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Native antimony and bournonite intergrowths in galena from the English Lake District

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ABSTRACT. The Driggith vein is representative of the lead-zinc mineralization in the Caldbeck Fells area, with a primary mineral assemblage consisting of quartz, baryte, calcite, chalcedony, pyrite, arsenopyrite, galena, sphalerite, bournonite, argentian tetrahedrite, and native antimony. Broadly similar assemblages are found in Pb-Zn mineralization of Upper Devonian to Permian age elsewhere in the Lake District. The paragenetic sequence appears to have been early pyrite and minor arsenopyrite associated with quartz; with later baryte, calcite, sphalerite, and chalcopyrite enclosed by galena. Within the galena occur inclusions of tetrahedrite, bournonite, and native antimony. A later stage of baryte mineralization was followed by the alteration of primary sulphides to secondary minerals. Elsewhere in the Lake District, galena occurring in this association also contains inclusions of native antimony, bournonite, and other sulphosalts, and in this respect differs from galena associated with earlier veins composed dominantly of chalcopyrite, pyrite, and arsenopyrite. The inclusions make a major contribution to the high antimony values reported in trace element analyses of galena from the Lake District. The occurrence of these inclusions, which in some cases display preferred orientation within the host galena, is discussed in terms of phase relations involving PbS and $AgSbS_2$.

METALLIFEROUS mines in the Caldbeck Fells area, about 12 km north-east of Keswick, were worked principally for lead, zinc, copper, and baryte. Many of the mines have a long and varied history (Postlethwaite, 1913; Eastwood, 1921, 1959; Shaw, 1970), but none are working at the present time, Potts Ghyll baryte mine being the last to close in 1965 (Shaw, 1970).

There are two main associations of galena in the Lake District. It occurs as a minor constituent of some of the Lower to Middle Devonian chalcopyrite-arsenopyrite-pyrite veins (Stanley and Vaughan, 1980), but it is found predominantly in later veins of Upper Devonian to Permian age (Ineson and Mitchell, 1974) associated with sphalerite, baryte, minor chalcopyrite, and carbonates (Stanley, 1979). Native antimony, bournonite, and other sulphosalt inclusions appear to be restricted to this later galena.

The principal lead-zinc veins worked in the Caldbeck Fells occur in the Driggith-Roughtongill vein system, which consists of two major northeast to southwest lodes and several minor offshoots. Most of the veins were emplaced along normal faults cutting andesites and tuffs of the Eycott Group of Ordovician age (Wadge, 1978); for part of its length, however, the Roughtongill South vein occupies a fault in the Carrock Fell Igneous Complex. Other lead-zinc veins in the Lake District occur in rocks of the Borrowdale Volcanic Group and Skiddaw Group, both of Ordovician age. The slates and siltstones of the Skiddaw Group appear to have been generally unfavourable host rocks for the mineralization, with the exception of those areas which suffered metamorphism and hardening caused by the emplacement of the underlying Lake District granite batholith.

Ore-bearing specimens were collected from many lead-zinc veins in the Lake District as part of a wider study of mineralization in the area. Specimens described in this paper from the Driggith vein (fig. 1) were collected from surface workings northeast of Driggith mine [NY 3280 3520] and from dumps at the Sandbeds end of the Driggith vein [NY 3320 3620]. These specimens were studied in thin and polished sections and, where necessary, qualitative examination was followed by determinations using X-ray powder diffraction and electron probe microanalysis as described in detail in Stanley (1979). It is important to note that galena specimens must have a near-perfect polished surface in order to observe the fine intergrowths.

Mineralogy. The mineralogy of the Driggith vein is representative of the lead-zinc mineralization of the Caldbeck Fells area, except that tetrahedrite was not found at other localities. Elsewhere in the Lake District, the assemblages of the lead-zinc mineralization are broadly similar, although they generally contain fewer secondary minerals than found at Driggith. In addition, while native antimony, bournonite, and other sulphosalt inclusions occur in galena from several other Lake District localities, they are considerably less abundant than in galena from the Caldbeck Fells area, and in particular from the Driggith-Roughtongill vein system.

