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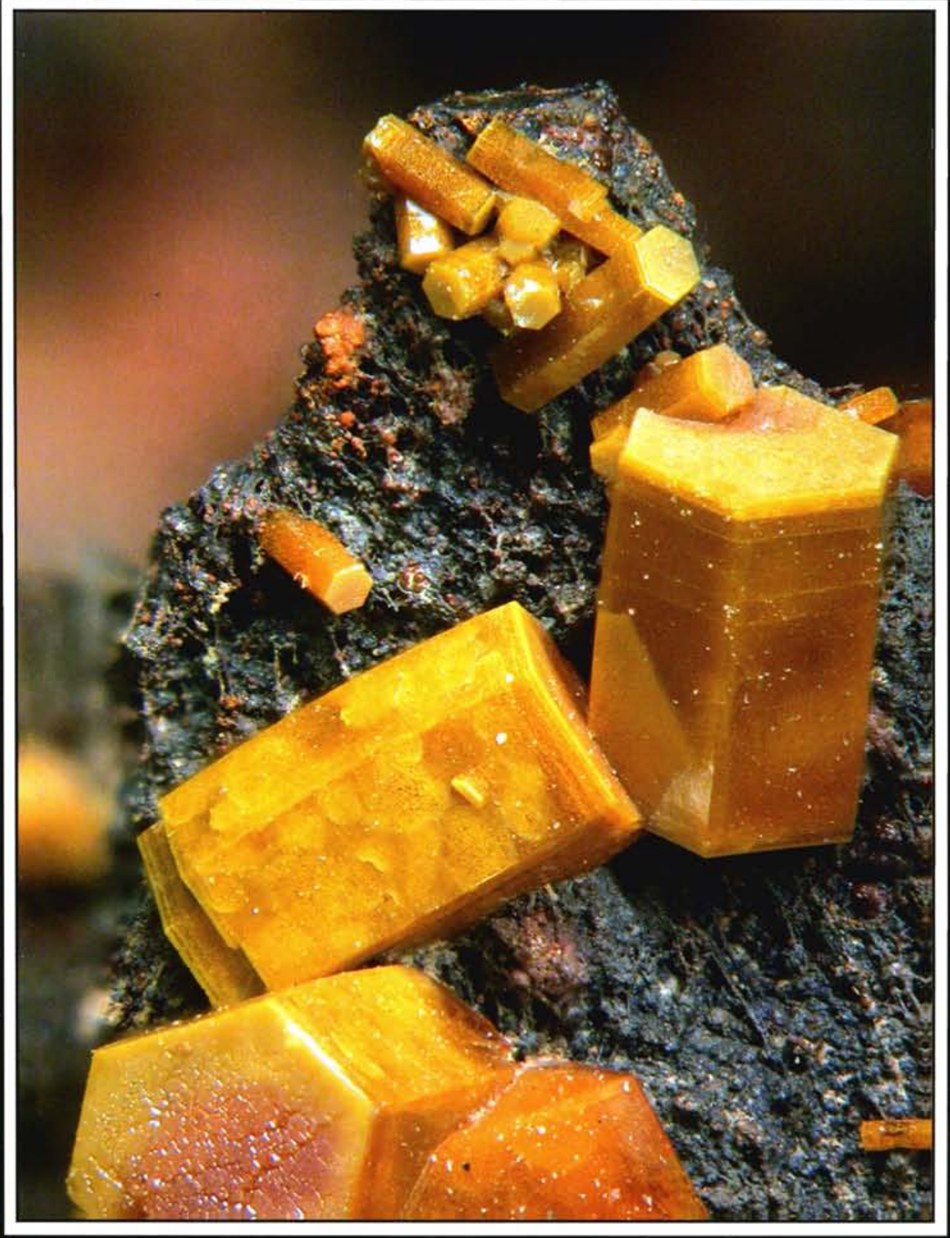

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The journal of British Isles topographical mineralogy

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FRONT COVER:
Hexagonal prismatic mimetite crystals to 4mm from Dry Gill mine,
Caldbeck Fells, Cumbria, collected in the 1970s by Jim Knight.
Photograph by David Green.

BACK COVER:
Ewaldite from Dolyhir Quarry, Old Radnor, Powys, Wales.
1.7mm. Julie Ballard collection and photograph.

Journal of the Russell Society

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PAPERS

Editorial

Welcome to volume 9 of the Journal. Not volume 9, part 1; at a recent meeting of the Russell Society Council it was agreed that the numbering system would be simplified to an annually increasing number: 2006 volume 9, 2007 volume 10, etc. Exceptions to this may arise if we have a sufficient quantity of articles to produce two parts in one year, or if a special or themed issue is spread between two parts to avoid problems associated with printing and binding an extra thick edition. Astute readers may notice that the font size in this volume is smaller than in recent issues; this is to accommodate all of the articles submitted within a reasonable number of pages.

Thanks again to the authors and stalwart reviewers, we have an appetising set of articles on British mineralogy for you to digest (metaphorically). Half of the articles, occupying well over half of this volume, describe mineral localities in Cumbria, including three reviews of localities in the Caldbeck Fells. We start with a note by Trevor Bridges and David Green on the first British occurrence of köttingite, an uncommon zinc-rich member of the vivianite group. This discovery extends the already lengthy list of supergene minerals known from the Hilton Mine updated by these authors in the previous volume. Next are comprehensive reviews of the mineralisation at Driggith and Sandbed Mines, at Brae Fell Mine and at Arm O'Grain. David Green and co-authors report 18 minerals new to the Driggith and Sandbed Mines of which annabergite, brianyoungite, gersdorffite, lavendulan, parnauite, strashimirite, yarrowite and zálesíite are reported for the first time in the Caldbeck Fells and mawbyite for the first time in the British Isles. A.W.G. Kingsbury's claims to have collected specimens of several of these species from this locality and from Brae Fell Mine are probably fraudulent; however, the authors conclude that many of his reported species have now been found, albeit in much smaller specimens. This does not apply to Arm O'Grain which is one of the few localities in the Caldbeck Fells that was not known to Arthur Kingsbury.

A pair of articles by Richard Braithwaite and his co-authors describes secondary species associated with weathering of smelter residues from Castleside in Co. Durham and Tindale Fell in Cumbria. At the site of Castleside smelting mill, the presence of antimony and copper together has resulted in the formation of some unusual phases, including copper antimonate which has not previously been reported from slags or from natural occurrences. Continuing the theme of post-mining secondary minerals, Tom Cotterell reports the first Welsh occurrence of hydronium jarosite within opencast iron ore workings at the Brynycastell mine near Dolgellau.

In the next article, Alan Dyer and his co-authors report chemical analyses of millimetre-sized crystals labelled as 'heulandite' from Wheal Hazard, St Just, Cornwall and demonstrate that most of their compositions lie within the closely related clinoptilolite series of zeolite minerals.

Witherite replacement of baryte has been recognised for a long time in the Northern Pennines orefield. Trevor Bridges and David Green document baryte replacement by barium carbonate minerals and calcite in specimens from mines from the Nenthead area, Cumbria, and discuss the geochemistry of the replacement process with reference to conditions in the orefield. Studies of fluid inclusions in witherite and barytocalcite are required and the authors offer to make available well crystallised material for such research. Any takers?

Tim Neall and co-authors then review British occurrences of scotlandite. This rare lead sulphite mineral has been found in the Caldbeck Fells, in the Leadhills-Wanlockhead district, and at Whitwell quarry in Derbyshire. By studying its paragenesis, the authors constrain the conditions under which scotlandite formed and suggest that it is likely to be identified at further localities as analytical techniques (and awareness!) improve.

The final article is a note by Stephen Moreton and David Green on an unusual association of cavity-fill zeolites and skarn minerals at Barnahallia in Connemara, Ireland. Corrosion of calcite may have formed the cavities.

Norman Moles

THE FIRST BRITISH OCCURRENCE OF KÖTTIGITE, FROM HILTON MINE, SCORDALE, CUMBRIA

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Köttigite, $Zn_3(AsO_4)_2.8H_2O$, is an uncommon member of the vivianite group of minerals, monoclinic and triclinic arsenates and phosphates with a general formula that can be written $A_3(XO_4)_2.8H_2O$. In the vivianite group, the A-site in this group is usually occupied by a divalent transition metal cation and the XO_4 group is either phosphate or arsenate (Gaines *et al.*, 1997). Köttigite was named in 1850 in honour of Otto Köttig, a German chemist. It forms a solid solution series with erythrite and annabergite and is dimorphous with metaköttigite. The unit cells of the iron, cobalt, nickel and zinc bearing members of the vivianite group, parasymplesite, erythrite, annabergite and köttigite, are almost identical in size and since the transition metal cations have very similar scattering factors their XRD powder patterns are almost identical. It is difficult to differentiate them by XRD alone. Analytical data, either EDS or WDS, in combination with XRD is required to characterise the minerals to species level.

Recent investigations of iron, cobalt, nickel and zinc-bearing members of the vivianite group from a number of localities in the British Isles have identified köttigite at two localities in Britain and one in Ireland. The first British occurrence, at Hilton mine in Cumbria, is described here. A second occurrence at Sandbed mine in the Caldbeck Fells, Cumbria is described in a companion paper (Green *et al.*, 2006). An article including a description of the first Irish köttigite occurrence at Moll Doyle mine in the Wicklow Mountains of Ireland is in preparation.

Hilton Mine is situated near the head of the Scordale valley on the western escarpment of the Pennine Hills, Cumbria in the vicinity of NGR NY 762 228. The geology, mineralogy and structural setting are described by Dunham (1990). The mine is internationally well known for beautiful specimens of golden yellow fluorite and also for excellent specimens of tabular baryte, which occurred in veins and metasomatic replacement flats, particularly just below the Whin Sill. Bridges (1982) reported an unusual assemblage of nickel minerals from the south wall of the Dow Scar level, a little below the Whin Sill. The assemblage includes nickeline, gersdorffite, minor millerite and the oxidation product annabergite. Bridges and Green (2005) updated the supergene mineralogy of the mine with eight previously unreported species including the arsenates adamite and mimetite, these latter minerals occurring as part of the oxidised nickel-rich assemblage. Recent re-examination of some of this material has resulted in the identification of a specimen containing köttigite.

The köttigite was initially examined by energy dispersive spectrometry (EDS), zinc and arsenic being the dominant elements found with an atomic number greater than 10. Since the specimen appeared visually different to adamite from the site (see Bridges and Green, 2005) it was examined by X-ray diffractometry. The XRD pattern (reference number MANCH: XRD1102) was an excellent match to köttigite.

The whole specimen approximates to a 40 mm cube of mainly galena and gersdorffite. One side is freshly broken; other sides are highly oxidised and coated with annabergite and ferruginous earthy encrustations. The köttigite occurs on the latter and covers an area of approximately 10 mm by 3 mm. The individual crystals reach about 1 mm, but are generally much smaller. They are colourless and transparent with an appearance similar to minute crystals of stilbite. Interestingly, there is no sphalerite on the specimen, which came from a nickel-rich pod. Supergene zinc-bearing minerals including adamite, aurichalcite, hemimorphite, hydrozincite and smithsonite have been found at Hilton mine and zinc is relatively mobile in the supergene environment.

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A REVIEW OF THE MINERALISATION AT THE DRIGGITH AND SANDBED MINES, CALDBECK FELLS, CUMBRIA

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Low temperature lead-zinc-copper veins are developed within a NE-SW trending fracture system in rocks of the Eycott Volcanic Group at Driggith and Sandbed mines in the Caldbeck Fells, Cumbria. The lead veins were worked by a succession of mining companies from the 18th century onward, first at Driggith mine and later at Sandbed mine. East-west trending baryte-quartz-carbonate veins were worked for baryte in the mid-20th century. The dumps from these mines surround and in some cases cover those of the earlier lead workings.

Several episodes of primary mineralisation can be distinguished. The primary lead vein mineralisation comprises major quartz, calcite, sphalerite, galena and chalcopyrite. Sparse antimony-rich sulphide mineralisation is present as inclusions in the galena. There is rich, localised, iron sulphide-arsenopyrite mineralisation, which pre-dates the lead-copper-zinc vein mineralisation; sparse nickel- and cobalt-bearing mineralisation of unknown affinity, and baryte mineralisation with quartz and carbonates that post-dates the lead-copper-zinc vein mineralisation. The later baryte is present in distinct E-W trending veins and as a later stage of mineralisation in the fractures that host the lead-copper-zinc vein mineralisation.

Supergene oxidation is extensive. About sixty supergene minerals have been identified. Distinctive specimens of curved green arsenate-rich pyromorphite on hackly quartz are well known from the opencut above Driggith mine. Bayldonite, cerussite, mimetite and malachite are widespread and abundant. Anglesite, aurichalcite, hemimorphite, linarite and philipsburgite are relatively common in micro-crystalline specimens. The arsenate minerals barium-pharmacosiderite, beudantite, mimetite, segnitite and scorodite form distinct localised gossans, which are closely associated with primary arsenopyrite. A variety of sulphate minerals including brochantite, langite, linarite, serpierite and schulenbergite have been formed by post-mining oxidation.

Minerals discovered for the first time at the Sandbed and Driggith mines as a result of this study include arsendescloizite, annabergite, brianyoungite, djurleite, erythrite, gersdorffite, köttigite, lanarkite, lavendulan, olivenite, mawbyite, parnauite, philipsburgite, pyrrhotite, redgillite, strashimirite, yarrowite and zálesíite. Of these, annabergite, brianyoungite, gersdorffite, lavendulan, parnauite, strashimirite, yarrowite and zálesíite are reported for the first time in the Caldbeck Fells and mawbyite for the first time in the British Isles.

The published mineralogy of the Driggith and Sandbed mines is complicated by the claims of Arthur Kingsbury, many of which are fraudulent. Rare species claimed by Kingsbury, which should be removed from the list of minerals from Driggith and Sandbed include allophane, chalcanthite, conichalcite, chlorargyrite, planchéite, plumbogummite, phosgenite, pseudomalachite, turquoise and wulfenite. In addition, many fine specimens in the Kingsbury collection which are labelled from Driggith or Sandbed mine, including common species such as adamite, brochantite, cerussite, leadhillite, linarite and malachite, are fraudulent, although undoubted specimens (almost always of much poorer quality) are well known at both localities.

INTRODUCTION

The Caldbeck Fells, at the northern edge of the English Lake District in Cumbria, host one of the richest and most diverse assemblages of minerals in the British Isles (Young, 1987; Cooper and Stanley, 1990, 1997). As part of a review of mineralisation in the area, two of the better known localities, the Driggith (sometimes written as Driggeth) and Sandbed (also written as Sandbeds) mines have been investigated. The purpose of the study is two-fold: to update the mineralogy fifteen years after Cooper and Stanley produced their seminal description of the mineralogy of the area and to review some of the specimens claimed from the mines by Arthur Kingsbury, whose descriptions of minerals from the area have subsequently proved unreliable (Ryback *et al.*, 1998; 2001).

Although they are usually described separately, the Driggith and Sandbed lead mines were generally worked as a single mine. The spoil heaps are derived from interconnected levels on the same vein (Shaw, 1970; Adams, 1988); because of their geological and mineralogical similarity they are considered together here.

HISTORY

The Driggith and Sandbed workings were described in detail by W.T. Shaw (1970) who had first hand experience of mining the baryte veins and had explored the lead mines. Further descriptions are provided by Adams (1988) and Cooper and Stanley (1990). This historical summary is based primarily on their accounts.

