# Bismuth-bearing assemblages from the Northern Pennine Orefield

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## Abstract

Bismuthinite-bearing quartz veins from the Alston Block of the North Pennine Orefield are all close to, or above, the Rookhope and Tynehead cupolas of the buried Weardale Granite. They are uniform in composition and paragenesis and are earlier than the main fluorite–baryte–galena–sphalerite mineralization of the orefield. Rhythmical crystallization of quartz, chalcopyrite and minor pyrite is followed by fluorite–quartz–chalcopyrite–minor sphalerite–altered pyrrhotite mineralization. Early tin-bearing (up to 0.29 wt.% Sn) chalcopyrite encloses trace amounts of bismuthinite ($Bi_2S_3$), synchysite ($CaREE(CO_3)F_2$), argentopentlandite ($Ag(FeNi)_8S_8$) (close to being stoichiometric), pyrrhotite, cubanite and cosalite ($Pb_2Bi_2S_5$), while early pyrite carries monoclinic pyrrhotite (close to $Fe_7S_8$) and tungsten-bearing cassiterite (up to 1.03 wt.% $WO_3$). Bismuthinite is macroscopically visible and is associated with native bismuth and small, fine-grained, spherical aggregates that qualitative analysis suggests may be cosalite crystals. Synchysite and more rarely monazite, xenotime and adularia are intergrown with bismuthinite. These mineralogical data form part of the basis for an increasing awareness of the contribution of the Weardale Granite to the early phases of mineralization in the Alston Block.

KEYWORDS: bismuthinite, synchysite, argentopentlandite, cosalite, cassiterite, Northern Pennine Orefield.

## Introduction

THE zoned Mississippi Valley style lead-zinc-fluorite-baryte orefield of the Alston Block is hosted by Lower Carboniferous carbonates and siliciclastics. These unconformably overlie Lower Palaeozoic clastic and volcanic rocks which are intruded by the Caledonian Weardale Granite. The geology, nature and especially the origin of the area's mineralization have been the subject of study and speculation for many years. The most recent comprehensive accounts are those of Dunham (1990) and Ixer and Vaughan, (1993).

