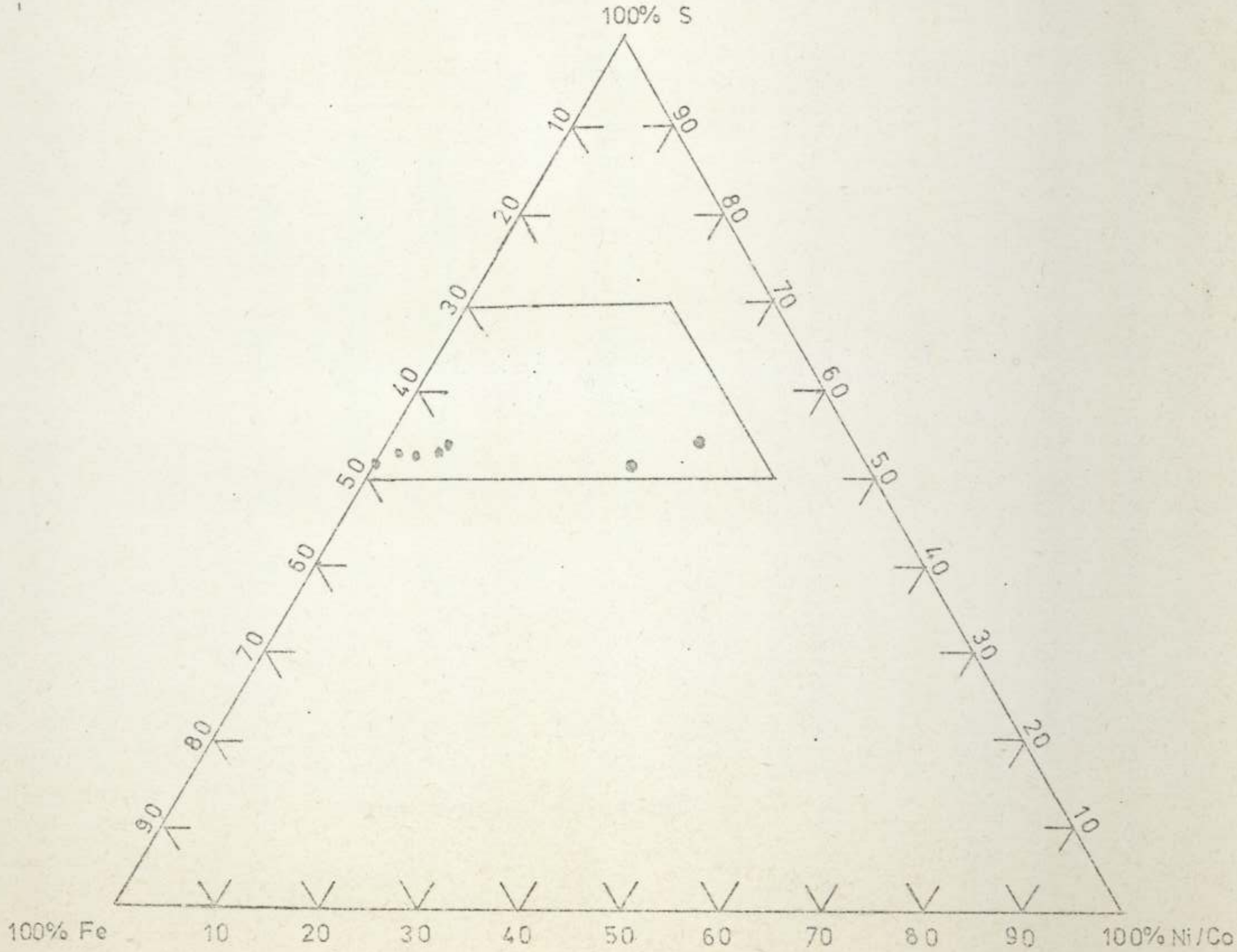


Fig 8. Analyses of nickeliferous marcasite.