There are records of mining from the beginning of the eighteenth century. It seems likely that the early workings exploited the highly oxidised ores which crop out in the vein exposures above Driggith mine. These would have been relatively easy to process and smelt. Thomas Hillary was working a level in 1724 and in 1790, Driggith mine was leased to William Roe and Thomas Smyth of Liverpool who had extended the workings to a depth of 25-fathoms. Roe and Smyth appear to have done well, but had abandoned their efforts by 1810 when the mine was taken by Messrs Richardson and Lowrey of Carlisle. With a workforce of around 40, they produced about 200 tons of lead ore annually and also returned a profit. They sold out to Thomas Braddyll of Ulverston who drove the 60-fathom level from the Sandbed end of the vein to make it easier to work the orebody at depth. The cost of this long drivage bankrupted Braddyll in 1834 and the next two groups who took the mine, Barratt and Bennett, between 1834 and 1840 and Dickinson and Company between 1840 and 1849 faired little better. The complex ore, which contained galena, baryte, sphalerite, chalcopyrite and quartz, presented a considerable processing problem with the technology available at the time. George Brocklebank and William Jeffrey, who took the mine in the 1850s installed a new processing plant and this returned the workings to profit for a time. By 1859 a lower level was desperately needed and so in the Caldbeck tradition of driving levels at intervals of 30-fathoms, the 90-fathom level was begun. Repeated surveying errors meant this took eight years to complete, much longer than was originally anticipated. With their funds running short, Brocklebank and Jeffrey sold out in 1865 to the West Cumberland Silver Lead Mining Company, for whom Jeffrey acted as manager. The crash in world lead prices, the relatively low returns of ore and lawsuits from local farmers forced the company into bankruptcy in 1874. This ended the last serious attempt to work the mines for lead. A number of attempts to reopen the mines in the first half of the twentieth century were short lived and met with no success.

Although it is the lead workings that are of primary interest in this account, there are large baryte workings dating from the middle of the twentieth century at Sandbed mine. By the middle of the twentieth century, baryte had become a valuable commodity. A vein was discovered at Sandbed in 1927, but mining did not begin until 1946 at what would become Sandbeds East mine. A crosscut driven from near the site of the old lead mine opened into a rich vein, which was followed east and west along the lode. The eastern drive was productive along the whole of its length until it came to surface in Blea Gill, the western drive proved unproductive. A 100-fathom level was driven from Blea Gill to work ore in the sole of the eastern drive, but it was surprisingly poor. A separate working, the Howthwaite baryte level, was opened up further east, near to Calebrack, but this was even less productive as the vein contained no workable baryte.

Sandbeds West mine worked the western continuation of the Sandbed Baryte Lode. It was initially exploited via a crosscut level driven at about the same height as the 60-fathom lead level. The vein was cut in 1956 and a drivage made west along the vein. Although initially promising, at about 300 feet west of the intersection, its character changed. It was filled with dolomite and quartz, with local masses of water clear baryte and a considerable amount of manganese oxide. Levels were driven into the hillside above at 50, 40, 30 and 20-fathoms. The last two of these intersected a NE-SW trending arsenopyrite-rich quartz vein marked as Low Pike Vein by Adams (1988, p.88). The 20-fathom level was driven to a point where it was only 400 feet from the most easterly of the baryte workings driven from Potts Gill. Below the 60-fathom baryte level, crosscuts were put in at about 70-fathoms (described as 67-fathoms by Shaw, 1970) and from the old 90-fathom lead level. Large vughs were encountered in stopes above the 90-fathom baryte level some lined with water clear baryte up to 2 feet thick.

TOPOGRAPHIC SURVEY

The Driggith and Sandbed mines are large and complex sites, which cover several square kilometres of moorland. A survey was carried out using a hand held GPS to locate major features of interest. The grid references quoted below are accurate to plus or minus one in the last digit and are plotted on the accompanying sketch map (Fig. 1).

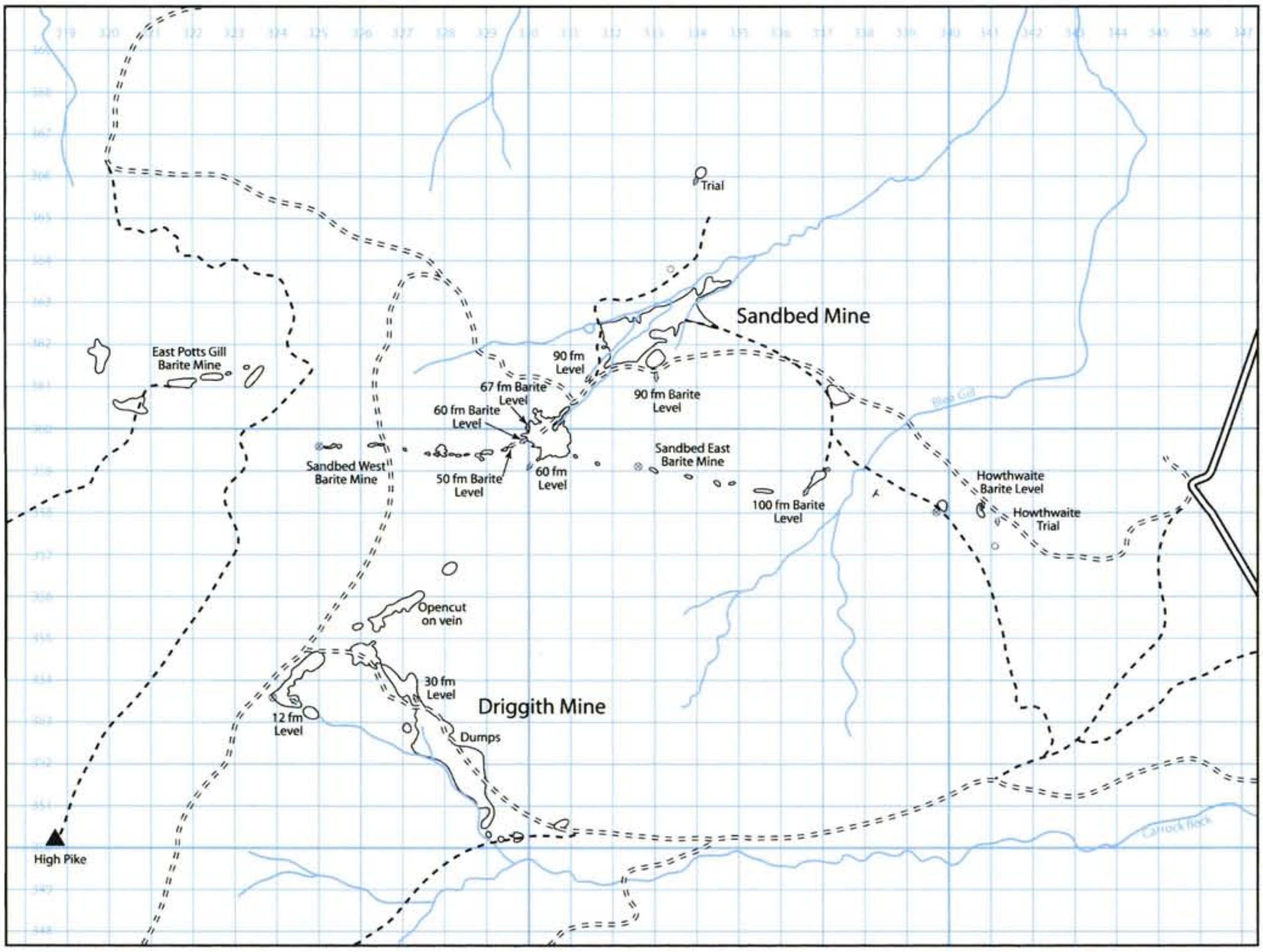


Figure 1. A sketch plan based on a GPS survey of the Driggith and Sandbed mine sites and the surrounding area. All of the major features described in the text are marked.

Driggith mine was worked by opencuts which run northeast-southwest across the flank of High Pike and from two crosscut levels driven into the fellside. The 12-fathom is driven from NY 3244 3534 and the 30-fathom from NY 3273 3535. Two deeper levels, the 60-fathom (NY 3300 3591) and the 90-fathom (NY 3314 3612) constitute the major workings of Sandbed (lead) mine.

There are a number of smaller workings in the immediate area and these are described, beginning in the northeast near Calebrack, to give a complete picture of the localities. About 500 m west of Calebrack on the south side of the track to Sandbed mine, there is an inconspicuous trial driven at about 190° (NY 3411 3577) and 50 m to the south a grassed-over bellpit or shaft with a tiny dump containing quartz-arsenopyrite mineralisation (NY 3411 3572). This is described as the Howthwaite trial here, but it does not appear to have been identified in any other work. A very short distance to the west of the Howthwaite trial, at NY 3407 3581, a larger dump marks the position of the Howthwaite baryte level, which was driven onto the Sandbed baryte vein, but yielded nothing of value (Adams, 1988). The dumps contain a little baryte and vein quartz and an open shaft remains on the hillside above.

A large dump in Blea Gill (NY 336 359), containing baryte and quartz, marks the 100-fathom level of Sandbed West mine (Shaw, 1970). The adit entrance (or possibly two nearby entrances: Adams, 1988, p.88) is at NY 3365 3584. Subsidence craters and shafts, running west across the hillside toward Sandbed mine, mark the position of the vein, which was first worked via a crosscut level (the 90-fathom Sandbed West) driven from NY 3331 3612 just east of the site of Sandbed lead mine. A large spoil heap containing baryte and country rock remains near the adit entrance which is immediately south of the track to the lead mine.

The 90-fathom level at Sandbed mine, which was driven to provide access to the lead vein and also used as an access drivage by the baryte mining operations is marked by a large subsidence crater at NY 3314 3612. A considerable volume of water issues from it. The valley for about 300 m to the northeast is covered by a thin veneer of mineralised spoil, and contains a few elongated finger dumps. Little remains of any of the mine buildings. A tiny trial at NY 3334 3639 exposes a small amount of arsenic mineralisation. Some distance to the north, the dump from a larger trial (NY 3340 3659), which must represent significant underground development, lies largely forgotten. It appears to have intersected a quartz vein containing sparse supergene lead mineralisation although a copper vein is marked by the British Geological Survey (1997).

The large and conspicuous dumps about 150 m southwest of the 90-fathom level at Sandbed mine contain spoil from the lead vein, which was worked from the 60-fathom level (NY 3300 3591) and material from the later baryte mining operations on the Sandbed Baryte Vein (the 50-fathom, 60-fathom and 67-fathom levels of Sandbeds West baryte mine). They cover an area of several hundred square metres and are up to about 10 m deep (Fig. 2). The Sandbed Baryte Vein is marked by a conspicuous series of collapses, which run up the hillside to the west and conceal the remains of the 40-, 30- and 20-fathom levels which were also part of the Sandbeds West baryte mine. The surface remains of the baryte mine end in a shaft at NY 3250 3595.

Figure 2. The large, conspicuous dumps from the 60-fathom level at Sandbed mine seen from the northwest. The grey dump on the left hand side of the picture is from the Sandbed West baryte mine.

The Driggith-Sandbed Lead Vein runs southwest from the 60-fathom level dumps and can be traced at surface as a conspicuous gulley and a series of collapses. At NY 3290 3578, an area rich in arsenate mineralisation is exposed in one such collapse, which probably marks the position of an old shaft. As the vein rises up the flank of High Pike, the workings of Driggith mine are encountered. The main vein is exposed in opencuts above the site of the mine as a conspicuous rib of white quartz.

The vein at Driggith mine was worked from 12-fathom and 30-fathom levels. Extensive spoil heaps stretch for several hundred metres down a gulley to the southeast of the 30-fathom level, which was driven as a crosscut from NY 3273 3535. The foundations and some of the walls of mine buildings and a few items of equipment still remain in the gulley (Fig. 3). There are conspicuous spoil heaps higher up the hill around the entrance to the 12-fathom level (NY 3244 3534). An open shaft at NY 3239 3536 marks the approximate point where this level intersects the vein and is the most southwesterly surface feature of Driggith mine.

Figure 3. Spoil heaps in the gulley below the 30-fathom level at Driggith mine.

METHOD

This account is based partly on a critical review of published references to the mineralogy of Driggith and Sandbed mines, partly on our own analyses of material in public and private collections and partly on field surveys carried out during 2005 and 2006 with the permission of the Lake District National Park Authority (LDNPA).

Two references contain significant original data on the mineralisation at Driggith and Sandbed mines: Hartley (1984) provides a summary list of material supposedly collected in the 1950s, while Cooper and Stanley (1990), in addition to their summary of previous work, report new discoveries prior to the end of the 1980s. Unfortunately many of these records in both of these works are based on specimens from the Arthur Kingsbury collection now held at the Natural History Museum, London. In this study, descriptions based solely on specimens in the Kingsbury collection are automatically considered suspect as a result of the reputation he has acquired for making fraudulent claims (*e.g.* Ryback *et al.*, 1998, 2001). It is worthwhile recording that although many of Kingsbury's false claims were published by Hartley (1984) and there are numerous descriptions of Kingsbury specimens in Cooper and Stanley (1990), all the data were published in good faith and the authors had no knowledge of the fraudulent nature of some of the specimens. Other published data in peer-reviewed journals are considered reliable, but are judged in the context of the identification techniques used by the authors.

The principal public collections examined in this study were those of the Natural History Museum (NHM), the National Museum of Wales (NMW) and the Manchester Museum (MM). Private collections belonging to Richard Bell (RB) (also comprising material from the late Mike Rothwell and John Dickinson), Mike Leppington (ML), Trevor Bridges (TFB), Norman Thomson (NT), George Wilson (JGW), Neil Hubbard (NH), David Middleton (DM), Tim Neall (TN) and Peter Todhunter (PT) were also examined. A significant database, collated by Mike Leppington, provided the basis for the initial species list; further analytical work was carried out wherever possible to confirm the identifications.

A large number of specimens were examined. Initially a detailed visual inspection was made using a stereomicroscope. Where this revealed material that appeared to merit further study, small fragments were detached and analysed by energy dispersive X-ray spectroscopy (EDS) on a scanning electron microscope (SEM). Those specimens that appeared unusual, either because of their crystal morphology or chemical composition, were prepared for X-ray diffractometry (XRD). Tiny fragments were hand-picked with a needle, finely ground, and applied in solvent suspension to a glass slide. The thin uniform film so produced was mounted in an X-ray diffractometer (CuK_α radiation, 40 kV, 20 mA) and the diffraction pattern recorded. Pattern matching software was used in combination with the chemical data to match the XRD pattern to known standards.

In a limited number of cases only a few microscopic crystals were present and it was impossible to separate enough material for analysis by XRD. In some cases, optical and morphological data, in combination with the data produced by EDS, were considered sufficient to give a reliable identification. In others the data were not considered sufficiently reliable and a tentative identification is made.

Certain mineral groups require quantitative chemical analyses in addition to XRD data to identify them to species level. Analyses by wavelength dispersive spectrometry (WDS) were carried out in a limited number of cases to establish precise chemical compositions. Crystallites were hand-picked from the specimens under study, embedded in resin and polished to produce a flat surface. Analyses were made at 20kV, 20nA with a 15 micron beam diameter using a Cameca SX100 electron microprobe. Count times of 10 seconds were used to minimize volatilization or decomposition effects during data collection.

The ore minerals present in the lead-zinc-copper vein are described in detail by Stanley (1979) and Stanley and Vaughan (1981) and readers are referred to these accounts for a full description of the ore minerals present in this assemblage. A few polished sections of material from two of the less well studied vein assemblages were prepared and examined by reflected light microscopy using x8 air, x16 oil and x40 oil immersion lenses. One of the sections was also examined by WDS. The full results of the WDS analyses are not generally included in tabular form, as we intend to publish them in shorter separate articles (*e.g.* Neall *et al.*, 2006).

GEOLOGY

The Driggith-Sandbed lead vein occupies the northeastern portion of a NE-SW trending mineralised fracture system that can be traced between the Thief gills and the edge of the Caldbeck Fells near Wood Hall (British Geological Survey, 1997). Beyond this point in the fracture continues as a normal fault in younger Carboniferous sediments, but it is not known to be mineralised.