The marked zonal distribution of minerals within the deposits of the orefield has long been recognised as a function of the temperature of deposition: the comparatively high temperature inner fluorite zone is surrounded by a lower temperature zone in which barium minerals are dominant. The principal sulphide minerals of the orefield, galena and sphalerite, occur in greatest abundance near the outer portion of the fluorite zone and inner margins of the barium zone (Dunham, 1990). Chalcopyrite, although relatively common in small amounts throughout the orefield, is only abundant in the central, highest temperature, parts of the fluorite zone (Dunham, 1990). The close coincidence between the shape of the exposed fluorite zone and the subcrop of the concealed Weardale Granite (Fig. 1) and the concentration of copper-rich mineralization above
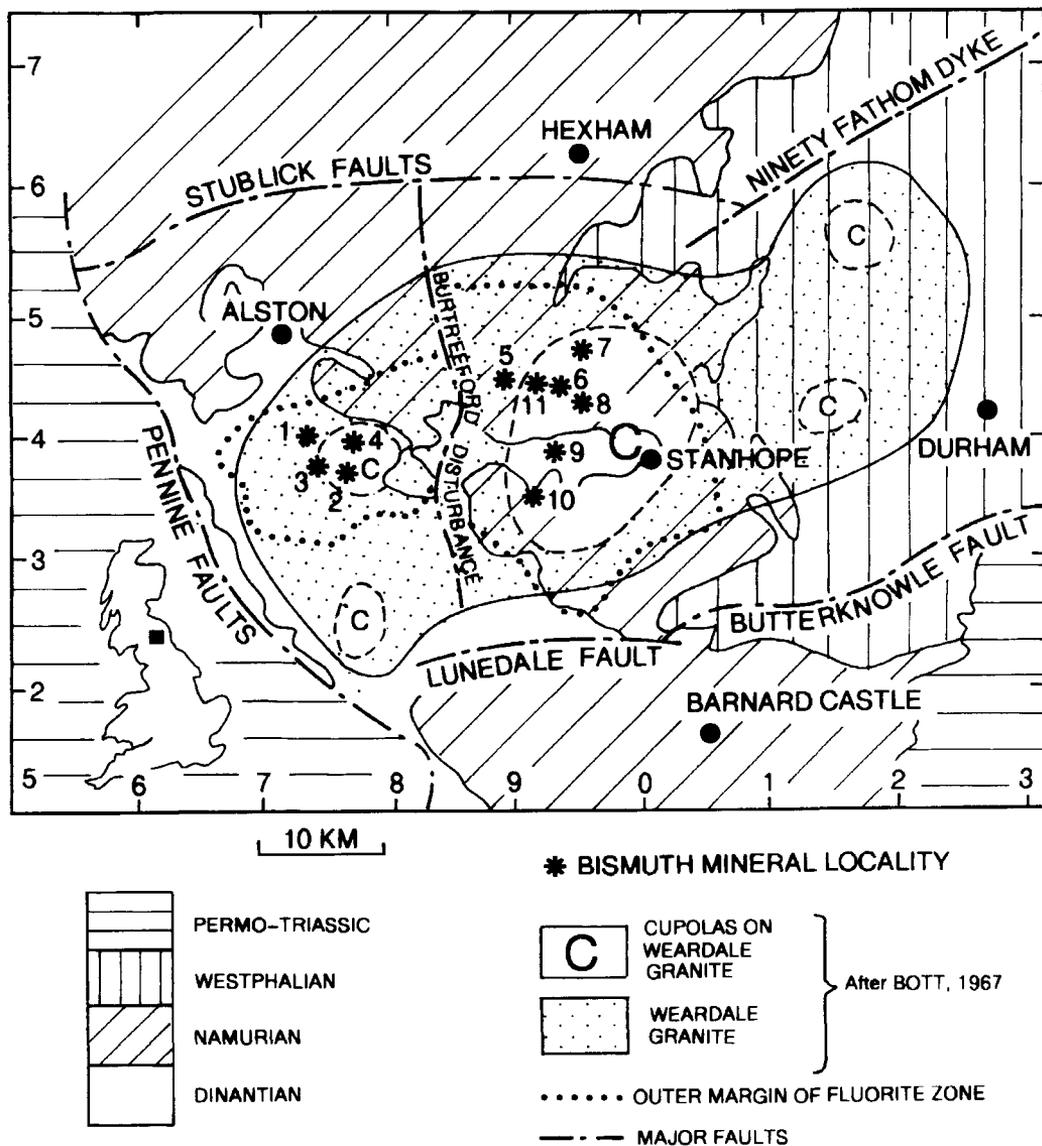
FIG. 1. Map of bismuth mineral localities of the Northern Pennine Orefield.

the Rookhope and Tynehead cupolas of this granite have figured prominently in the debate over the origin of the mineralization (Ixer, 1986; Brown *et al.*, 1987; Dunham, 1990; Ixer and Vaughan, 1993).

Mineralogical studies of the ore-bearing assemblages in recent years have revealed a great variety of minor elements, notably Ag, Co, Ni, As, Sb, Bi, Sn, *REE* (rare earth elements) and their resulting minerals within the main sulphide-fluorite-baryte-quartz mineralization (Ixer *et al.*, 1979; Vaughan and

Ixer, 1980; Ixer, 1986; Brown *et al.*, 1987; Young *et al.*, 1985; Ixer, 1990; Dunham, 1990). The significance of these elements and minerals and the role of the concealed Weardale Granite in their formation and in the formation of the orefield as a whole has been discussed by Brown *et al.*, (1987); Rankin and Graham (1988); Dunham (1990); Ixer and Vaughan, (1993).