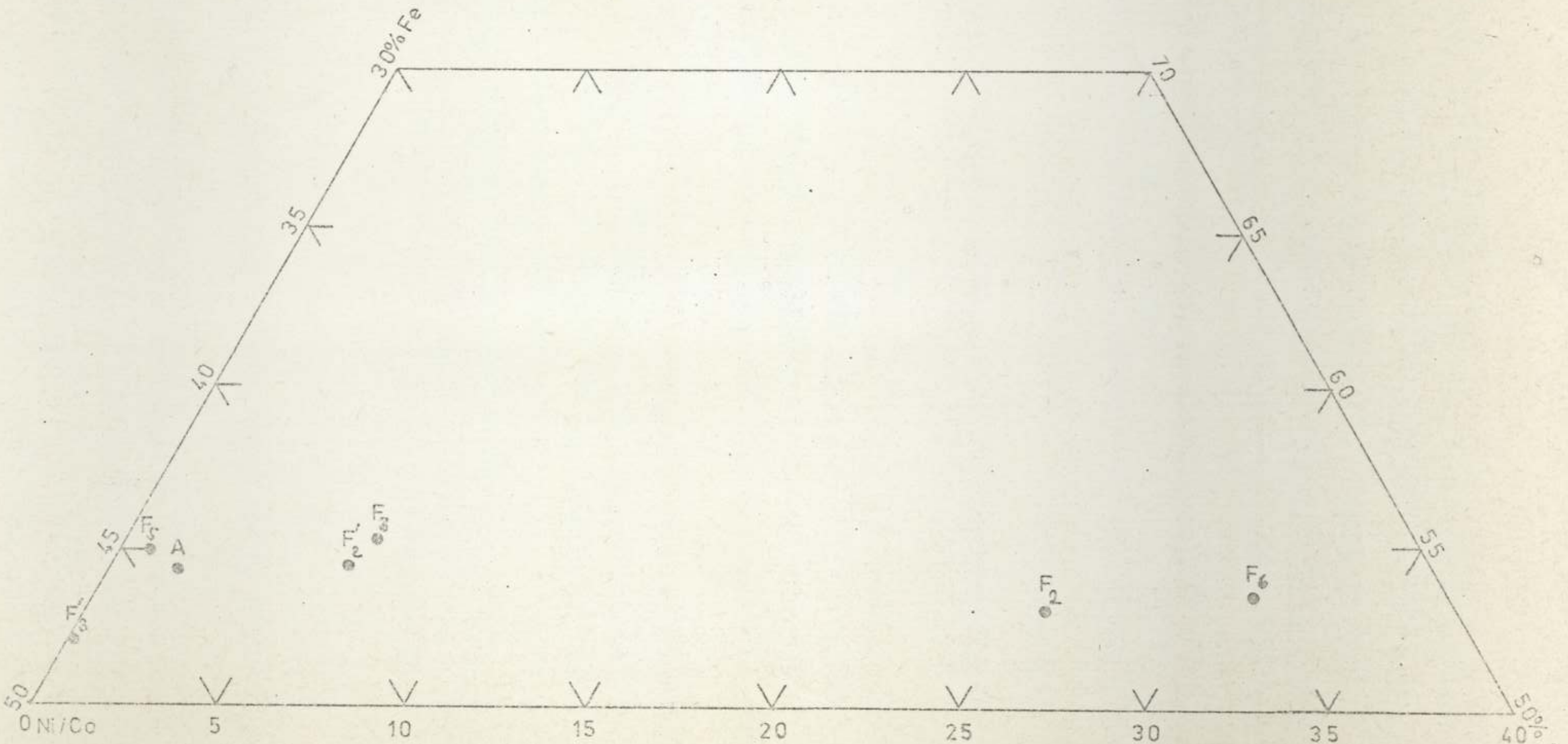


Fig 9. Analyses of nickeliferous marcasite, enlargement of portion of Fig 8.

6.4 Arsenical nickel/iron/cobalt sulphides, Alston Block

Arsenic rich sulphides were found in pieces of Tynebottom Limestone near Garrigill, which exhibited a characteristic pink cobalt bloom. Optical examination revealed bundles of sheaf-like anisotropic crystals, each crystal bounded by a narrow rim of anisotropic pale yellow material. The central part of each crystal was much fractured, and frequently bent. Chemical analysis of whole sample showed 38.2% arsenic, and the electron probe results are presented in table 4. Sulphur, Arsenic, Iron, Nickel and Cobalt X-ray traces are shown, together with the respective X-ray pictures. Plates 14, 15, 16.

The analyses fall into two groups, high arsenic, around 45% and low arsenic around 8.5%. High arsenic occurs with high cobalt and nickel, and vice-versa. In the low arsenic group, sulphur at 46.5% is over twice the value in the high arsenic group. In the low arsenic group iron is high at 39.8% whereas in the high arsenic group it is lower and variable, and antipathetic towards cobalt and nickel.

It is inferred that there are probably two or more phases present. X-ray diffraction studies demonstrated the presence of marcasite. The phases containing the high cobalt and nickel are as yet unidentified.

Table 4 Arsenical Nickel/Cobalt/Iron Sulphides.

Designation	S%	As%	Fe%	Ni%	Co%	Total
51	20.64	45.689	12.037	2.217	22.025	102.616
53	20.02	46.697	4.857	19.277	11.448	102.301
55	21.93	43.979	9.856	5.795	21.055	102.622
56	21.13	31.395	19.215	6.589	21.394	99.723
52	46.671	8.597	39.833	1.244	3.336	99.682
54	46.443	8.676	39.770	1.144	3.754	99.788

6.5 Bornite, Odin Mine

A semi-quantitative probe analysis of a brown isotropic phase revealed the presence of copper and suggested the presence of bornite. (See Plate 5, No. 2.)