At the Driggith and Sandbed mines, the lead vein is hosted by a thick sequence of relatively competent lavas and volcaniclastic rocks of the Eycott Volcanic Group (Ordovician). Between the late Silurian and mid Devonian, these rocks were subject to low-grade regional metamorphism. The Lake District batholith was also emplaced. At the same time as the granite was intruded, the Lake District was raised to form a block, dipping gently toward the south, and bounded at its northern edge by a major fault system. Subsequent marine transgressions in the Dinantian (early Carboniferous) resulted in the deposition of a thick carbonate sequence until only a few islands of older rock remained exposed (notably around Carrock Fell). The limestone present in a broad belt two kilometres to the north of the Driggith and Sandbed mines dates from this period.

The fault system occupied by the Driggith-Sandbed lead vein is a major structural feature. To the north and west of it, the Eycott lavas are cut by numerous broadly northeast-southwest trending faults with relatively small displacements. To the south and east of the vein, the faults are broadly north-south in orientation and are structurally continuous with those that host the high temperature quartz-arsenopyrite-wolframite mineralisation at Carrock Mine (British Geological Survey, 1997).

PRIMARY MINERALISATION

The main stage lead-zinc-copper mineralisation at the Sandbed and Driggith mines typically comprises intergrowths of galena, sphalerite and lesser chalcopyrite in vein quartz with the carbonates calcite and dolomite and white baryte. It is described in detail by Stanley (1979) and the ore mineralogy is summarised by Stanley and Vaughan (1981). The paragenetic sequence is early pyrite and arsenopyrite enclosed in quartz with later baryte, calcite and base-metal sulphides (mainly sphalerite and chalcopyrite) overgrown by galena. Antimony, bournonite and tetrahedrite are present as trace inclusions in the galena.

Baryte, which is very abundant in the lead vein, is largely contemporary with the main lead-zinc-copper mineralisation, although a rather coarser sometimes slightly pink baryte, which is also relatively abundant belongs to a later episode of vein mineralisation, which is also developed in the east-west trending veins that were worked for baryte at Sandbed and Potts Gill mines (*e.g.* Stanley and Vaughan, 1982 p.571). The east-west baryte veins contain quartz, dolomite and manganese oxides and were thought by Ineson and Mitchell (1974) and Stanley and Vaughan (1982) to be late Carboniferous to Permian in age, which is younger than the lead-zinc-copper mineralisation, which is described by the latter authors as early Carboniferous.

Minor cobalt- and nickel-rich mineralisation (containing cobaltian gersdorffite and tetrahedrite) in thin brecciated veins in quartz is present on the dumps at Sandbed mine. It may represent a distinct episode of mineralisation but is more likely to be part of the main lead-zinc-copper mineralisation. The lack of any *in situ* exposures and the small size of the fragments we have been able to study make its relative age and affinities difficult to assess. Since this assemblage has not been described in detail before, four polished sections were examined by reflected light microscopy.

Pyrite is present in small amounts as 20 to 30 µm diameter grains or aggregates up to 160 µm across in quartz. More often, 2 to 30 but up to 90 µm diameter, irregular to rounded grains are enclosed within a 2 to 10 µm wide, pink-lilac to blue-lilac gersdorffite rim that itself is enclosed in chalcopyrite. Trace amounts of 5 to 30 µm diameter marcasite is intergrown with pyrite in quartz or forms cores to euhedral gersdorffite as do very rare, 4 µm diameter, pink nickeliferous pyrite/bravoite aggregates.

Subhedral to euhedral, pentagonal dodecahedral gersdorffite crystals are 2 to 20 µm in size and form loose aggregates, greater than 200 µm across, that are spatially separated from much of the base metal mineralisation. Elsewhere, single gersdorffite crystals up to 30 µm in diameter occur in quartz, chalcopyrite or very locally in tetrahedrite, itself enclosed by chalcopyrite. Many gersdorffite crystals show colour zoning from pink-white to blue-white.

Tetrahedrite is present in small amounts. Much of it is intergrown with chalcopyrite as inclusion-free masses up to 200 µm across surrounded by chalcopyrite. Trace amounts are present as 1 to 5µm diameter grains enclosed in gersdorffite. Very minor amounts of an unidentified sulphosalt up to 5 µm in size are intergrown with tetrahedrite in chalcopyrite. Trace amounts of galena altering to 50 x 2 µm size acicular cerussite and 60 µm diameter sphalerite are present in quartz. Elsewhere galena as 10 to 30 µm diameter grains is present as single inclusions or mixed galena-tetrahedrite or galena-sphalerite intergrowths in chalcopyrite.

Chalcopyrite is the major base metal sulphide in the cobalt- and nickel-rich assemblage and forms discrete masses up to 200 µm across enclosing gersdorffite or intergrown with tetrahedrite. Chalcopyrite occurs as rims up to 60 µm wide surrounding tetrahedrite. Locally chalcopyrite alters along its cleavage to 1 to 5 µm wide bornite or covellite, but mainly chalcopyrite alters to successive, 5 to 20 µm wide, digenite, yarrowite and limonite rims. Cuprite with deep red internal reflections is present as 5 to 10 µm diameter discrete crystals or thin 100 µm long veinlets cross-cutting gersdorffite aggregates. Discrete masses of covellite and pale blue djurleite are up to 50 µm, digenite up to 100 µm, and yarrowite up to 200 µm in diameter. Limonite up to 40 µm across fills void spaces.

Rich localised concentrations of supergene lead, iron and arsenate minerals crop out between Driggith and Sandbed mine, at Howthwaite trial and in a small exposure below the 90-fathom level at Sandbed mine. An arsenopyrite-rich vein was cut by the Sandbed West Baryte Vein according to Shaw (1970). The major arsenic-bearing mineralisation in the northern Caldbeck Fells pre-dates the lead-zinc-copper vein mineralisation (Stanley and Vaughan, 1982). Our observations corroborate this. In the opencut between Driggith and Sandbed mines, arsenopyrite and iron sulphides are abundant as sub-millimetre size idiomorphic crystals in volcaniclastic quartz rock, which is cut by later milky white quartz veins. The milky quartz veins contain arsenopyrite, which may have been remobilised from the surrounding arsenopyrite-rich wall-rocks, as well as lead-zinc-copper mineralisation.

Two polished sections were examined. Fine-grained, pale-coloured TiO_2 minerals up to 10 µm in diameter are common in the wallrocks. Arsenopyrite is also common and forms discrete, euhedral, rhombic or lath-shaped crystals 2 to 40 µm in diameter, that locally form aggregates; larger arsenopyrite crystals, up to millimetres in size, are shattered and are replaced by scorodite. Arsenopyrite encloses small TiO_2 minerals, pyrrhotite and galena grains, all 2 to 20 µm in diameter.

Pyrrhotite is present in the arsenopyrite or forms discrete very rare crystals in quartz up to 120 x 40µm in size. Lath-shaped intergrowths of marcasite and pyrite are more common and form sheaf-like masses 20 x 1µm but up to millimetres in length. These are pseudomorphs after pyrrhotite and suggest that pyrrhotite was probably an important early phase. Pyrite occurs as 5 to 100 µm diameter pentagonal dodecahedral crystal associated with the base metal sulphides. Sphalerite with deep orange internal reflections and galena enclosing rare, 20 µm diameter bravoite are intergrown with each other and are up to a few millimetres in diameter. Chalcopyrite is uncommon but is present as 20 to 80 µm masses surrounding arsenopyrite; it encloses small 1 to 5 µm diameter galena grains. This mineralisation is similar to the chalcopyrite-pyrite-arsenopyrite type mineralisation described by Stanley and Vaughan (1982) and seems likely to be part of it.

MINERALS

The suite of minerals present at Driggith and Sandbed mines is described below. Where an identification is based on modern analytical techniques or sound literature references, the sub-title is capitalised; if there is some uncertainty associated with an identification or further investigation is required the sub-title is typed in lower case; if an identification is likely to be based on a fraudulent specimen the title is italicised. In some cases (*e.g.* adamite) some of the specimens are fraudulent, while others are genuine. In these cases the genuine material takes priority; it is usually described first.

ADAMITE, $Zn_2(AsO_4)OH$

In the 1980s, adamite was identified by XRD at both Driggith and Sandbed mines as drusy crusts of pale mint to apple green crystals in fractures in quartz veinstone. Our analyses have shown that most of this material is not strictly adamite. Typical green specimens analysed recently by WDS contain more copper than zinc. Although they produce adamite-like XRD patterns they cannot be labelled as such where more than 50 atom% copper substitutes for zinc. The most copper-rich composition we have identified at Sandbed mine is $(Cu_{1.5},Zn_{0.5})(AsO_4)OH$; furthermore, EDS analyses suggest that most of the green 'adamite' from both mines contains more copper than zinc. Nonetheless, some of the pale green, colourless and pale blue crystalline crusts have more zinc than copper and can be labelled adamite (Fig. 4).

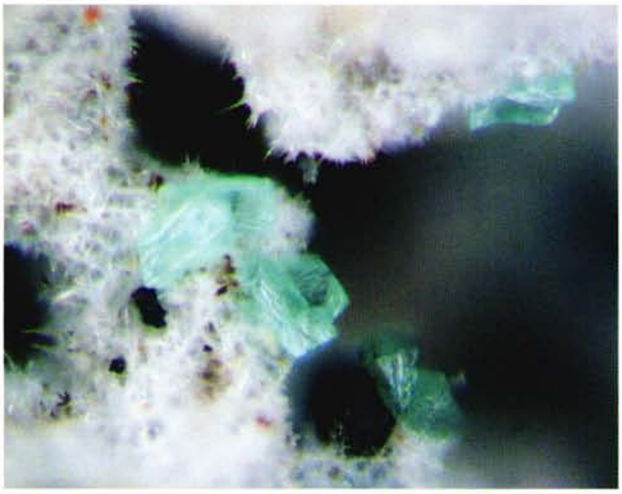


Figure 4. Pale blue blocky adamite crystals 0.15 mm across with white calcium-rich mimetite from the 60-fathom level dumps at Sandbed mine.

Adamite is usually found on its own, but may be associated with bayldonite, mimetite or hemimorphite. The crystals rarely exceed 1 mm in length, they sometimes develop blocky prismatic habits with low angle terminations (Fig. 5), but are more usually grown together in drusy crusts. Unusual pale green 'adamite' crystals from Driggith mine are figured by Cooper and Stanley (1990, p.76).

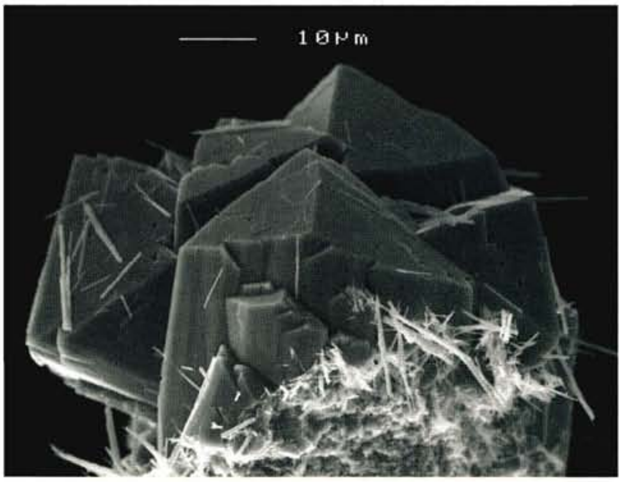


Figure 5. Blocky adamite crystals up to about 50 µm long from the 60-fathom level dumps at Sandbed mine.

Pale blue blocky sodium-rich adamite crystals from a tiny dump near the Howthwaite trial (NY 3411 3577) were collected in the early 1990s. The dump has been completely removed by erosion. A single specimen preserved in Manchester Museum under accession number N12162 was analysed by WDS, a typical formula, based on one trivalent anion per formula unit is: $Na_{0.2}Zn_{2.0}[(AsO_4)_{0.9}(PO_4)_{0.1}]OH_{1.1}$.

The claimed occurrence of adamite at Sandbed mine represented the first British report of the mineral when L. J. Spencer noted it on the basis of a specimen 'collected' in 1951 by Arthur Kingsbury (Spencer, 1958; Cooper and Stanley, 1990). This specimen and others supposedly collected by Kingsbury at Driggith mine were discredited by Ryback *et al.* (2001, p.52), who proved beyond reasonable doubt that they came from Lavrion in Greece.

Agardite, $(REE,Ca)Cu_6(AsO_4)_3(OH)_6.3H_2O$

The 'agardite group' includes bismuth lead, calcium and rare-earth bearing copper arsenates all of which have similar XRD patterns. A survey of about a dozen specimens from Driggith and Sandbed mine revealed crystals containing calcium, lead and rare earth elements (REE). Most of the specimens contained both calcium and rare earth elements and are intermediate between agardite and zálesíite. None could be unequivocally identified as agardite. The minute size of the fibres, with cross-sectional areas of a few square micrometres made preparation of samples for analysis by WDS impossible. Agardite almost certainly does occur at both mines but further analytical work is needed to establish it beyond reasonable doubt.

Allophane, $Al_2SiO_5.H_2O$

Most of the possible allophane specimens examined by EDS in this study contained no aluminium. A few powdery aluminium silicates were found, but they did not have allophane's characteristic hyaline lustre (Anthony *et al.*, 1995).

Allophane was noted from the 12-fathom level at Driggith mine by Hartley (1984), almost certainly on the basis of material in the Kingsbury collection. Since allophane is amorphous (Anthony *et al.*, 1995) and the principal identification technique used by Hartley was XRD, the claim must be regarded with scepticism. An extensive search of the Kingsbury collection failed to produce any specimens of allophane from Driggith or Sandbed mines. Allophane is best removed from the list of minerals from Driggith mine.

ANGLESITE, $PbSO_4$

Anglesite is reasonably common at both Driggith and Sandbed mines as small colourless euhedral blocky to prismatic crystals associated with partly oxidised galena in cavities with other supergene lead minerals including bindheimite, cerussite, caledonite, leadhillite and linarite. Cavities in decomposed galena lined with small, brilliant anglesite crystals were collected by W. F. Davidson during exploratory work on the Driggith-Sandbed opencut in the late 1940s (Davidson and

Thomson, 1951; Norman Thomson, *personal communication*).

Steep bipyramidal anglesite crystals to 20 mm were noted by Cooper and Stanley (1990) from the Driggith-Sandbed opencut on the basis of a specimen donated to the NHM by Arthur Kingsbury. This specimen is likely BM 1957,487, a steep bipyramid about 16mm in length nestled in a cavity in galena. Along with three other anglesite specimens in Kingsbury's personal collection it can be reassembled to form a single, fine piece with a slight museum patina. Recent research has shown that fine mineral specimens broken into smaller fragments are a common feature of many Kingsbury frauds and because the anglesite specimen is of a quality better than has otherwise been recorded from the locality it must be treated with extreme caution.

ANKERITE, $Ca(Fe,Mg,Mn)(CO_3)_2$

Ankerite was identified by XRD and EDS as typical brown curved crystals in cavities in quartz veinstone. It occurs at both Driggith and Sandbed mines.

ANNABERGITE, $Ni_3(AsO_4)_2.8H_2O$

Annabergite is present on the 60-fathom level dumps at Sandbed mine as white, pale pink, blue and green crusts, which are composed of minute bladed crystals. It is almost certainly post-mining in origin. There are extensive chemical substitutions in the material we have examined: cobalt, zinc, iron and copper substitute in varying amounts for nickel. Copper with zinc and cobalt produces an unusual turquoise coloured annabergite while cobalt on its own or with zinc produces white to pale pink crystals. Annabergite forms a solid solution with the isomorphous cobalt arsenate erythrite, but the colour transition from pink to green does not occur at the halfway point of the chemical substitution. Many of the pale pink minerals from Sandbed mine that are labelled erythrite in collections are annabergite or köttigite.

Annabergite typically occurs in brecciated quartz-carbonate veinstone with tennantite, chalcopyrite and gersdorffite. It was first identified by XRD at the British Geological Survey (Mike Leppington, *personal communication*) and was confirmed by XRD and WDS in this study.

ANTIMONY, Sb

Minute, micrometre-size grains of antimony were identified with bournonite as inclusions in galena from Driggith mine by Stanley and Vaughan (1981).