Bismuthinite was first recorded from the Alston Block by Ixer (1986) who noted that minor amounts

TABLE 1. Bismuth mineral localities of the Northern Pennine Orefield (numbers refer to localities shown on Figure 1)

| | Locality | Grid reference | Veins worked or explored |
|---|---|---|---|
| 1. | Rotherhope Fell Mine | NY 699 426 | Rotherhope Fell Vein |
| 2. | Sir John's Vein | NY 761 378 | Great Sulphur Vein |
| | | | Sir John's Vein |
| 3. | Crossgill trials | NY 739 383 | Great Sulphur Vein* |
| 4. | Windy Brow trials | NY 765 381 | Windy Brow Vein |
| 5. | Groverake Mine | NY 896 442 | Rookhope Red Vein |
| | | | GroverakeVein* |
| | | | Greencleugh Vein |
| 6. | Redburn Mine | NY 929 431 | Rookhope Red Vein |
| 7. | Whiteheaps Mine | NY 949 466 | White Vein |
| | | | Hunstanworth Red Vein |
| | | | Company's Vein |
| | | | Ferneygill Vein |
| 8. | Stotfield Burn Mine | NY 943 424 | Rookhope Red Vein |
| 9. | Cambokeels Mine | NY 935 383 | Slitt Vein* |
| 10. | Westernhope Old Mine | NY 920 345 | Westernhope Old Vein |
| 11. | Rookhope Borehole | NY 937 428 | In Little Limestone* |

* Bismuth mineralization recorded *in situ*.

occur in the early high-temperature quartz–chalcopyrite-rich assemblages close to the Rookhope Cupola. Further localities and an association between bismuthinite, monazite and other *REE* minerals were described briefly by Flowers (1986) and additional localities were listed by Young in Dunham (1990). To date there has been no detailed or systematic account of these bismuth-bearing associations or indeed of the inner zone, high-temperature mineralization to which they belong.

The bismuth-bearing assemblages described in this paper occur within the innermost portions of the fluorite zone above the concealed granite cupolas of Rookhope and Tynehead. In four instances at Groverake, Cambokeels Mine, the Crossgill outcrop of the Great Sulphur Vein and the Rookhope Borehole bismuth mineralization has been collected *in situ*. At Groverake Mine and Cambokeels, bismuthinite-bearing quartz–chalcopyrite veinstone occurs as a narrow selvage to the main fluorite mineralization of the vein and is paragenetically early. At Crossgill bismuthinite-bearing iron sulphide-rich veinstone was collected from an outcrop of the sulphide-rich zone of the Great Sulphur Vein and in the Rookhope Borehole the mineralization is at 943 feet depth within the Little Limestone. At all other localities samples were obtained from mine spoil.

Localities from which specimens were obtained are listed in Table 1 and shown in Fig. 1.

*Experimental methods*

Samples have been studied using reflected and transmitted light microscopy and electron probe microanalysis. The instruments used were a Cambridge Microscan V employing an accelerating voltage of 15 kV using synthetic sulphides and standard correction procedures (at Aston University) and a Cameca SX50 using an accelerating voltage of 20 kV and pure elements, $SnO_2$ and FeS standards (at The Natural History Museum).

**Mineralogy of the bismuth-bearing assemblages**

Examination of fine-grained chalcopyrite-bearing quartz veinstone from the dumps of ten mines within the Northern Pennine Orefield has revealed very small but locally conspicuous, amounts of bismuthinite with minor amounts of native bismuth. The veinstone samples from all localities are extremely similar in composition and texture both in hand specimen and microscopically. Hence, the descriptions which follow are generalised with individual locality characteristics noted only where necessary.

In hand specimen bismuthinite-bearing veinstone consists of a compact aggregate of fine-grained colourless, pale grey or white quartz, although a crude irregular colour-banding of different coloured quartz is apparent in some samples. Small vugs, up to

5 mm across, lined with pyramidal white or colourless quartz crystals are locally present. Samples collected *in situ* from the margins of Groverake Vein in Groverake Mine, Rookhope contain abundant masses of chalcopyrite over 50 mm across.