CHAPTER 7

CONCLUSIONS

Main Research Findings

From the results of this research and the literature search, it is confirmed that bravoite and nickelian pyrite are common accessory minerals in the majority of Mississippi Valley Type low temperature hydrothermal deposits. (Heyl, 1956).

Previous Research

Examination of the literature revealed two main associations of bravoite, 1) Magmatic associations where it occurred as an alteration product of pentlandite. 2) Low temperature hydrothermal associations where it occurred as an accessory mineral in the Mississippi Valley type and 'Red Bed Sandstone' type deposits.

Nomenclature

Nomenclature of nickel iron cobalt sulphide is very unsatisfactory and one based entirely on appearance is proposed.

Distribution

Bravoite and nickeliferous pyrite are found commonly throughout all the mineralised areas of Derbyshire and the Askrigg Block of the North Penninnes. They occurred more rarely in the Mendips and the Alston block of the North Pennines, and the Shelve area of Shropshire. An examination of one specimen from Strontian, Scotland, revealed a zoned nickelian pyrite.

Nickel Concentration and Geographical Location

No significant correlation could be found in the Derbyshire Dome between nickel concentration in the iron sulphides and geographical location. Apart from confirming a general tendency towards a coarse overall calcite, barite, fluorite zoning, no evidence to support Mueller's hypothesis concerning the subdivisions of the fluorite zone could be detected on the basis of fluorite colour or of concentration of pyrites.

Bravoite Host Minerals

Bravoite and nickelian pyrite, and more rarely, nickelian marcasite occurred equally in calcite, fluorite, and barite, and much more rarely in quartz, galena, chalcopyrite and sphalerite. They are frquently found as many minute (5μ to 50μ) crystals in calcite, fluorite or barite which is otherwise completely devoid of other mineralisation.

Bravoite Physical Properties

Nickel cobalt pyrites exhibited a range of colours ranging from pale yellow through lilac, violet and purple to brown of varying shades and saturation. Electron probe studies enabled a subjective assessment of the reflectance to be correlated with nickel/cobalt content, but no correlation could be arrived at between colour and nickel cobalt composition. However, in general, the deeper the colour, the less the iron content. This agreed with other worker's findings (Vaughan, 1969).

They exhibited diverse habits and zoning patterns, often zoned and un-zoned crystals co-existing together, except when as inclusions in a single non-metallic crystal. The 3,4,5,6, and 8 sided figures exhibited by the crystals and the complicated zoning patterns are all derived from different sections of the basic pyritohedral form.

Bravoite Solid Solution Series

No major discontinuity in the iron nickel/cobalt solid solution series between a nickel/cobalt content varying between 0% and 25% could be detected. The concentration of results for nickel cobalt concentration between 6% and 15% probably reflected the choice of the deepest coloured specimens for electron probe examination. In general nickel and cobalt exhibited a sympathetic relationship, cobalt not usually coming in until the nickel content reached greater than 15%.

Nickeliferous Marcasite

Certain nickel rich iron sulphides varied from weakly to violently anisotropic and were identified as nickeliferous marcasite. Colour zones cut directly across crystal or twin boundaries delineated by the anisotropic boundaries, and in certain specimens sinuous violet coloured bands were superimposed on apparently normal marcasite crystals, and enclosing one or more highly nickeliferous, (up to 65% nickel cobalt sulphides), centres. Further investigation is needed to determine the structure and nature of these apparently anomalous findings.

Nickeliferous Arsenical Pyrites

An arsenic rich nickel iron cobalt sulphide was found in the North Tyne Valley in Tynebottom Limestone of the Alston Block. Micro-probe analyses revealed the presence of two phases, with arsenic and nickel cobalt showing an antipathetic relationship. X-ray diffraction showed the presence of marcasite, but the presence of other cobalt and nickel rich phases are suspected. Further work is necessary to resolve this problem.

Paragenesis

In every specimen of a nickel cobalt iron sulphide examined, bravoite or nickeliferous pyrite was always the earliest metallic phase, preceeding pyrite and marcasite. This paragenesis confirmed that of Ixer (1974).

Owing to the obvious limitations of the study it is impossible to say definately whether bravoite mineralisation could be used as a pointer towards locating economic deposits of lead and zinc, since all the collecting was carried out in areas rendered accessible by previous mining activities for these minerals. The existence of bravoite in other areas has not been conclusively disproved, but failure to detect the iron/nickel sulphide otherwise than in material associated with mineralised vein material was suggestive that the hydrothermal fluids, when mineralised conveyed simultaneously all the mineral species without selection and distributed them all in a fairly uniform manner in the now mineralised areas.

Economical Exploitation

There is no possibility that either cobalt or nickel are present in anything approaching economic quantities.

APPENDIX A

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