Antlerite, $Cu_3SO_4(OH)_4$

Antlerite was reported with bayldonite on a specimen (NMW:3.41G.M.8484) collected by R.J. King at Sandbed mine (Young, 1987; Cooper and Stanley, 1990). It has subsequently been shown to be malachite (X-ray reference number NMW:X-443). Geochemical arguments can be used to show that antlerite is unlikely to be present on the dumps at Sandbed mine (*e.g.* Bridges *et al.*, 2005). It should be deleted from the list of minerals from the locality.

ARAGONITE, $CaCO_3$

Aragonite was identified as radiating sprays of acicular white crystals up to about a millimetre across on the surfaces of fragments of dump material affected by post-mining oxidation. It also occurs as pale blue-green sheaves with calcium-rich pyromorphite. Aragonite is present in post-mining assemblages where dolomite- or ankerite-bearing vein material has oxidised.

ARSENDESCLOIZITE, $PbZn(AsO_4)(OH)$

The rare lead zinc arsenate arsendescloizite was identified by XRD and WDS as pale green crusts of lenticular crystals up to about 0.05 mm long covering areas to several square centimetres on a few specimens from the 60-fathom lead level dumps at Sandbed mine (Neall *et al.*, 2006). Quantitative chemical analyses showed substitution of calcium for lead and of copper for zinc. The average chemical formula can be written $(Pb_{0.66},Ca_{0.22})(Zn_{0.71},Cu_{0.23})[(AsO_4)_{0.95},(PO_4)_{0.04},(VO_4)_{0.01})](OH)$, based on one trivalent cation per formula unit. Arsendescloizite is associated with calcium-rich pyromorphite and minor adamite in hairline fractures in quartz-rich wall rock (Fig. 6).

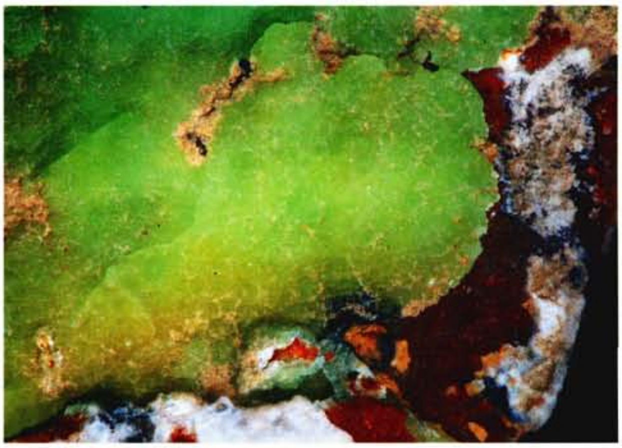


Figure 6. A pale green arsendescloizite crust a few millimetres across from the 60-fathom level dumps at Sandbed mine. Part of a specimen from the Tim Neall collection which was donated to the Oxford University Museum of Natural History.

ARSENIOSIDERITE, $Ca_2Fe_3(AsO_4)_3O_2.3H_2O$

Arseniosiderite occurs in the opencut above Sandbed mine as minute scaly brown crystal groups and as dark brown masses with a well-developed cleavage. Minute feathery masses of a calcium lead arsenate associated with scorodite and barium-pharmacosiderite from Howthwaite trial are also probably arseniosiderite (Fig. 7).

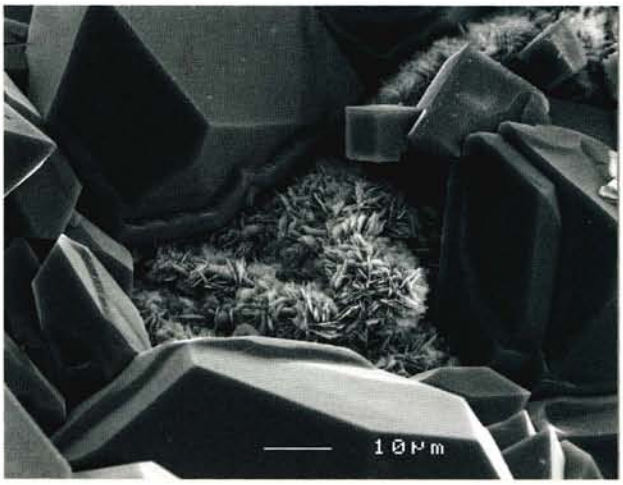


Figure 7. Minute feathery arseniosiderite masses from the Howthwaite trial associated with barium-pharmacosiderite and scorodite.

ARSENOPYRITE, FeAsS

Arsenopyrite is locally abundant. It was described by Stanley and Vaughan (1981) as corroded inclusions in chalcopyrite and galena at Driggith mine. In the opencut between Driggith and Sandbed mines, arsenopyrite is abundant as sub-millimetre size idiomorphic crystals in volcaniclastic quartz rock which is cut by later milky white quartz veins. The milky quartz veins also contain arsenopyrite, rarely as well-formed crystals up to 5 mm on edge, with galena and sphalerite. Scorodite pseudomorphs and epimorphs with the characteristic morphology of arsenopyrite are present in some of the highly oxidised arsenate-rich vein material in this area.

Brecciated arsenopyrite, shot through with later clear to milky quartz is present at Howthwaite trial. Where this has oxidised it produces a cellular quartz box-work containing powdery supergene arsenates.

Asbolane, $(Ni,Co)_xMn(O,OH)_4.nH_2O$

Minute black mammiliary masses associated with zálesíite and erythrite from the 60-fathom level dump at Sandbed mine were examined by EDS, which showed that they contained manganese, cobalt and nickel. They are likely to be asbolane. The tiny amounts of material present did not allow analysis by XRD.

AURICHALCITE, $(Zn,Cu)_5(CO_3)_2(OH)_6$

Aurichalcite was identified by XRD and EDS in this study as aggregates and frothy masses of pale blue to blue-green lath-like crystals up to a few millimetres in length (Figs 8 and 9). Small specimens collected during recent fieldwork at Driggith mine display radiating sprays of pale blue feathery lath-like crystals up to 2 mm in length with hemimorphite.

Aurichalcite was noted without description from both Driggith and Sandbed mines by Hartley (1984). Cooper and Stanley (1990) describe a specimen with brochantite, linarite and malachite in the NHM collection labelled Driggith mine, which likely corresponds to linarite specimen BM 1956,431 which will be covered later under linarite. In Kingsbury's personal collection there are three groups of aurichalcite specimens all of which are very different. The first group were collected in 1949 from the Driggith 12-fm level and registered under Kingsbury's number 1837. It consists of two small specimens of iron stained quartz coated by velvety patches up to 7 mm across of sub-millimetre pale sky-blue crystals. The matrix of the specimens is typical of localities in the Caldbeck Fells and they are comparable to others from Driggith mine and are very likely to be genuine. It has been noted previously (Alan Hart, *personal communication*) that specimens such as these, collected by Kingsbury before 1951 are almost always legitimate.

Figure 8. Well crystallised pale blue aurichalcite crystals up to about 2 mm across with colourless hemimorphite from Sandbed mine. Mike Leppington collection.

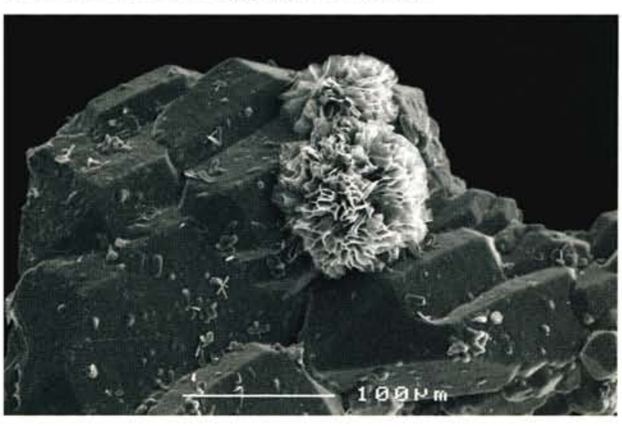


Figure 9. Masses of feathery aurichalcite up to about 70 µm across on mimetite from Sandbed mine.

The second group comprises a tube of fragments and a box containing a specimen about 30 mm across and some smaller fragmentary pieces all labelled "*Sandbeds 1951*". Radiating feathery blades of pale sky-blue aurichalcite to 5 mm are present associated with white botryoidal smithsonite to 1 mm on a dark brown earthy matrix. The specimens are light and porous and likely came from an extensive zone of supergene alteration. They are far richer than anything else from the locality and the matrix and form are atypical of the Caldbeck Fells. However they are a very good match with specimens from the Kelly Mine, New Mexico, USA in the NHM collections (BM 1949, 268). They are likely to be fraudulent.

The third group of specimens is labelled "*Driggith 30 fathom dumps*". The specimens consist of a mass of pale blue-green finely acicular porous-looking brochantite overgrown in places by pale sky-blue feathery aurichalcite crystals to 1 mm that form in regions up to 10 mm across. The aurichalcite is associated with white and straw-brown globular to botryoidal smithsonite. The association of aurichalcite with well-crystallised brochantite and smithsonite is unlike anything otherwise reported from the Caldbeck Fells. The specimens are labelled as 1952, are exceptionally rich, remarkably undamaged, and do not appear to have been collected from a mine dump. They have a passing similarity to material from the Grandview Mine, Arizona, USA and are almost certainly fraudulent.

AZURITE, $Cu_3(CO_3)_2(OH)_2$

Azurite was listed from Driggith mine by Thimmaiah (1956) and Stanley and Vaughan (1981).

It has been identified using wet chemistry as small groups of rounded crystals on limonitic quartz-baryte matrix on a specimen from the 60-fathom level dumps at Sandbed mine (Peter Todhunter, *personal communication*).

Azurite was noted from the top level dumps at Sandbed mine by Hartley (1984), probably on the basis of a Kingsbury specimen. In common with a number of other Kingsbury azurites from the Caldbeck Fells the specimen can no longer be found.

BARYTE, $BaSO_4$

Baryte is abundant in the northeast-southwest trending lead vein deposits and was worked in east-west trending veins at Sandbed mine. Much of the vein quartz at Driggith and Sandbed mines contains planar voids which are almost certainly contained baryte, suggesting extensive dissolution and remobilisation. Quartz is commonly intergrown with white laminar baryte and vughs in the quartz veinstone are commonly filled by a later generation of coarse white to very pale pink or brown baryte. Well crystallised specimens of primary baryte are rare. A specimen in the Mike Leppington collection shows a white cockscomb baryte aggregates about 30 mm across on drusy quartz.

Thin transparent baryte blades have been identified by EDS in goethite encrusted quartz or on malachite on specimens collected from both Sandbed and Driggith mines. Their occurrence as well formed crystals in cavities in highly oxidised vein material suggests that they are supergene. White rhombic crystals of lead-rich baryte up to 1.5 mm on edge which occur on cerussite at Sandbed mine are also likely to be supergene. Analyses by WDS show that lead substitutes for barium at up to about 5 atom% in this material.

Shaw (1970) describes high grade water clear spar (baryte) with dolomite and quartz at Sandbed West mine. Large vughs between the 70- and 90-fathom levels at Sandbed West mine were lined with "beautiful crystal clear barytes up to two feet thick". Nothing appears to have been preserved from this find.

BARIUM-PHARMACOSIDERITE, $Ba_{0.5}Fe_4(AsO_4)_3(OH)_4.{\sim}6H_2O$

Barium-pharmacosiderite was reported from an isolated exposure in the opencut above Sandbed mine by Young *et al.* (1992). A number of pharmacosiderite group minerals from the arsenic-rich area between Driggith and Sandbed mines and at Howthwaite trial were examined by XRD and EDS in this study. Most proved to be barium-pharmacosiderite. Drusy crusts composed of minute pale green to yellow-brown cubic crystals of barium-pharmacosiderite are common in the arsenate gossans (Fig. 10).

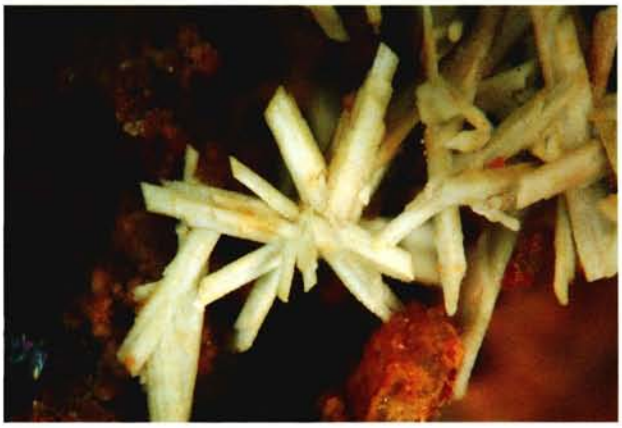
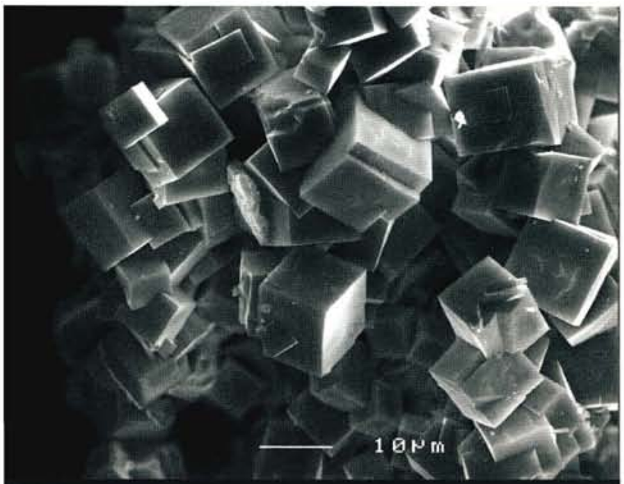


Figure 10. Pale green pseudomorphs up to 2 mm in length of barium-pharmacosiderite after an unknown iron arsenate mineral, possibly parasymplesite, from the arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

Barium pharmacosiderite is commonly intergrown with scorodite and associated with beudantite-segnitite and occasionally carminite and mimetite. Pale green to white or brown pseudomorphs and epimorphs of barium-pharmacosiderite and scorodite after a monoclinic iron arsenate, possibly parasymplesite, are present on a few specimens (Figs. 10 and 12).



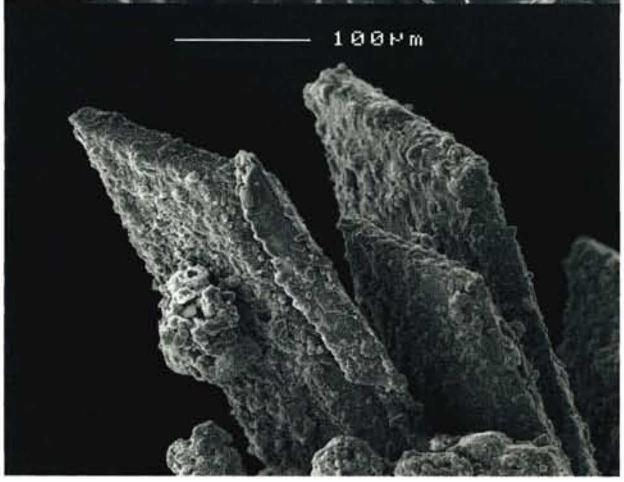


Figure 11 (upper). Typical cubic crystals of barium-pharmacosiderite from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

Figure 12 (lower). Typical monoclinic barium-pharmacosiderite pseudomorphs 0.2 mm long probably after the iron arsenate mineral parasymplesite from the arsenate-rich gossan in the opencut between Driggith and Sandbed mines.