Much of the quartz–sulphide mineralization fills voids between clasts of silicified argillaceous and locally carbonaceous wallrocks. Within these clasts, detrital, zoned zircons, mainly 10–30 μm but locally up to 60 μm in length, 10–40 μm diameter $TiO_2$ pseudomorphs after original Fe Ti oxide minerals, 2–10 μm long graphite flecks and up to 40 μm diameter irregular carbonaceous matter (including spores) are present. At Stotsfieldburn Mine, Rookhope, carbonaceous clasts are up to 200 μm across and carry abundant 10–20 μm framboidal pyrite. Diagenetic components in the wallrocks include 1–10 μm acicular $TiO_2$ and 5–30 μm diameter framboidal pyrite much of which is progressively recrystallized to produce pentagonal dodecahedral crystals. Where the wallrocks have been extensively pyritized, relict carbonaceous matter, $TiO_2$ minerals and zircon are enclosed in coarse-grained pyrite.

Rhythmically interbanded quartz–chalcopyrite with minor pyrite is the first phase of breccia cementation or vug infill. Fluorite–quartz–chalcopyrite–minor sphalerite–altered pyrrhotite mineralization is later and occurs as cross-cutting veinlets or infills the centre of veins and open void spaces.

Chalcopyrite is the most abundant and usually the first sulphide deposited in the veinstone. It is interbanded with quartz generations of different grain sizes. The earliest generation of chalcopyrite, locally accompanied by minor pyrite and rare earth minerals, directly overgrows the host rocks, forming aggregates, up to several centimetres across, comprising coarse-grained twinned crystals. These are overgrown by fine-grained quartz with sparse bismuthinite and synchysite crystals passing into barren coarse-grained quartz. This, in turn, is overgrown by fine-grained cloudy quartz enclosing chalcopyrite, bismuthinite and spherical aggregates of fine-grained unidentified bismuth-bearing minerals (Fig. 2A) that again pass into barren coarse-grained quartz. Much chalcopyrite is inclusion-free but locally it encloses and replaces pyrite, bismuthinite and pyrrhotite. Elsewhere chalcopyrite encloses discrete crystals of rare earth element minerals, 5–40 μm diameter grains of argentopentlandite, 10–30 μm diameter mackinawite, pyrrhotite and cubanite plus intergrowths of quartz, bismuthinite and spherical aggregates of one (or more) very fine-grained lead, bismuth and sulphur-bearing minerals. An analysis of argentopentlandite (Table 2) shows it to be almost stoichiometric but
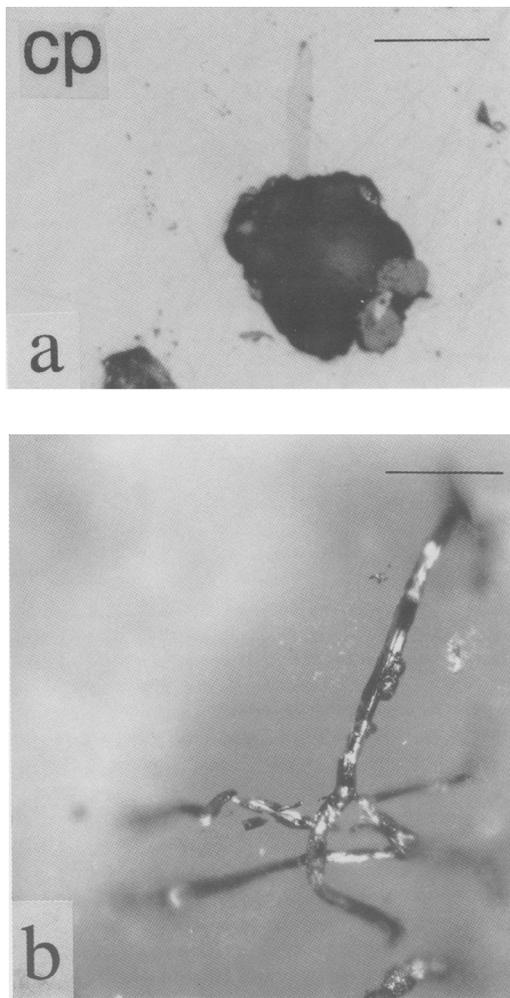


FIG. 2. (A) Chalcopyrite (cp) encloses a rounded area of quartz (dark). Bismuthinite is present as a single bladed crystal within chalcopyrite and as a small lanceolate crystal overgrown by two, lower reflectance, 'spheres'. Scale bar 20 μm. (B) Bismuthinite fibres growing within chalcedonic quartz. Intergrowths between randomly oriented fibres form untidy 'nests'. Small spheres are seen overgrowing the fibres. The plane of focus is within the quartz, below the surface of the section. Scale bar 50 μm.