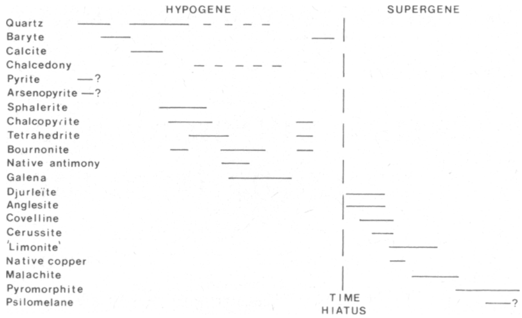


FIG. 2. Paragenetic diagram for Driggith vein.

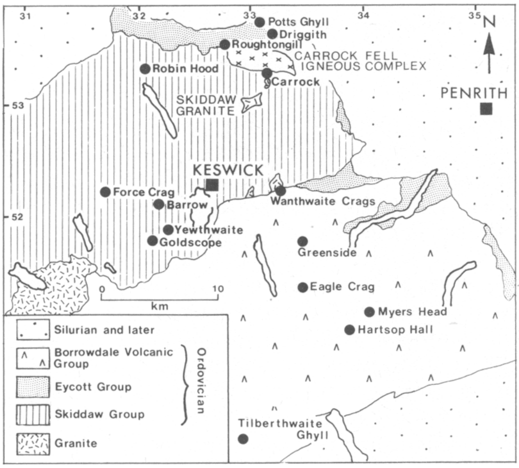


FIG. 1. Sketch map of the Lake District, showing localities referred to in the text.

The study of hand specimens, and of thin and polished sections, indicates a primary mineral assemblage for the Driggith vein of quartz, baryte, calcite, chalcedony, pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, bournonite, tetrahedrite, and native antimony. Minerals regarded as later secondary alteration products, on the basis of textural evidence, include djurleïte, covelline, goethite, native copper, 'limonite', azurite, anglesite, pyromorphite, and psilomelane. In addition, bornite was found by Thimmaiah (1956), although it was not observed in the present study.

The antimony-bearing minerals present are native antimony, bournonite, and tetrahedrite. Electron microprobe analyses of bournonite and tetrahedrite are given in Stanley (1979). Tetrahedrite, $(Cu_{0.84}, Ag_{0.16})_{10.1}$ $(Fe_{0.43}, Zn_{0.57})_{2.0}$ $Sb_{4.2}$ $S_{12.7}$, contains 10-12 wt% silver, and X-ray diffraction studies show it to have interplanar spacings in agreement with Berry and Thompson's (1962) data for argentian tetrahedrite. Native antimony occurs as very fine grains and was determined by qualitative electron probe microanalysis.

Paragenetic relations. The paragenetic relations determined for mineral assemblages from the Driggith vein are summarized in fig. 2. Pyrite occurs both as small euhedra in the fine-grained tuffaceous country rock and as an early phase in the vein itself where, along with minor amounts of arsenopyrite, it is found as corroded inclusions in chalcopyrite and galena. The early age of the first generation of baryte mineralization is shown clearly by field observations of baryte on either side of the main central quartz vein, and by later quartz pseudomorphs after baryte. Calcite also appears to be an early phase, as it is found at the external margins of the later sulphide filling.

Sphalerite and chalcopyrite generally exhibit mutual boundary relationships and are interpreted as having been deposited at roughly the same time. Sphalerite is particularly abundant and commonly occupies interstices in corroded quartz pseudomorphing baryte. Galena encloses sphalerite and chalcopyrite, and appears to be later.

Argentian tetrahedrite appears olive-grey against galena and is mostly in anhedral grains (<200 μm). Commonly it grows on euhedral quartz or is found as isolated grains in galena, and it may contain inclusions of bournonite.