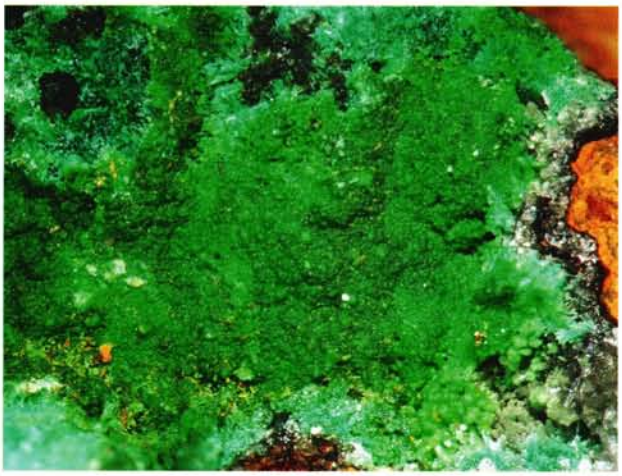


Figure 13. A typical dark green resinous bayldonite crust from the 60-fathom level dumps at Sandbed Mine, the field of view is 7 mm across. Mike Leppington collection.

BAYLDONITE, $PbCu_3(AsO_4)_2(OH)_2$

Bayldonite is widespread and common. Arthur Kingsbury and Heinrich Neumann found it in 1949 on the dumps of the Sandbed and Driggith mines. The Kingsbury specimens at the Natural History Museum all appear legitimate and the discovery was corroborated by Davidson and Thomson (1951). Bayldonite typically occurs as dark green resinous encrustations in thin fractures and cavities in vein quartz with malachite, mimetite (which it commonly encrusts and replaces) and philipsburgite. Distinct crystals are rare.

BEAVERITE, $Pb(Fe,Cu)_3(SO_4)_2(OH,H_2O)_6$

An examination of a number of specimens from the dumps of both Driggith and Sandbed mines, coated in yellow-brown drusy crusts or yellow powdery encrustations, produced one XRD pattern and several EDS analyses that are consistent with beaverite.

Powdery yellow aggregates of beaverite, coating cerussite and altered galena, were claimed from the Driggith-Sandbed opencut by Kingsbury and Hartley (1957). The rich bright yellow crusts associated with cerussite, galena and scorodite that we have examined from this area have all proved to be the arsenate-rich mineral segnitite or beudantite-segnitite intermediates. It is difficult to be absolutely certain about the provenance the Kingsbury specimens of beaverite and beudantite from the Driggith-Sandbed opencut since they came from outcrop workings that are no longer extant (Norman Thomson, *personal communication*). The matrix and association with galena and cerussite are reasonable for the area and the specimens are not unusually rich. They may be genuine, but Kingsbury's proven reputation for mis-labelling even unremarkable specimens gives cause for concern.

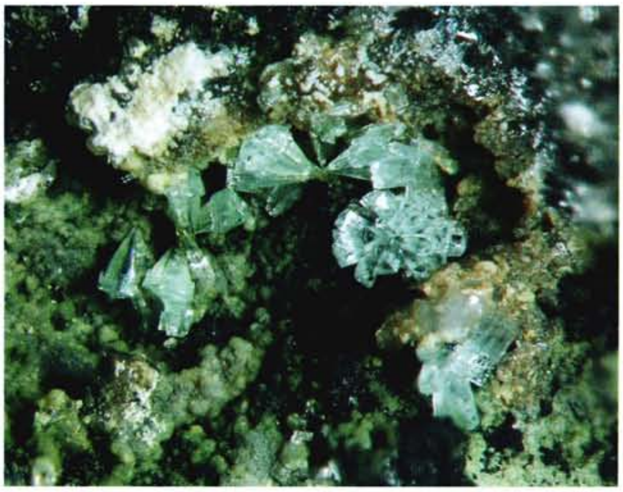


Figure 14. Ice blue inverted pyramidal bechererite crystals with conspicuous pedion faces, up to about 0.3 mm across from the 30-fathom level dumps of Driggith Mine. Richard Bell collection.

BECHERERITE, $Zn_7Cu(OH)_{13}[SiO(OH)_3SO_4]$

The rare zinc copper silicate sulphate bechererite was identified on specimens collected in1996 from the 30-fathom level dumps at Driggith mine (Rust *et al.*, 2003). It occurs in cavities in oxidised galena as characteristic inverted pale blue trigonal pyramids up to 0.3 mm in length terminated by conspicuous pedion faces. Similar specimens were collected more recently on the 12-fathom level dumps (Mike Leppington, *personal communication*).

BEUDANTITE, $PbFe_3[(As,S)O_4]_2(OH,H_2O)_6$

Beudantite was reported by Kingsbury and Hartley (1957) as yellow-brown to brown powdery aggregates from the outcrop of the main vein between Sandbed and Driggith mines. It was recorded from the same area above Sandbed mine by Young *et al.* (1992). We have identified beudantite by XRD and WDS on specimens collected from the opencut above Sandbed mine, where it occurs as yellow-brown drusy encrustations on prismatic mimetite with scorodite and barium-pharmacosiderite. A beudantite-segnitite intermediate occurs as yellow-brown glistening masses in cavities in cellular quartz at Howthwaite trial (Fig. 15). It appears to have formed by the oxidation of primary arsenopyrite. Beudantite occurs sparsely as blocky yellow-brown to brown crystals on the main dumps of Sandbed lead mine and is also found in drusy crusts of brown sparkling crystals at Driggith mine.

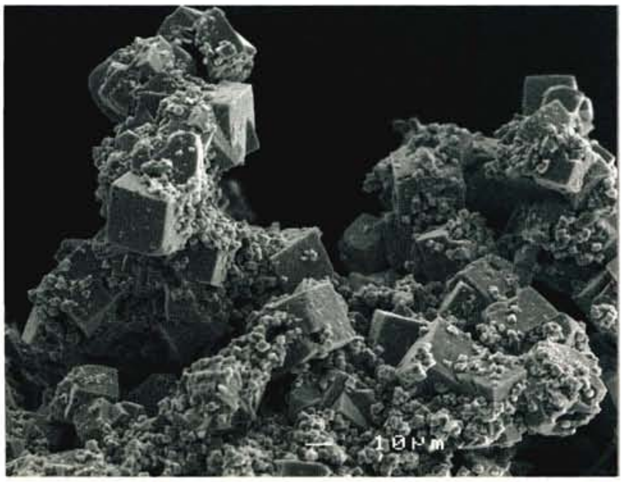


Figure 15. Blocky pseudo-cubic beudantite crystals up to about 20 µm across from the Howthwaite trial.

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Bindheimite was identified by EDS as yellow powdery crusts at both Driggith and Sandbed mines. It is reasonably common in cavities in quartz veinstone containing partly oxidised galena and cerussite.

Bindheimite was described from the 30-fathom level dumps at Driggith mine in cavities in vein quartz with malachite (by J. Hartley, *personal communication*, in Cooper and Stanley, 1990) probably on the basis of a Kingsbury specimen. Specimen K53/71 matches Hartley's description. It is a piece of quartz veinstone 10 cm across richly invested with malachite and sporadically coated in pale yellow bindheimite. The malachite is relatively rich for the area, but the quartz matrix is typical of the Caldbeck Fells. Given Kingsbury's penchant for falsification it is not possible to be confident of its provenance, though it seems possible that it is from the Caldbeck Fells.

BORNITE, Cu_5FeS_4

Bornite was recorded replacing chalcopyrite at Driggith mine by Thimmaiah (1956) and was also noted by Eastwood (1921) at "Driggith-Sandbeds". It was identified in this study as thin alteration rims surrounding chalcopyrite from Sandbed mine.

BRIANYOUNGITE, $Zn_3(CO_3,SO_4)(OH)_4$

White crusts composed of minute pearly lath-like crystals in slightly oxidised quartz-sphalerite veinstone were identified as brianyoungite by XRD on specimens from both Driggith and Sandbed mines. Two specimens are preserved in the Manchester Museum collections (N14182 and 14183) Individual crystals reach about 0.5 mm in length (Fig. 16).

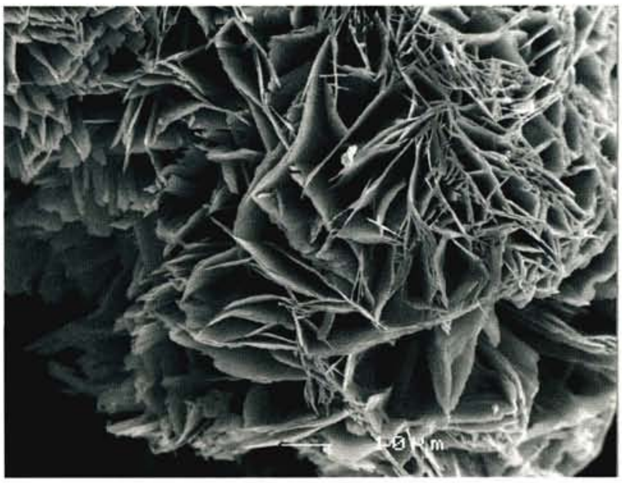


Figure 16. Curved lath-like crystals of brianyoungite up to c. 0.1 mm from the 60-fathom level dumps of Sandbed mine.

BROCHANTITE, $Cu_4(SO)_4(OH)_6$

Powdery masses of brochantite were described from Driggith mine by Davidson and Thomson (1951). In this study, brochantite has been identified by XRD and EDS at both Driggith and Sandbed mines as a component of the blue-green crusts produced by the post-mining oxidation of broken fragments of ore. It is commonly associated with linarite and langite. Rarely, small bladed to prismatic brochantite crystals occur in cavities in vein quartz with linarite and cerussite. Brochantite was recorded in panned concentrates from How Beck, downstream of Sandbed mine, by Wadge *et al.* (1977).

A considerable number of chalcopyrite specimens with greenish coatings of brochantite are present in the Kingsbury collection at the NHM. Most of Kingsbury's brochantite is genuine, but two specimens donated to the NHM prior to his death are almost certainly fraudulent. The first specimen, BM 1958,139, collected by Kingsbury in 1951 from Driggith is 50 mm across and encrusted with acicular sprays of velvety brochantite. Two tiny cavities within the brochantite contain a royal blue finely acicular mineral, probably cyanotrichite. The habit of this brochantite is different to any found in the Caldbeck Fells, the matrix is atypical, the specimen is remarkably rich and the occurrence of cyanotrichite is unique. It is almost identical to the fraudulent specimen described under aurichalcite. Interestingly, in Kingsbury's XRD notebook, the aurichalcite and brochantite specimens are sequentially numbered, the aurichalcite is "K53/36" and the brochantite is "K53/37" but the claimed collection dates are different, one is August 1952 the other August 1951. The second specimen, BM 1961,219 contains numerous blocky dark green prismatic brochantite crystals to 3 mm upon microcrystalline linarite in a centimetre-sized cavity in an impure, baked quartz matrix. The matrix is atypical of the Caldbeck Fells, the specimen has an old museum patina and the crystals are far larger than anything otherwise reported at Driggith mine. The specimen is a good match for material from Llaillay, Valparaiso, Chile in the NHM collection (BM 82228) and is almost certainly fraudulent.

BOURNONITE, $PbCuSbS_3$

Bournonite was identified as microscopic intergrowths with other sulphides at Driggith mine by Stanley and Vaughan (1981).

CALCITE, $CaCO_3$

Calcite forms part of the carbonate gangue at both lead mines and is also present in the east-west baryte veins. It occurs rarely as minute corroded crystals in cavities in vein quartz.

Figure 17. A striated blue caledonite crystal 0.8 mm tall in quartz from the 30-fathom level dumps of Driggith mine. Richard Bell collection.

CALEDONITE, $Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$

Caledonite is uncommon but fairly widespread on the dumps at Driggith mine, it is rare at Sandbed mine, though it was noted by Davidson and Thomson (1951) as tiny crystals. Well crystallised specimens have been found in recent years on the 30-fathom level dumps at Driggith mine, where caledonite occurs as deep blue striated prismatic crystals up to 3 mm in length with leadhillite and linarite (Figs 17 and 18). Smaller prismatic crystals of an unusual green colour have been found in the same area (Fig. 19). Elongated prismatic to acicular crystals are not uncommon on the 12-fathom level dumps, they are often found with linarite in the oxidation rims surrounding galena.

Specimens in the Kingsbury collection dated 1949 and 1950 from Sandbed mine contain prismatic blocky caledonite crystals 2 to 3 mm across on iron stained quartz with leadhillite, linarite, bindheimite and anglesite (see Cooper and Stanley, 1990). These are relatively large, but the early collection date and the characteristic matrix suggest they are probably genuine.

Figure 18. A blue caledonite crystal 1.1 mm tall in quartz from the 30-fathom level dumps of Driggith mine.

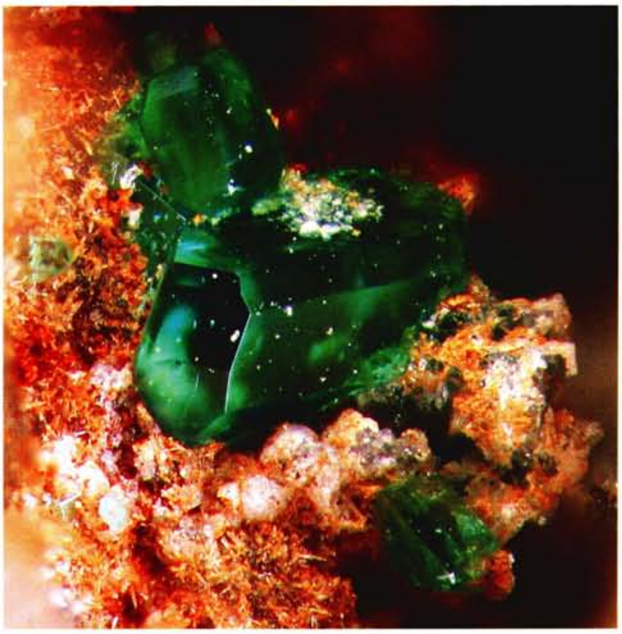
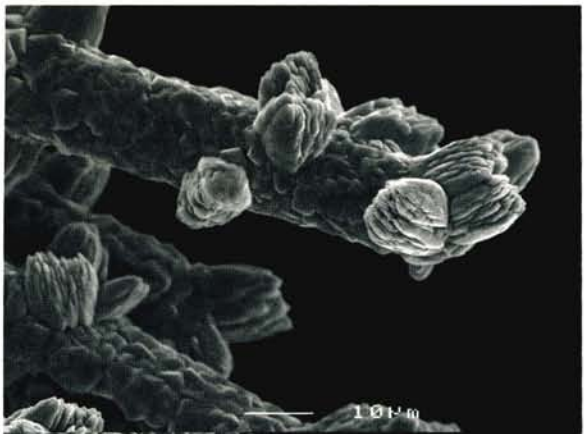


Figure 19. An unusual green caledonite crystal 0.6 mm in length from the 30-fathom level dumps of Driggith mine.

CARMINITE, $PbFe_2(AsO_4)_2(OH)_2$

Carminite was reported by Kingsbury and Hartley (1960) from the outcrop of the main vein at Driggith mine and by Cooper and Stanley (1990) (in a *personal communication* from George Wilson) from an exposure near Sandbed mine. These both probably refer to lead- and arsenic-rich outcrops above the 60-fathom level on the vein between the Driggith and Sandbed mine sites. Carminite was identified by XRD in this study as drusy crusts of minute red crystals associated with scorodite and barium-pharmacosiderite on material collected by George Wilson (Manchester Museum specimen, N14636). It occurs as rich crystalline crusts overgrowing mimetite and associated with segnitite and mawbyite in the same area. Carminite commonly overgrows segnitite, which is replacing mimetite (Fig. 20). Small red masses and patches in arsenate-rich gossan from the Howthwaite trial have also been identified as carminite (Fig. 21).