(The photomicrographs are of Specimen 20933 (Durham Collection) taken in oil immersion, plane polarized light.)

to be slightly bismuth-bearing with 0.30 wt.% Bi. Table 3 shows chalcopyrite to be close to stoichiometric in composition but to be tin-bearing with up to

TABLE 2. Representative electron microprobe analyses of iron sulphides from bismuth-bearing assemblages (all data in wt.%)

| Locality/Mineral species | Fe | Ni | Co | Cu | As | S | Total | Formula | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Groverake (20908) | 59.37 | 0.04 | n.a. | 0.02 | n.a. | 38.99 | 98.42 | $Fe_{0.88}S$ | Relict pyrrhotite |
| | 58.92 | 0.03 | n.a. | 0.03 | n.a. | 39.10 | 98.08 | $Fe_{0.87}S$ | grains in pyrite itself |
| | 59.59 | 0.03 | n.a. | 0.02 | n.a. | 39.18 | 98.82 | $Fe_{0.87}S$ | within marcasite |
| | 59.15 | 0.06 | n.a. | b.t. | n.a. | 39.19 | 98.40 | $Fe_{0.87}S$ | Pseudomorphs after |
| Pyrrhotite MS | 59.26 | 0.09 | n.a. | 0.02 | n.a. | 39.36 | 98.73 | $Fe_{0.86}S$ | pyrrhotite |
| | 60.00 | b.t. | n.a. | 0.03 | n.a. | 39.66 | 99.69 | $Fe_{0.87}S$ | |
| Groverake (20908) | 46.39 | 0.09 | b.t. | 0.05 | b.t. | 54.09 | 100.62 | $Fe_{0.98}S_2$ | |
| | 46.33 | 0.02 | b.t. | 0.03 | b.t. | 53.63 | 100.01 | $Fe_{0.99}S_2$ | Pyrite matrix to |
| | 46.30 | b.t. | b.t. | 0.03 | b.t. | 53.68 | 100.01 | $Fe_{0.99}S_2$ | relict pyrrhotite |
| Pyrite MS | 45.79 | 0.15 | b.t. | b.t. | b.t. | 53.44 | 99.38 | $Fe_{0.98}S_2$ | |
| Whiteheaps | 46.63 | b.t. | 0.12 | n.a. | 0.78 | 54.27 | 101.80 | $Fe_{0.99}S_2$ | Bladed marcasite |
| | 46.71 | b.t. | 0.09 | n.a. | 0.21 | 53.46 | 100.47 | $Fe_{1.00}S_2$ | pseudomorphs |
| Marcasite AF | 46.47 | b.t. | 0.09 | n.a. | 0.19 | 53.88 | 100.63 | $Fe_{0.99}S_2$ | after pyrrhotite |

| | Fe | Ni | Ag | Cu | Bi | S | Total | Formula | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Groverake (20908) CJS Argentopentlandite | 27.63 | 26.58 | 13.37 | 1.24 | 0.30 | 31.40 | 100.52 | $Ag_{1.01}(Fe_{4.04}, Ni_{3.70}Cu_{0.16}) S_8$ | Argentopentlandite inclusion in chalcopyrite |

n.a., not analysed; b.t., below detection limit; MS, Dr M. Sweeney; CJS, Dr C. Stanley; Groverake 20908, (Durham University Mineral Collection); AF, Mr A. Flowers.

0.29 wt.% Sn at Groverake. Average tin values for Groverake and Rotherhope Fell are 0.09 wt.%, similar to those from Whiteheaps (0.07 wt.% Sn) (Flowers, 1986) and Redburn mine namely up to 0.06 wt.% (Stanley in Ixer, 1986). Neither cassiterite nor any member of the stannite group of minerals have been recognised as inclusions within chalco-pyrite from the orefield, suggesting that the tin occurs structurally within chalcopyrite.