At Driggith and other lead-zinc veins in the Caldbeck Fells, bournonite occurs in three forms: (i) as relatively large grains (<100 μm) commonly enclosed in argentian tetrahedrite; (ii) along cleavages in galena, with chalcopyrite and minor tetrahedrite, possibly the result of post-cleavage remobilization; (iii) as intergrowths in galena, either as platelets or rods, usually no more than a few microns in width and clearly oriented along structural planes of the galena (fig. 3), or as rounded blebs (<5-10 μm) arranged in irregular curved strings, possibly along galena grain boundaries. Irregular grains of bournonite (20-30 μm) also occur either associated with native antimony (fig. 4) or as somewhat smaller grains at chalcopyrite/galena grain boundaries.

Native antimony is intimately associated with bournonite where the latter occurs as intergrowths and small blebs in galena (figs. 3 and 4). It has a high reflectance and appears bright white against galena, generally occurring as minute (<1 μm) rounded grains and rarely larger than 5 μm.

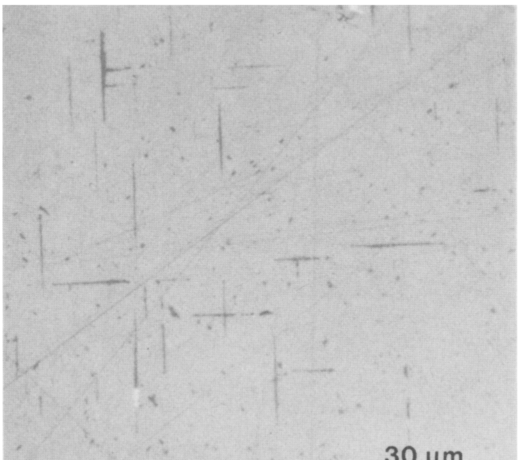
A further period of baryte mineralization took place after the deposition of galena and the antimony-bearing minerals. Following the remobilization of some of the sulphides, the primary mineralization suffered considerable alteration by later fluids. Galena was extensively replaced along cleavages and grain boundaries by djurleïte and covelline, the djurleïte being intimately associated with very fine (<1 μm) grains of anglesite. In this replacement, galena was replaced preferentially to the bournonite and native antimony intergrowths. Additional secondary minerals include cerussite, 'limonite', native copper, malachite, psilomelane, and pyromorphite.

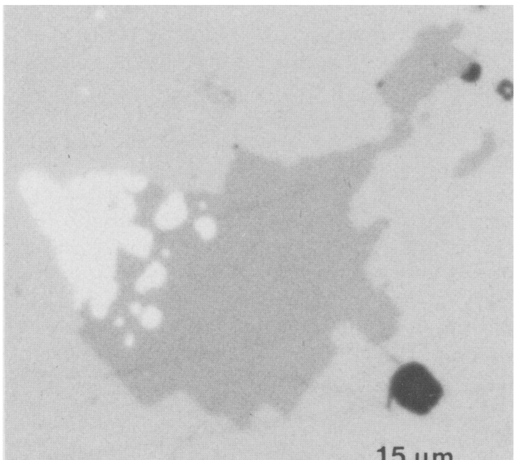
Comparison with other Lake District lead-zinc deposits. Intergrowths of bournonite and native antimony, similar to those described from the Driggith vein although in considerably smaller amount, were identified in galena from lead-zinc veins at Force Crag [NY 2020 2175], Yewthwaite [NY 2400 1955], Goldscope [NY 2255 1850], Greenside [NY 3595 1880], Eagle Crag [NY 3545 1435], Hartsop Hall [NY 3960 1200], and Myers Head [NY 4155 1275]. At Barrow mine [NY 2320 2180] two other phases, boulangerite and ullmannite, occur in addition to these intergrowths as minute inclusions in galena (Stanley, 1979). Tetrahedrite was identified in material from Eagle Crag, near Patterdale and from Tilberthwaite Ghyll, near Coniston [NY 3030 0060].