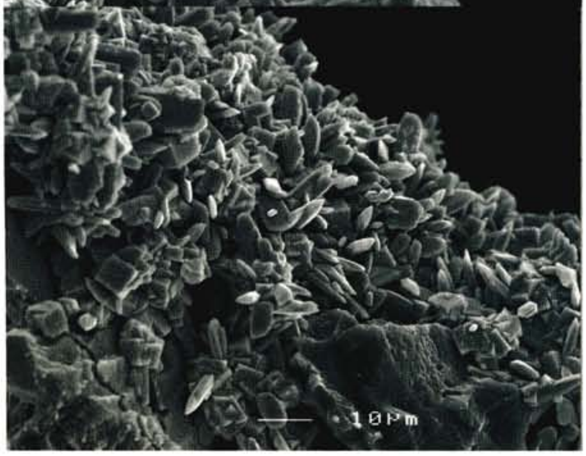


Figure 20 (upper). Tubular epimorphs of segnitite after mimetite up to about 0.1 mm long overgrown by carminite from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

Figure 21 (lower). A drusy crystalline carminite crust with crystals up to about 10 µm long from the Howthwaite trial.

One carminite specimen, which is broken into four pieces, is present in the Kingsbury collection at the NHM. Thin orange-red carminite crusts to 3 mm are scattered in granular gossanous quartz matrix, associated with mimetite and cerussite patches each to around 3 mm. It is difficult to assess the legitimacy of this specimen, the matrix is not wholly atypical of the Caldbeck Fells and it may well be genuine even though it is split into pieces and was collected in 1951.

CERUSSITE, $PbCO_3$

Cerussite was reported at Driggith mine (mis-spelled Driggath) by Greg and Lettsom (1858). It is common as acicular to prismatic or tabular colourless to white crystals, up to about 10 mm in length, often showing characteristic 60° twinning (Fig. 22). It occurs as microcrystalline crusts and masses in quartz veinstone surrounding partially oxidised galena. Cerussite is rather less abundant and typically occurs in smaller crystals on the dumps at Sandbed mine (Fig. 23). In the arsenate gossans between the main mine sites, cerussite occurs as colourless equant pyramidal crystals up to several millimetres long in cavities in arsenopyrite.

Figure 22 (upper). A 4 mm cerussite twin with minor blue linarite from the 12-fathom level dumps of Driggith mine.

Figure 23 (lower). Platy twinned cerussite crystals to 1.75 mm long from the 60-fathom level dumps of Sandbed mine. Mike Leppington collection.

An unusual specimen studded with star-shaped cerussite twins on malachite, which Arthur Kingsbury claimed to have collected at Driggith mine, is described and illustrated by Ryback *et al.* (2001, p.63), who make a very convincing case it came from Zellerfield, Germany. This specimen is important in that it shows even the provenance of common minerals from the Kingsbury collection cannot be relied upon. Nonetheless, many of the other cerussite specimens in the Kingsbury collection are clearly genuine.

Chalcanthite, $CuSO_4.5H_2O$

An oxidised quartz-chalcopyrite specimen from the "*60-fathom level, Driggith mine*", (possibly a mistake for Sandbed mine) is labelled as chalcanthite in Arthur Kingsbury's hand. It is an early specimen and was one of the first sent by Kingsbury for XRD analysis at the University of Leeds. The specimen in coated in a pale blue poorly crystalline crust which probably contains more than one supergene phase. It appears to be dump formed. The identification was considered suspect by Cooper and Stanley (1990) and analyses by EDS at the NHM showed that the crust was a copper sulphate, but not chalcanthite since the copper to sulphur ratio was wrong. This does not appear to be an intentionally fraudulent specimen, as the specimen genuinely appears to be from where it is claimed: it probably represents an analytical error. Chalcanthite should be removed from the list of minerals from Driggith mine.

Chalcocite, Cu_2S

Chalcocite was recorded as a replacement of bornite at Driggith mine by Thimmaiah (1956) and from the 12- and 30-fathom level dumps by Hartley (1984). It is not easy to differentiate chalcocite from other black copper sulphides digenite and djurleite and the report should be considered in this light. All of the black copper sulphides which we have examined in this study proved to be either digenite or djurleite.

CHALCOPYRITE, $CuFeS_2$

Chalcopyrite is abundant as golden metallic masses, which are often intergrown with sphalerite and surrounded by galena in vein quartz at both Driggith and Sandbed mines. Well formed sphenoidal crystals occur rarely in cavities in quartz veinstone (Fig. 24).

CHENITE, $Pb_4Cu(SO_4)_2(OH)_6$

Chenite forms translucent sky-blue equant to prismatic crystals up to 0.6 mm long with caledonite, linarite and leadhillite and an as yet unidentified lead-copper sulphate on material collected from the dumps of the 12-fathom level at Driggith mine (Fig. 25) (Green and Hubbard, 1996). A single specimen from the Ken Savage collection, in the Manchester Museum collection (accession number N14168), shows pale blue chenite crystals to 0.5 mm with anglesite, leadhillite and lanarkite. This is also from Driggith mine.

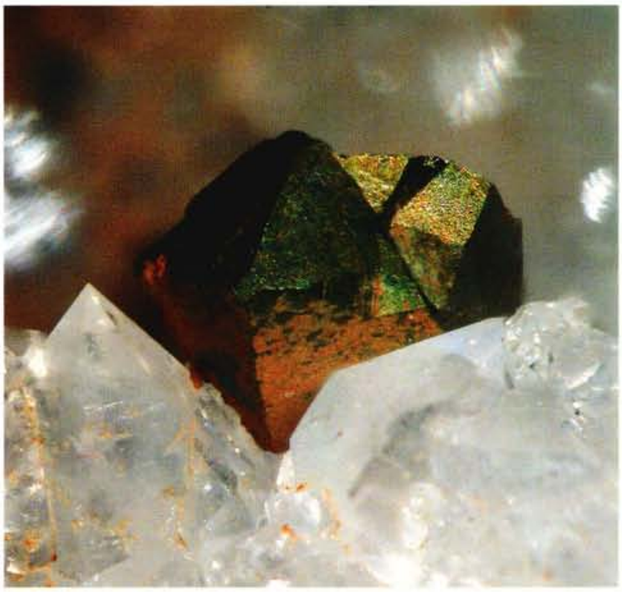


Figure 24. Sphenoidal chalcopyrite crystals 2.2 mm on edge from Sandbed mine. Mike Leppington collection.

Figure 25. A well formed sky blue chenite blade 0.6 mm long from the 12-fathom level dump at Driggith mine. Neil Hubbard collection.

Chlorargyrite, AgCl

Traces of chlorargyrite are noted at Driggith mine in unpublished manuscript notes by Arthur Kingsbury held at the NHM (Cooper and Stanley, 1990). The mineral was recorded by Hartley (1984) as ceragyrite, from the outcrop workings between the Driggith and Sandbed mines. The records, which are all based on material in the Arthur Kingsbury collection, have not been corroborated by other collectors. Furthermore, a recent search through Kingsbury's collection failed to find any specimens. Although silver and silver-rich tetrahedrite have been reported at Sandbed mine, the record of chlorargyrite must be considered suspect. It should be deleted from the list of minerals from the locality.

CHRYSOCOLLA, $(Cu,Al)_2H_2Si_2O_5(OH)_4.nH_2O$

Chrysocolla is widespread in the copper and lead veins in the Caldbeck Fells. It was noted from Driggith mine by Davidson and Thomson (1951) and from both Driggith and Sandbed mines by Hartley (1984). Chrysocolla occurs as blue to blue-green spherules and masses, often displaying syneresis cracks, filling cavities in copper-rich veinstone. It is commonly associated with malachite and hemimorphite.

CINNABAR, HgS

Earthy red-brown crusts of supergene cinnabar, which appear to have been produced by the oxidation of sphalerite, have been identified by EDS at Driggith mine. A very similar looking mineral occurs at Sandbed mine as minute earthy brick-red encrustations, but has not been analysed.

CLINOCHLORE, $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$

Minute colourless crudely hexagonal aggregates of clinochlore are common but inconspicuous in sulphide-rich vein quartz in the opencut above Sandbed mine. They were identified by XRD. Some specimens have been mis-labelled as muscovite.

Conichalcite, $CaCu(AsO_4)(OH)$

Conichalcite was noted from the outcrop workings between Driggith and Sandbed mines by Young (1987) and Cooper and Stanley (1990) on the basis of specimens in the Kingsbury collection. The finds have not been repeated by other collectors.

The descriptions are based on two specimens, one in the main NHM collection BM 1958,109 donated by Kingsbury and another in Kingsbury's personal collection. The latter specimen is broken up into about ten small fragments, which can be reassembled along with the NHM specimen to produce a single larger piece. A single good specimen broken into numerous fragments is often a sign of a Kingsbury fake. The abundant presence of an agardite group mineral on some of the smaller fragments, which apparently went un-noticed by Kingsbury, is also surprising. The occurrence of conichalcite in the Caldbeck Fells remains unproven and the Kingsbury specimen is likely to be untrustworthy. Conichalcite should be deleted from the list of minerals from Driggith and Sandbed mines.

CONNELLITE, $Cu_{19}Cl_4(SO_4)(OH)_{32}.3H_2O$

Small dark blue spherules from Driggith mine were identified as connellite at Oxford University (Mike Leppington, *personal communication*). Similar specimens have since been identified by EDS at Sandbed mine (Fig. 26). Although we have no reason to doubt the specimens, there has been a suggestion that some connellite specimens found at Sandbed mine were Cornish in origin and were left at the site by a thoughtless collector (Mike Leppington, *personal communication*).

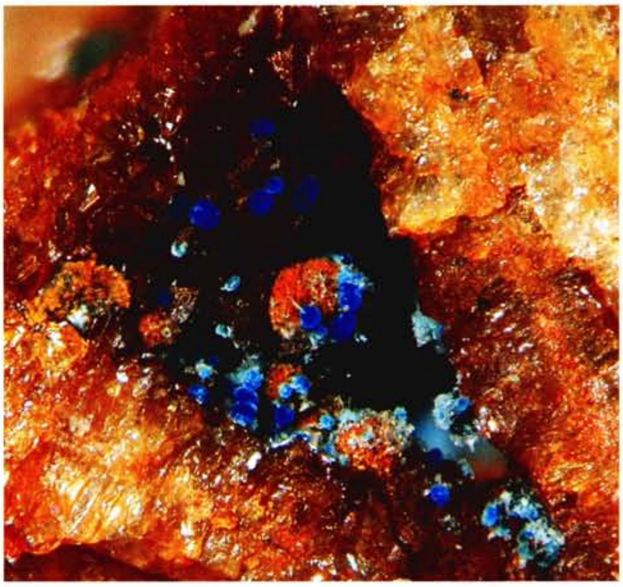


Figure 26. Minute deep blue connellite spherules 0.2 mm across from Sandbed mine. Richard Bell collection.

COPPER, Cu

Copper was reported at Driggith mine by Stanley and Vaughan (1981).

CORNWALLITE, $Cu_5(AsO_4)_2(OH)_4$

Cornwallite is present on specimens from Sandbed mine in the R.J. King collection at the NMW according to Young (1987) and Cooper and Stanley (1990). There are two specimens in the collection (NMW:83.41G.M.7988 and 7989). Cornwallite occurs as rich green globular crusts overgrowing malachite on limonitic quartz with minor supergene baryte in both cases (Tom Cotterell, *personal communication*).

COVELLITE, CuS

A number of reports of covellite from Driggith mine are summarised by Cooper and Stanley (1990) and the mineral has been identified in this study at Sandbed mine. Specimens in the Kingsbury collection from the openwork above Sandbed mine appear to be genuine. Covellite commonly forms metallic blue to purple rims around other sulphides. In addition to specimens of undoubted natural origin, covellite occurs as masses of minute metallic blue-black plates on the surfaces of some specimens. These are post-collecting in origin.

CUPRITE, Cu_2O

Tiny red octahedral cuprite crystals partially altering to green copper secondaries have been collected recently at Sandbed mine and massive to poorly crystallised specimens also occur at Driggith mine (Mike Leppington, *personal communication*).

Cuprite was recorded from the Driggith-Sandbed opencut on the basis of a specimen in the Kingsbury collection by Cooper and Stanley (1990). The only cuprite specimen in the Kingsbury collection from Driggith-Sandbed is accompanied by the hand written note "*Sandbeds upper 1953*". It consists of irregularly etched and corroded deep red cuprite grains to 8 mm oxidising to powdery malachite in hackly white quartz. As this cuprite is considerably larger than anything otherwise reported, it was collected in 1953 and it is an excellent match for cuprite specimen BM 1964R,2367 from Wheal Prosper, St. Hilary, Cornwall, it is almost certainly fraudulent.

DEVILLINE, $CaCu_4(SO_4)_2(OH)_6.3H_2O$

Devilline occurs in green to blue green crusts of post-mining origin surrounding blocks of unaltered vein material at both Driggith and Sandbed mines. It was recorded by Hartley (1984), and verified independently by Mike Rothwell (*personal communication*) and by EDS in this study. It occurs as white to pale blue or green lath-like crystals up to a few millimetres long. No specimens labelled devilline have been found in the Kingsbury collection, but it is likely that Hartley's record is based on an XRD of the blue crust such as that described under chalcanthite.

DIGENITE, Cu_9S_5

Digenite was identified in alteration rims, 5 to 20 µm wide, surrounding chalcopyrite from the 60-fathom level dumps at Sandbed mine. It is associated with yarrowite and limonite.

DJURLEITE, $Cu_{31}S_{16}$

Djurleite replacements of galena were recorded in small amounts at Driggith mine by Stanley and Vaughan (1981) and identified in this study as grains to 50µm across in the cobalt-rich assemblage found on the 60-fathom-level dumps at Sandbed mine.

DOLOMITE, $Ca,Mg(CO_3)_2$

Creamy white to brown dolomite occurs commonly as a late stage mineral in fractures and fissures in the lead vein. It is rarely replaced by yellow-brown crusts of the zinc carbonate smithsonite at Sandbed mine. Dolomite was abundant in the 60-fathom level at the Sandbed West baryte mine according to Shaw (1970). Some of the dolomite was a very dark variety containing 12% manganese, its oxidation may well account for the abundant manganese soot described from the mine. Small white rhombs of dolomite occur with chalcopyrite on quartz at Driggith mine.

DUFTITE, $PbCu(AsO_4)(OH)$

Ten possible duftite specimens were examined by XRD and EDS in this study but only two were conclusively identified. One was collected from the 60-fathom level dumps at Sandbed mine by Tim Neall (registration number TN 1403) and displays a rich apple green crust about half covering a 40 x 40 mm fragment of wallrock with a thin quartz vein running through it (Fig. 28). Analyses by EDS indicated calcium was present in addition to lead, copper and arsenic, but the XRD pattern was clearly duftite rather than conichalcite. The second specimen was a thin yellow-green crust on quartz, which XRD showed to be a mixture of duftite and a descloizite-group mineral. Analyses by EDS indicated that lead, copper, vanadium, arsenic and a trace of calcium were present so it is likely that the crust is a mixture of duftite and mottramite. A minute specimen in the Mike Leppington collection from Driggith mine is also likely to be duftite, as it has a similar EDS spectrum to XRD confirmed material, however, there was insufficient material for confirmation by XRD.

Figure 27. Creamy white dolomite rhombs about 2 mm on edge from Sandbed mine. Mike Leppington collection.

Figure 28. A rich crust of bright green duftite on vein quartz from the 60-fathom level dumps of Sandbed mine. Tim Neall collection registration number TN 1403.

Duftite was recorded from an old trial on a copper vein near the 30-fathom level at Driggith mine on the basis of unpublished information in a manuscript by Arthur Kingsbury and Jack Hartley held at the Natural History Museum (Cooper and Stanley, 1990). We were not able to locate the trial in our field survey of the area. There is a single poorly curated tray of duftite fragments in the Kingsbury collection material labelled "*1952 Driggith 30ftm level*" which oddly does not look as though it was considered to be anything important. It contains half a dozen fragments and one larger specimen about 20 mm long. There is no matrix visible on any of the pieces, which are a complex intergrowth of microcrystalline apple green duftite clusters associated with fibrous emerald green malachite that is possibly pseudomorphing anglesite and transparent brownish cerussite. The late collection date, atypical assemblage and unusual richness of all the specimens strongly suggest that they are fraudulent.