Locally tabular aggregates, up to 500 × 40 μm in size, of fine-grained twinned marcasite surround pyrite and both minerals enclose relict pyrrhotite. They form a characteristic texture and are the 'bladed marcasite' of Phillips and Smith (1974) that were later recognised as pseudomorphs after pyrrhotite (Ixer *et al.*, 1979; Ixer, 1986). The aggregates are cemented together by coarse-grained marcasite, quartz, chalcopyrite or more rarely by pyrite, sphalerite and cobalt-nickel sulpharsenides (Ixer *et al.*, 1979). Analyses of relict pyrrhotites in pyrite in Table 2 show them to be monoclinic, close to $Fe_7S_8$ in composition and to carry trace amounts of nickel and copper (up to 0.09 wt.% and 0.03 wt.% respectively). The pseudomorphing pyrite and marcasite are close to stoichiometric with a little nickel and copper in pyrite, up to 0.15 wt.% and 0.03 wt.% respectively, and cobalt and arsenic in marcasite, up to 0.12 and 0.78 wt.% respectively. Elsewhere, high cobalt and arsenic contents, up to 3.8 and 8.7 wt.% respectively, are reported for marcasite pseudomorphs after pyrrhotite from Tynebottom Mine (Ixer *et al.*, 1979). A recent re-examination of this material using high magnification scanning electron microscopy suggests that 'arsenical marca-site' may be a very complex intergrowth of cobalt-bearing, but nickel-arsenic-poor, marcasite and glaucodot (Gwilt, pers. comm.).

Pyrite is a major component of the veinstone and is present in quartz and to a lesser extent in fluorite, chalcopyrite and sphalerite. It forms anhedral to euhedral crystals up to 400 μm in diameter. Large pyrite crystals show 5–20 μm partially recrystallized framboidal or poorly crystalline cores (up to 150 μm across) within well polished margins. These display 2–5 μm wide, pink-brown, or up to 10 μm paler coloured, optical zones that lie parallel to the crystal edges. Many crystals are inclusion-free but others enclose 2–5 μm marcasite and 5–10 μm euhedral

rhombic to tabular cassiterite crystals. These crystals form discontinuous veinlets or aggregates, up to 50 μm across, infilling vugs in pyrite and are especially common in ores from Groverake. As Table 3 shows, cassiterite carries minor amounts of iron (up to 1.3 wt.% FeO) and tungsten (up to 1.0 wt.% $WO_3$), and so is the first tungsten-bearing mineral to be recognised from the North Pennine Orefield. Pyrite is cemented and replaced along fractures, cleavage and grain boundaries by chalcopyrite, bismuthinite and sphalerite and hence carries these phases as small inclusions.

The rare earth mineralogy of the veinstone is complex with a number of minerals being present. Their presence was first noted by Flowers (1986) who identified monazite, xenotime and synchysite and these together with bastnäsite have been confirmed by P. Webb (pers. comm.) and will be described and discussed elsewhere. Monazite and xenotime form discrete 20–40 μm equant crystals that overgrow bismuthinite whereas texturally later, acicular (5 × 1 μm) to tabular (up to 120 × 10 μm) crystals of synchysite/bastnäsite are present in quartz and fluorite and locally overgrow bismuthinite. Rare, euhedral adularia crystals are present close to rare earth minerals in fine-grained radiating quartz.

Sphalerite, up to 20 μm in diameter, is dark-coloured, iron-rich and free of chalcopyrite disease. Together with minor amounts of galena it infills voids between quartz and fluorite or overgrows chalcopyrite.