Several previous accounts of Lake District mineralization mention isolated occurrences of antimony-bearing minerals, although some of these appear not to be associated with lead-zinc mineralization. Postlethwaite (1913) recorded stibnite from Robin Hood mine, Bassenthwaite, and also from Wanthwaite Crags to the south-east of Keswick. Davidson and Thompson (1948) found stibnite from St. Sunday Crag in the Helvellyn region. The occurrence of stibnite, zinckenite, jamesonite, and boulangerite in Grainsgill, near Carrock mine, was described by Kingsbury and Hartley (1956), but it is not known if these minerals were from the north-south tungsten veins or from the east-west lead-zinc crosscourse. Gough (1963) found bournonite and tetrahedrite inclusions in galena from the Greenside lead vein.

Antimony-bearing phases have recently been reported from the area of the North Pennine orefield around Alston (Vaughan and Ixer, 1980). In particular, oriented spindles and veinlets of bournonite occur in galena, as do grains of ullmannite.

Discussion. In the Lake District lead-zinc veins, bournonite and native antimony inclusions in galena are locally abundant and commonly oriented, as described from the Driggith vein and the Caldbeck Fells area. There can be little doubt that these inclusions account, at least in part, for the high antimony contents (500 to 5000 ppm) of some Lake





FIGS. 3 and 4. FIG. 3 (*left*). Reflected light photomicrograph: Oriented bournonite (dark grey) and native antimony (white) intergrowths in galena (grey). Driggith vein. FIG. 4 (*right*). Reflected light photomicrograph: Native antimony (white) with bournonite (dark grey) in galena (grey). Driggith vein.

District galenas reported by Gough (1963) and El Shazly *et al.* (1957). These trace element studies indicate a consistent excess of antimony over silver, most galenas having Sb/Ag ratios of 3:1 or greater, up to 20:1. Argentian tetrahedrite was the only silver-bearing phase identified in the present work, and it seems unlikely, on account of its limited distribution, to be responsible for the 200 to 1000 ppm of silver reported in galena.

Synthetic studies have indicated that silver in argentiferous galena is unlikely to be present as argentite (Ag_2S) solid-solution. Van Hook (1960) found that only 0.4 mole% Ag_2S could be in solid-solution at 700 °C and an insignificant amount at temperatures below 500 °C. Amcoff (1976), in an extension of work by Hoda and Chang (1975), found complete solid-solution between PbS and $AgSbS_2$ above 390 °C and determined that the maximum solubility of $AgSbS_2$ in PbS is about 4 mole% $AgSbS_2$ at 300 °C and 2 mole% $AgSbS_2$ at 250 °C. Fluid-inclusion studies of fluorite and sphalerite (Stanley, 1979) from Lake District lead-zinc veins indicate mineralization temperatures in the range 100–130 °C.

It is therefore considered that silver and some antimony occur in solid-solution in galena in the form of $AgSbS_2$, and that the excess of antimony over silver in the trace element analyses may be explained by the presence of fine-grained inclusions of native antimony and sulphosalts such as bournonite. Intergrowths of bournonite and native antimony in galena, particularly those from the Driggith vein, oriented along structural planes, are thought to be due to exsolution. Hydrothermal solutions containing lead and sulphur, and possibly some antimony and silver, could have gained additional antimony, silver, copper, and sulphur from the alteration of early minerals in the Driggith vein, such as argentian tetrahedrite and chalcopyrite. On cooling and crystallization of the $AgSbS_2$–PbS solid-solution, excess antimony could combine with any other remaining elements and be exsolved in the form of oriented lamellae, or as discrete grains, of bournonite. According to Brett (1964), oriented exsolution lamellae may develop during either rapid cooling and crystallization or slow cooling, provided that the degree of supersaturation is low. Since exsolution lamellae are stable only as long as the lamellar phase is in crystallographic continuity with the host phase (Brett, 1964), the oriented exsolution of bournonite and native antimony in galena would be unstable. This may explain the limited occurrence of this type of intergrowth and the more widespread presence of the more stable texture of larger unoriented blebs of bournonite and native antimony.

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