ELYITE, $Pb_4Cu(SO_4)O_2(OH)_4.H_2O$

Elyite occurs as acicular to lath-like crystals up to 0.5 mm in length of a characteristic deep purple colour in small cavities in partly oxidised galena with leadhillite, chenite, caledonite and an as yet unidentified lead-copper sulphate (Fig. 29). It was identified on specimens in the Neil Hubbard collection from the 12-fathom level dumps at Driggith mine on the basis of its EDS spectrum, colour and association.

Figure 29. Deep purple acicular to lath-like elyite crystals up to 0.4 mm long from the 12-fathom level dumps at Driggith mine. Neil Hubbard collection.

ERYTHRITE, $Co_3(AsO_4)_2.8H_2O$

A considerable number of 'erythrite' specimens were collected in the early 1990s from a small area on the 60-fathom level dumps at Sandbed mine (Mike Leppington and Richard Belson, *personal communications*). Pink crusts on specimens to large hand size with occasional well formed bladed crystals were found in brown iron-rich matrix containing quartz, carbonates, gersdorffite, tennantite and tetrahedrite. Similar specimens occur much less commonly, at Driggith mine (Tim Neall, *personal communication*). Our analyses have shown that much (but not all) of the so called erythrite falls within the annabergite or köttigite composition fields. The most extreme case was a pink feathery crust which had a formula $(Zn_{1.3},Ni_{1.1},Co_{0.3})(AsO_4)_2.8H_2O$. In this case nickel and zinc exceed cobalt by a factor of eight, yet because of its pink colour the specimen was labelled erythrite. Visual identifications of erythrite from Driggith and Sandbed mines cannot be considered reliable.

GALENA, PbS

Galena is abundant on the dumps of both Driggith and Sandbed mines. It occurs in the arsenate gossans at Howthwaite trial and in the Driggith-Sandbed opencut, where it is commonly surrounded by oxidation rims containing beudantite-segnitite and carminite. Rarely small euhedral blocky crystals occur in cavities in quartz veinstone.

GERSDORFFITE, NiAsS

Gersdorffite was identified by XRD in carbonate-rich quartz vein material containing the supergene nickel and cobalt minerals annabergite and erythrite from the 60-fathom level dumps at Sandbed mine. It is an abundant early-stage primary phase in this assemblage, where is commonly occurs as minute pentagonal dodecahedral crystals that are spatially separated from the other base-metal sulphides. It is occasionally overgrown by chalcopyrite or tetrahedrite. Analyses by EDS show that the gersdorffite is always cobalt-rich. Gersdorffite is a relatively unstable mineral in the supergene environment. It is almost certainly the source of the cobalt, nickel and arsenic required for the formation of annabergite and erythrite.

GOETHITE, FeO(OH)

Goethite is abundant as the major component of pale to dark brown friable limonitic crusts and as hard black encrustations on vein quartz. Rarely, velvety brown botryoidal goethite encrusts cavities in vein quartz (Fig. 30).

HEMATITE, Fe_2O_3

Hematite was listed without description from Sandbed mine by Hartley (1984). There are no specimens specifically listed as hematite from the mine in the Kingsbury collection.

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2.H_2O$

Hemimorphite is widespread but usually inconspicuous at Driggith and Sandbed mines. Pale blue crusts were noted from Sandbed mine by Davidson and

Thomson (1951). Hemimorphite typically occurs as small radiating sprays of bladed crystals, not usually exceeding a millimetre in length, in cavities in vein quartz (Fig. 31). Aurichalcite and adamite are rare associates. A few pale yellow cadmium-rich specimens have been found at Sandbed mine.

Figure 30. A plush brown goethite crust from Driggith mine. Richard Bell collection.

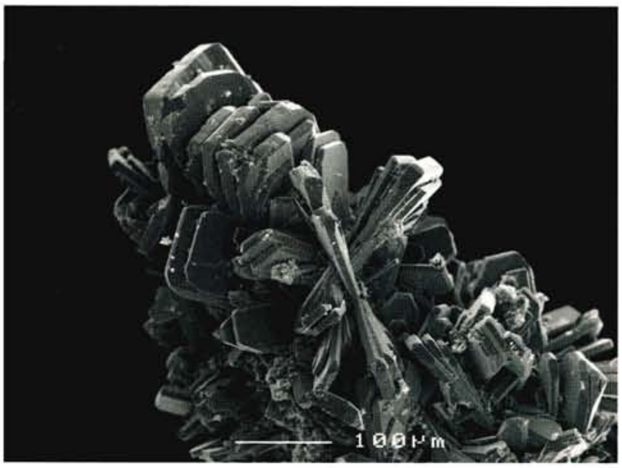


Figure 31. Typical well formed platy hemimorphite crystals in radiating clusters up to 0.2 mm across from the 60-fathom level dumps at Sandbed mine.

There are three hemimorphite specimens in the Kingsbury collection found in 1949 on the Driggith 12-fathom level dumps. They are typical of the locality and appear to be genuine. A fourth specimen of rich sky blue botryoidal hemimorphite is considerably different. The accompanying data suggest that it was collected from the Sandbed top level dumps in 1952. Sky blue botryoidal hemimorphite up to 10mm thick covers the whole of the upper surface (70 mm x 20 mm) of the specimen. Although pale blue crusts of good quality were noted by Davidson and Thomson (1951) this is far better than anything that Norman Thomson recalls collecting at Sandbed mine (*personal communication*). The specimen is almost identical to material from the Glencoyne adit dump at Greenside mine in the central Lake District which was found in about 1950. Its provenance must be considered highly suspect.

HYDROCERUSSITE, $Pb_3(CO_3)_2(OH)_2$

Hydrocerussite was identified as white bladed masses in association with bechererite on a specimen collected from the 30-fathom level dumps at Driggith mine (Rust *et al.*, 2003). It was recorded by Hartley (1984) at both Driggith and Sandbed mines and there seems no reason to doubt this, although during a recent search no specimens labelled as such could be found in the Kingsbury collection.

HYDROZINCITE, $Zn_5(CO_3)_2(OH)_6$

Pale blue crystalline crusts of hydrozincite were described from Sandbed mine by Young (1987) on the basis of specimens in the Natural History Museum. Hydrozincite was identified by XRD at both Driggith and Sandbed mines in thin crusts of a bright to dirty white colour and may be post-mining in origin. It also occurs as globular aggregates to about 1 mm across composed of minute lath-like crystals with a pearly lustre.

JAROSITE, $KFe_3(SO_4)_2(OH)_6$

Jarosite was identified by EDS at Sandbed mine in thin fractures in pyrite-rich quartz matrix as pale yellow-brown earthy crusts made up of crystals up to a few microns across. Similar material has been collected from the dumps of Driggith mine. Jarosite is restricted to fractures in the matrix, where it is exposed to the atmosphere it alters to goethite.

According to Hartley (1984) jarosite was found at the outcrop workings between the Driggith and Sandbed mines. The basis for this record appears to be specimen K53/174, which was part of a larger specimen that was sent in three pieces (K53/173-175) to Hartley for XRD identification. In Kingsbury's notes made after analysis it is recorded that "*K53/174 – Driggith Outcrop – Close to j*", because K53/173 came back as "*K53/173 – Driggith Outcrop – Maybe Pj*" it is assumed, that "j" means jarosite and "Pj" means plumbojarosite. Although it maybe genuine, the identification does not appear to have been conclusive and the provenance of the specimen has to be treated with caution, it is discussed further under plumbojarosite.

KÖTTIGITE, $Zn_3(AsO_4)_2.8H_2O$

Pale pink crystals of nickel and cobalt-rich köttigite, which had been labelled as erythrite, were identified by a combination of XRD and WDS. The most zinc-rich composition was on a pale pink feathery crystal and corresponds to the formula $(Zn_{1.3},Ni_{1.1},Co_{0.3})(AsO_4)_2.8H_2O$. Copper and iron were also detected but are not present in amounts sufficient to affect the formula. It is interesting to note that the crystals are distinctly pink in spite of the presence of a relatively small amount of cobalt. This underlines the observation that both köttigite and annabergite are visually indistinguishable from erythrite in specimens from Sandbed mine.

LANARKITE, $Pb_2O(SO_4)$

Lanarkite was identified by XRD on two specimens from Driggith mine in the Manchester Museum collection (N14168 and N14171). In both cases it occurs in cavities in corroded galena. On one specimen it is associated with leadhillite, anglesite and chenite and in the second with anglesite. Lanarkite forms sprays of very pale blue bladed crystals up to 0.7 mm long.

LANGITE, $Cu_4(SO_4)(OH)_6.2H_2O$

Langite is widespread as a component of the blue green crusts surrounding fragments of copper-rich ore on the dumps of both Driggith and Sandbed mines. It typically occurs as poorly formed crystals associated with brochantite and linarite, and is sometimes partly replaced by the former. Rarely, well-formed pseudo-hexagonal langite prisms or complex crystals with characteristic 60^O twinning occur in fractures in the rock (Fig. 32). These appear to have formed by post-mining oxidation.

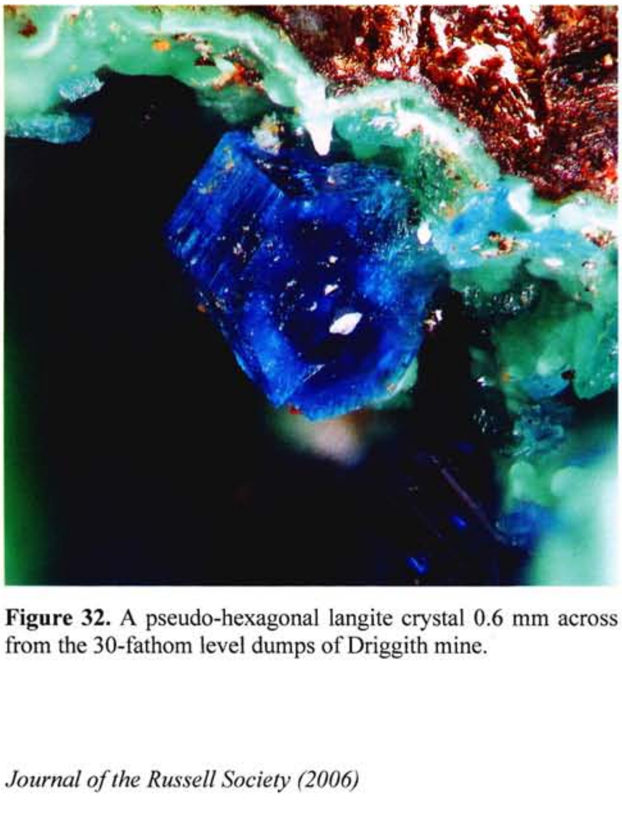


Figure 32. A pseudo-hexagonal langite crystal 0.6 mm across from the 30-fathom level dumps of Driggith mine.

LAVENDULAN, $NaCaCu_5(AsO_4)_4Cl.5H_2O$

A sky-blue mineral that forms hemispherical aggregates up to a few tenths of a millimetre across on specimens from the 60-fathom level dumps at Sandbed mine has an XRD pattern that is almost identical to lavendulan. Specimens examined by EDS is this study contained Ca, Cu, As and Cl in the correct ratios for lavendulan, but K rather than Na was detected in every case. The silicon detectors used in some EDS systems are not sensitive to small amounts of Na, and since Na_2O is only present at about 3 wt% (Anthony *et al.*, 2000) in lavendulan this may account for the lack of a detectable Na peak. Sodium was detected in some specimens analysed by Mike Rothwell in the 1990s and these are almost certain to be lavendulan (Mike Leppington, *personal communication*).

LEADHILLITE, $Pb_4(SO_4)(CO_3)_2(OH)_2$

Leadhillite is widespread but uncommon and inconspicuous in oxidised galena-bearing fragments on the dumps at both Sandbed and Driggith mines. It occurs as platy to blocky pseudohexagonal crystals up to about 3 mm across, which are commonly associated with caledonite, anglesite and cerussite at Driggith mine (Figs. 33 and 34).

Figure 33. A pseudo-hexagonal leadhillite crystal 1.2 mm across with blue caledonite from the 30-fathom level dumps of Driggith mine.

There are a number of specimens of leadhillite from the Driggith and Sandbed mines in the Kingsbury collection at the NHM, most of which are genuine. A few are clearly fraudulent, the most notable being a specimen with large platy crystals of leadhillite to 30 mm associated with grey-black cerussite. This specimen and a number of the others from Driggith and Sandbed mines are clearly from the classic locality at Leadhills in South Lanarkshire. The crystals are of a habit, size and colour that does not correspond to any that have otherwise been found in the Caldbeck Fells.

Figure 34. A pseudo-hexagonal leadhillite crystal 1.9 mm across in a cavity on quartz with caledonite from the 30-fathom level dumps of Driggith mine. Richard Bell collection.

LEPIDOCROCITE, γ-FeO(OH)

Lepidocrocite was identified by XRD as minute brown glistening hexagonal plates (up to about 0.3 mm) on a single specimen in the Mike Leppington collection. It occurs as a crystalline crust on cellular goethite-hematite boxworks and on goethite epimorphs after crystals with the characteristic morphology of ankerite and siderite.

LINARITE, $PbCu(SO_4)(OH)_2$

Linarite is common at both Driggith and Sandbed mines. It is a component of thin blue-green crusts on weathered sulphides that form by post-mining oxidation. It also occurs as euhedral bladed, prismatic and acicular crystals of a deep azure blue in cavities in blocks of oxidised ore (Figs 35 and 36). Linarite is commonly associated with brochantite and cerussite and sometimes with hemimorphite, leadhillite, schulenbergite and anglesite. Specimens are particularly common on the 12-fathom level dumps at Driggith mine.

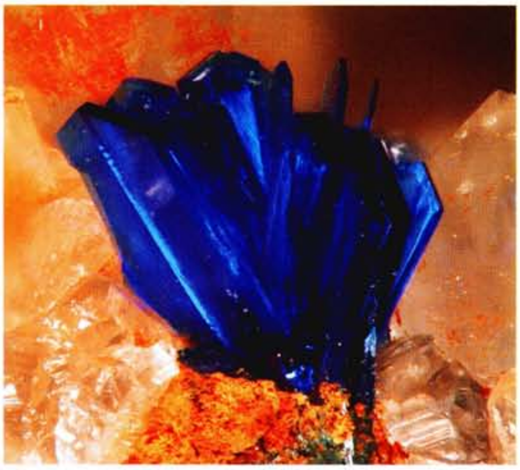


Figure 35. A radiating spray of tabular prismatic linarite crystal 1.5 mm tall from Driggith mine. Richard Bell collection.

Linarite is probably the most complicated of all of the Kingsbury frauds from the Driggith and Sandbed mines. The specimens in his collection range from linarite as an accessory phase on likely genuine specimens, through legitimate linarite specimens in their own right, to what is probably the most spectacular fake from the entire area. This specimen, donated to the NHM by Kingsbury and registered as BM 1956,431 from the 30-fathom level at Driggith mine, is noted by Cooper and Stanley (1990) as linarite crystals (<10 mm) with brochantite, malachite and aurichalcite. More accurately, tens of large well-formed and completely undamaged bladed linarite crystals to 9 mm cut a swath of brilliant blue across a 60 mm x 10 mm strip on the surface of the specimen. These are associated with brochantite, caledonite, aurichalcite, malachite and cerussite upon a matrix dominantly composed of solid partly oxidized chalcopyrite. The matrix is atypical of Caldbeck Fells material and the vast majority of the linarite crystals on this specimen are over 5 mm in length thus the specimen is of a quality that is much better than anything obtained from the Driggith mine. It is probably from one of the classic linarite localities, perhaps Llaillay in Chile or the Leadhills, South Lanarkshire or even the Roughton Gill or Red Gill mines themselves in the Caldbeck Fells.