Bismuthinite is the only bismuth mineral that can be recognised in hand specimens of the veinstone. It typically occurs as discrete, euhedral tabular crystals

TABLE 3. Representative electron microprobe analyses of sulphides and cassiterite from bismuth-bearing assemblages (all data in wt.%)

| Locality/Mineral Species | Fe | Cu | Sn | Bi | As | S | Total | Formula | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Groverake (20908) | 30.18 | 34.16 | 0.29 | b.t. | n.a. | 34.29 | 98.92 | $Cu_{1.01}Fe_{1.01}S_2$ | Interbanded |
|  | 30.47 | 34.11 | 0.11 | b.t. | n.a. | 34.53 | 99.22 | $Cu_{1.00}Fe_{1.01}S_2$ | with fine- |
| Chalcopyrite | 30.27 | 33.96 | 0.06 | 0.09 | n.a. | 35.26 | 99.64 | $Cu_{0.99}Fe_{0.99}S_2$ | grained quartz. |
|  | 30.89 | 34.38 | 0.07 | n.a. | n.a. | 34.95 | 100.29 | $Cu_{0.99}Fe_{1.01}S_2$ | Cassiterite |
|  | 30.98 | 34.64 | 0.12 | n.a. | n.a. | 34.86 | 100.60 | $Cu_{1.00}Fe_{1.02}S_2$ | present in pyrite |
| CJS | 30.82 | 34.20 | b.t. | n.a. | n.a. | 34.29 | 99.31 | $Cu_{1.01}Fe_{1.03}S_2$ | in specimen |
| Rotherhope Fell | 30.23 | 34.84 | 0.06 | n.a. | n.a. | 35.46 | 100.59 | $Cu_{0.99}Fe_{0.98}S_2$ |  |
| Chalcopyrite | 30.26 | 34.88 | 0.13 | n.a. | n.a. | 35.62 | 100.89 | $Cu_{0.99}Fe_{0.98}S_2$ |  |
| AF | 29.70 | 34.16 | 0.02 | n.a. | n.a. | 34.59 | 98.47 | $Cu_{1.00}Fe_{0.99}S_2$ |  |

| | Fe | Cu | Pb | Bi | Ag | S | Total | Formula | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Groverake 20908 | n.d. | 0.26 | 0.34 | 80.89 | b.t. | 17.87 | 99.36 | $Bi_{2.08}S_3$ |  |
| Bismuthinite | n.d. | 0.67 | 0.31 | 80.75 | b.t. | 18.12 | 99.85 | $Bi_{2.05}S_3$ |  |
| Groverake | 0.47 | 1.06 | n.a. | 79.81 | n.a. | 18.80 | 100.14 | $(Bi_{1.95}Cu_{0.08}Fe_{0.04})S_3$ | In chalcopyrite |
|  | 0.31 | 0.73 | n.a. | 80.04 | n.a. | 18.77 | 99.85 | $(Bi_{1.96}Cu_{0.06}Fe_{0.03})S_3$ |  |
| CJS | 0.20 | 0.60 | n.a. | 80.95 | n.a. | 18.87 | 100.62 | $(Bi_{1.97}Cu_{0.05}Fe_{0.02})S_3$ | In quartz |
| Whiteheaps | n.a. | n.a. | n.a. | 82.20 | b.t. | 18.27 | 100.47 | $Bi_{2.07}S_3$ |  |
| AF | n.a. | n.a. | n.a. | 82.58 | b.t. | 18.29 | 100.87 | $Bi_{2.08}S_3$ | In quartz |

| | $SnO_2$ | FeO | $WO_3$ | | | | Total | Formula | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Groverake 20908 | 98.43 | 0.65 | 0.93 | | | | 100.01 | $(Sn_{0.98}W_{0.01}Fe_{0.01})O_2$ | Discrete crystals |
| Cassiterite | 98.31 | 0.74 | 1.03 | | | | 100.08 | $(Sn_{0.98}W_{0.01}Fe_{0.02})O_2$ | in pyrite |
| CJS | 98.93 | 1.29 | 0.52 | | | | 100.74 | $(Sn_{0.98}Fe_{0.02})O_2$ |  |

n.a., not analysed; b.t., below detection limit; CJS, Dr C. Stanley; Groverake 20908 (Durham University Mineral Collection); AF, Mr A. Flowers.
Detection Limits: Sn in chalcopyrite 0.05 wt.%; Cu, Pb and Fe in bismuthinite, 0.10 wt.%; W in cassiterite 0.10 wt.%; Fe in cassiterite 0.15 wt.%.

20–60 μm long commonly within quartz (Fig. 2B) but also enclosed within chalcopyrite where it is intergrown with native bismuth and argentopentlandite. More rarely bismuthinite is found in pyrite, fluorite and sphalerite. In some samples bismuthinite forms long (up to 400 μm) spiralling fibres that are up to 5–40 μm in diameter and comprise single striated crystals or rarely, multiple crystals lying along the same axis. These fibres form small radiating 'nests' or are kinked and cross-cut chalcopyrite-quartz boundaries. In one specimen from Redburn Mine, Rookhope, bismuthinite is present as slightly curved bladed crystals up to 5 μm long. From Sir John's Mine, Stotfield Burn, Groverake and Cambokeels Mine free standing acicular crystals up to 1 mm long grow out from the surfaces of euhedral quartz crystals lining vugs in quartz-rich veinstone. On some margins of chalcopyrite and pyrite fine-grained complex intergrowths of bismuthinite and chalcopyrite are inferred to be the incomplete replacement of chalcopyrite by bismuthinite.

Bismuthinite analyses (Table 3) show them to be slightly bismuth-rich compared with their stoichiometric formula and to carry trace amounts of lead, up to 0.34 wt.%. The copper and iron content of some analyses may reflect a contribution from the enclosing chalcopyrite or be due to relict chalcopyrite within bismuthinite.

Associated with bismuthinite, often growing out from the fibres, are 2–10 μm but very rarely up to 60 μm, spherical aggregates of radiating <1 μm highly anisotropic crystals. Locally these aggregates show a poorly developed hexagonal outline or poor red-coloured internal reflections. The spheres, often with a 1–5 μm diameter bismuthinite core, occur in quartz, chalcopyrite, or overgrow pyrite and REE minerals but are themselves overgrown by argentopentlandite. Although the identity of this phase has not been established, qualitative analyses show the presence of lead, bismuth and sulphur, (together with a little copper and iron), which is consistent with the phase being cosalite, a mineral previously described from Teesdale (Vaughan and Ixer, 1980).

### Significance of bismuth-bearing assemblages.

Figure 1 shows that all the occurrences of bismuth-bearing mineralization within the orefield lie within the fluorite zone, above or very close to the Rookhope and Tynehead cupolas of the Weardale Granite. None has been found away from these areas despite a careful search of abundant mine spoil and investigation of many polished sections from elsewhere in the orefield.

The recent regional geochemical survey covering the western parts of the Alston and Askrigg Blocks (British Geological Survey, 1992) also supports the association of this mineralization with the Weardale Granite and its cupolas. The results show that some elements, in particular silver, have enhanced values that follow the outline of the buried granite (British Geological Survey, 1992) whereas others show more localized anomalies, for example, those shown by Sb, Bi and Mo at Weardale and by Bi in upper Teesdale. Yet other elements, notably Sn, show little sign of any coincidence with the granite subcrop. However, for all these elements comparison of the Alston and Askrigg Blocks shows there to be higher concentrations on the Alston Block than Askrigg where discrete Sn, Bi, Mo minerals have not been recorded and where Ag and Sb minerals are present only in minute amounts.

Both in situ and hand specimen materials show that the quartz-hosted bismuth-bearing assemblages are earlier than the main fluorite mineralization. Indeed the assemblages are paragenetically early, higher temperature and distinctive and Phillips and Smith (1974), Ineson (1976) and Dunham (1990) have suggested that they lie below the fluorite-galena-rich ores.

Polished section petrography and electron microprobe analysis show that bismuth is one of a characteristic suite of elements, including Sn, Ag, Sb, REE and now W that are present in the Alston Block despite being unusual for Mississippi Valley-type deposits (and are not present in any other British Mississippi Valley-type orefield). It is these elements, the 'granitic' ones of Ixer (1986) and Brown et al., (1987) that have played a role in the debate concerning the exact nature of the contribution of the Weardale Granite to the mineralization of the Alston Block (Brown et al., 1987).

The recognition of this relatively widespread, distinctive, bismuth-bearing veinstone invites further study of the early mineralization of the orefield particularly with regard to fluid inclusions, isotopic composition and, possibly, precious metal, especially gold content.

### Acknowledgements

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