Cooper and Stanley (1990) report linarite crystals, rarely greater than 5 mm, with leadhillite, brochantite and cerussite from Sandbed Mine on the basis of Kingsbury specimens at the NHM. Some smaller legitimate specimens in the Kingsbury collection labelled as being collected in 1949 do very rarely have linarite blades reaching this size. However the report was probably based on specimen BM 1961,221, donated by Kingsbury to the NHM and apparently collected in 1950 from the upper dumps at Sandbed mine. It is a rich specimen containing linarite crystals to 5 mm in cavities in iron stained quartz with malachite and cerussite. Although the quartz matrix looks like it may be from the Caldbeck Fells, the specimen is of a quality which seems unlikely to have been found in the relatively unoxidised material present on the dumps of Sandbed mine. A much more likely locality is the well-known and classic Red Gill mine.

Figure 36. A single thin lath-like linarite crystal 1.5 mm tall from Driggith mine. Richard Bell collection.

MALACHITE, $Cu_2(CO_3)(OH)_2$

Malachite is common at both Driggith and Sandbed mines and Davidson and Thomson (1951) recorded good crystals at the latter. Malachite occurs as pale to deep emerald green fibrous to long prismatic crystals and dark green botryoidal masses in small quartz-lined cavities. It is commonly associated with cerussite and small yellow barrel-shaped crystals of mimetite (Fig. 37).

Figure 37. Deep emerald green malachite crystals about 2 mm long overgrown by yellow blocky mimetite from Driggith mine.

There are many specimens in the Kingsbury collection that contain malachite in tiny acicular crystals or crusts. There is no reason to doubt them. A specimen of malachite from Zellerfeld which is clearly faked is described by Ryback *et al.* (2001). There are two other questionable specimens in the Kingsbury collection. The first labelled "*Sandbeds 1951*" is a mass of fibrous malachite 150 mm across which displays acicular crystal sprays up to 15 mm in size associated with tabular cerussite crystals to 12 mm on edge. The second specimen labelled "*Sandbeds 1953*" comprises rich fibrous malachite to 4 mm thick coating a 40 mm x 20 mm quartz specimen. Both specimens have late collection dates, are atypical of the Caldbeck Fells and are of a quality unlike anything otherwise found at the locality. It is likely that both specimens are fraudulent.

MARCASITE, FeS_2

Marcasite was identified by reflected light microscopy in the early arsenopyrite-rich assemblage which is exposed in the opencut between Driggith and Sandbed mines as 5 to 30 μm diameter grains intergrown with pyrite in quartz or forming the cores of euhedral gersdorffite grains ar intergrown with pyrite as pseudomorphs after pyrrhotite.

Mattheddleite, $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$

Mattheddleite was claimed to have been identified from Driggith mine by the late Ken Savage (*personal communication* to Mike Leppington). A specimen labelled anglesite and mattheddleite, now in the Manchester Museum collection (N14171), purchased from Ken Savage, was extensively analysed. It contained anglesite and lanarkite but no mattheddleite. Mattheddleite should be deleted from the list of minerals currently claimed from Driggith mine.

MAWBYITE, $PbFe_2(AsO_4)_2(OH)_2$

Mawbyite was identified by XRD as a component of a brownish-red to blood-red crystalline crust found in the arsenate-rich gossans above the Sandbed 60-fathom level. It occurs with carminite, segnitite and mimetite. The XRD patterns of carminite and mawbyite are similar, but have significant differences, notably in the peaks around 4.6 A. Peaks at 4.647 Å (-1.1.1. for mawbyite) and 4.584 Å (1.1.2 for carminite) were present in the diffraction pattern generated by the crust indicating the presence of both carminite and mawbyite. The two minerals cannot be distinguished visually on the specimen.

MIMETITE, $Pb_5(AsO_4)_3Cl$

Mimetite is common at both Driggith and Sandbed mines and occurs in a wide variety of colours and crystal habits. Colourless highly elongated prismatic crystals up to a few millimetres in length from an arsenate gossan in the Driggith-Sandbed opencut are end member mimetite. They are commonly associated with barium-pharmacosiderite, beudantite and scorodite. End member mimetite also occurs with adamite and bayldonite in thin fractures in quartz veinstone on the main dumps at Driggith and Sandbed mines. Mimetite is commonly colourless, yellow or yellow-green, and more rarely green, brown or orange. The crystals may be acicular to prismatic, barrel shaped, equant, curved or disk shaped, one habit sometimes grading insensibly into another. Rarely, mimetite pseudomorphs cerussite (Fig. 38). It also occurs in the erythrite-bearing assemblage at Sandbed mine as white silky fibres.

The well known specimens from the opencut above Driggith mine are arsenate-rich pyromorphite, but almost all of the other specimens we have examined from the lower workings at both Driggith and Sandbed mines are mimetite or phosphatian mimetite. In addition to its association with the supergene arsenate minerals described above, mimetite commonly occurs with malachite and cerussite. Calcium substitutes for lead in some mimetite specimens from the Driggith and Sandbed mines, but quantitative analyses have not found any that are sufficiently calcium-rich to be labelled hedyphane.

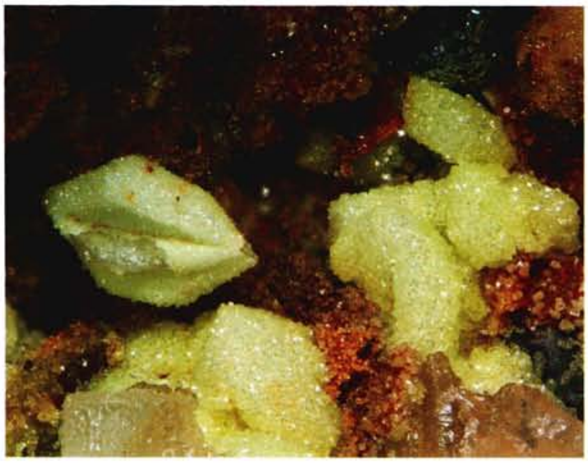


Figure 38. Pale yellow mimetite overgrowing and replacing cerussite to 3.5 mm from Sandbed mine. Mike Leppington collection.

MOTTRAMITE, $PbCu(VO_4)(OH)$

A yellow-brown crust from the 60-fathom level dumps of Sandbed mine was identified by a combination of XRD and EDS as mottramite.

Namuwite, $(Zn,Cu)_4(SO_4)(OH)_6.4H_2O$

A possible find of namuwite as pale blue-green hexagonal plates on the 30-fathom level dumps at Driggith mine was reported by Mike Rothwell (*British Micromount Society Newsletter*, **39**:18) on the basis of the similarity in the minerals EDS spectrum with undoubted namuwite from Wales. A likely confusion using this identification technique is with the similar zinc copper sulphate-carbonate schulenbergite. A search of both the Mike Rothwell and John Dickinson collections has revealed only schulenbergite from Driggith mine. Namuwite should be deleted from the list of minerals from the site.

OLIVENITE, $Cu_2(AsO_4)(OH)$

Olivenite was identified by XRD and EDS on a specimen from Sandbed mine in the Richard Bell collection. It occurs in small cavities in chalcopyrite-rich quartz veinstone as pale olive green prismatic to acicular crystals up to about 0.5 mm long with fibrous white terminations. Olivenite has also been identified with parnauite on a specimen from Sandbed mine in the Mike Leppington collection as drusy crusts of characteristic olive green acicular crystals.

PARNAUITE, $Cu_9(AsO_4)_2(SO_4)(OH)_{10}.7H_2O$

Aggregates of green lath-like parnauite up to about 0.7 mm long were identified by XRD and EDS on a fracture surface in iron stained quartz on a specimen in the Mike Leppington collection. Olivenite is present on the same specimen which was found on the 60-fathom level dumps at Sandbed mine.

Phosgenite, $Pb_2(CO_3)Cl_2$

Phosgenite was reported by Kingsbury (1957) associated with anglesite in decomposed granular galena from the outcrop workings between Driggith and Sandbed mines. The report is based on a single specimen supposedly collected in 1952, which contains stubby prismatic phosgenite crystals the largest of which is 8 mm x 5 mm x 5 mm, and is contained within a cavity in granular galena and associated with massive brownish cerussite. The specimen has been split into two pieces, is quite unlike anything otherwise recorded from the Caldbeck Fells, it would be an enormous crystal of phosgenite if it was genuine and its matrix is identical to classic material from Monteponi in Sardinia, Italy. Phosgenite requires a chloride ion activity of the order of that found in sea water to form in preference to cerussite (*e.g.* Bridges, 2003). Almost all of the known British occurrences are in lead veins that crop out on the sea coast. It is very difficult to see how such a high chloride ion activity could eventuate during the natural oxidation of the vein at Driggith mine. Phosgenite should be removed from the list of minerals from Driggith and Sandbed mines, the specimen is clearly fraudulent.

PHARMACOSIDERITE, $KFe_4(AsO_4)_3(OH)_4.6\text{-}7H_2O$

Recent analyses have shown that most of the material labelled 'pharmacosiderite' from the opencut above Sandbed mine is barium-pharmacosiderite however, a few pale green pseudomorphs, possibly after parasymplesite, which are identical to those described under barium-pharmacosiderite, proved to be made of pharmacosiderite intergrown with scorodite (Fig. 39).

Figure 39. Pharmacosiderite pseudomorphs after an unknown monoclinic mineral, possibly parasymplesite from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

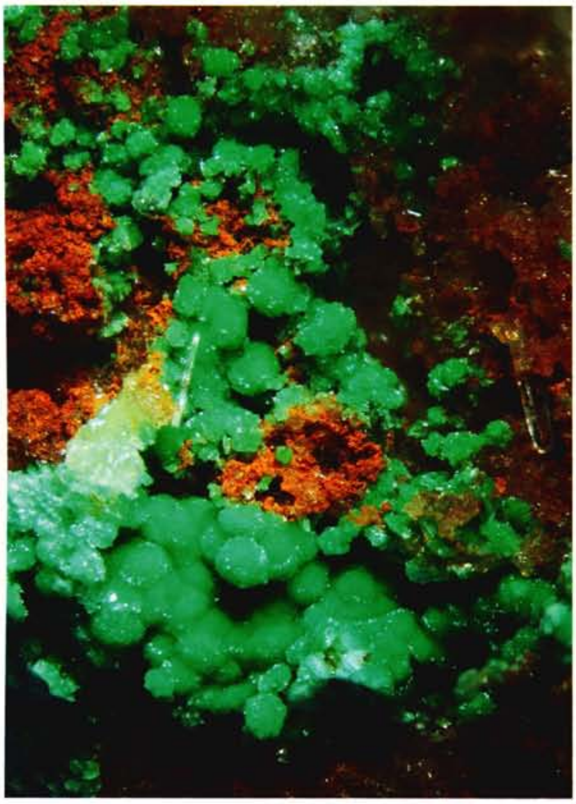


Figure 40. Drusy green philipsburgite spherules up to about 0.5 mm across on brown vein quartz from the 30-fathom level dumps at Driggith mine. Mike Leppington collection.

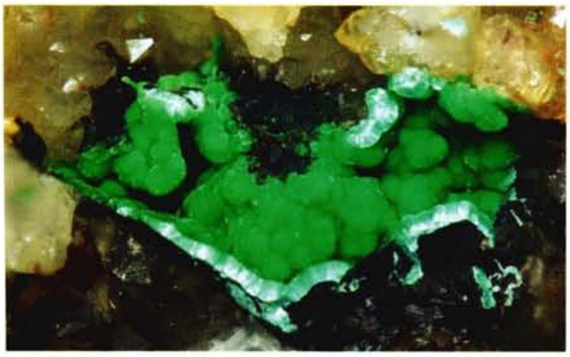


Figure 41. Rich botryoidal philipsburgite crusts in a cavity in vein quartz from the 60-fathom level dumps at Sandbed mine. Mike Leppington collection.

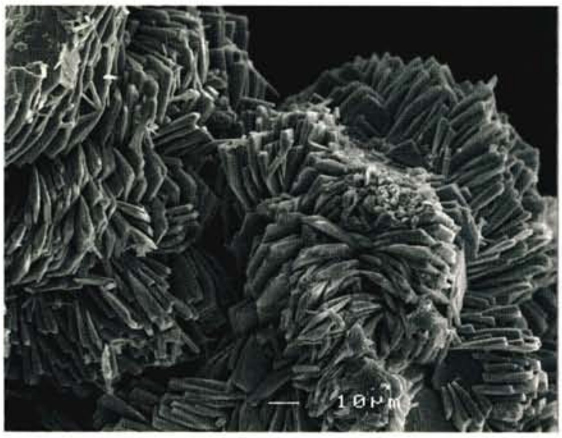


Figure 42. The surface of a drusy philipsburgite aggregate, showing typical pointed philipsburgite crystals from Driggith mine.

PHILIPSBURGITE, $(Cu,Zn)_6(AsO_4,PO_4)_2(OH)_6.H_2O$

Philipsburgite is widespread at both Driggith and Sandbed mines. At first glance, it is easily confused with malachite, but can be distinguished by a slightly pearly lustre and rather paler colour on fracture surfaces. Philipsburgite is common on the 30-fathom level dumps at Driggith mine (Fig. 40). Specimens to small hand size were found on the 60-fathom level dumps at Sandbed mine during recent surveys of the site. The best show rich green crusts, which sometimes break up into individual botryoidal aggregates, in cavities in vein quartz (Fig. 41). Examination by electron microscopy usually resolves the crusts into minute pointed bladed crystals up to about 10 µm long (Fig. 42).

Planchéite, $Cu_8(Si_4O_{11})_2(OH)_4.H_2O$

The claimed first British planchéite is listed from the 30-fathom level dumps at Driggith mine in an unpublished manuscript by Arthur Kingsbury held at the Natural History Museum, (Young, 1987; Cooper and Stanley, 1990). Serious doubt was cast on the provenance of the specimen by Ryback *et al.* (1998) and despite many years of searching no similar material has been found in the area. Planchéite should be deleted from the list of minerals from Driggith mine.

Plumbogummite, $PbAl_3(PO_4)_2(OH)_5.H_2O$

Sugary pale apple green masses of plumbogummite with pyromorphite were described from Sandbed mine on the basis of specimens in the Kingsbury collection by Cooper and Stanley (1990). The specimen was supposedly collected from Sandbed mine in 1951. A large piece of vein quartz is dominantly encrusted with two distinct generations of well formed olive green barrels and hexagonal prisms of pyromorphite-mimetite to 5 mm in length. The only associated mineral is a small isolated encrustation of pale apple-green to yellow drusy plumbogummite upon the quartz. The specimen is unlike anything otherwise reported from Sandbed mine and it is of a quality that could not have been dump collected. Kingsbury had a particular penchant for falsely claiming certain species and plumbogummite appears to be one of them (*e.g.* Bridges *et al.,* 2006). The specimen is likely fraudulent.

Plumbojarosite, $PbFe_6(SO_4)_4(OH)_{12}$

A few specimens, labelled as beudantite, from both Driggith and Sandbed mines contained only lead, iron and sulphur when examined by EDS. The analysis, colour and crystal habit when examined under SEM are consistent with plumbojarosite, but insufficient material was available for determination by XRD.

The first claimed British occurrence of plumbojarosite was described from the outcrop workings between Driggith and Sandbed mines by Kingsbury and Hartley (1957). A single specimen collected by Kingsbury in 1952 consists of greenish yellow to brown powdery crusts associated with dull green pyromorphite-mimetite and grey cerussite. It is labelled as Driggith or Driggith opencut and was split into three separate specimens K53/173-175 for the purpose of XRD analysis by Jack Hartley. One of these specimens "*K53/173*" was noted by Kingsbury before analysis as being "*Greenish-yellow earthy material on cerussite, ?beudantite or what? Driggith 1952*", although after analysis a different note states "*K53/173 – Driggith Outcrop – Maybe Pj*". It is assumed that "Pj" means plumbojarosite. The identification of plumbojarosite does not appear to have been conclusive and even though the specimen may be genuine, it is difficult to be absolutely certain since it may have been collected from outcrop workings that are no longer extant (Norman Thomson, *personal communication*). Given Kingsbury's well established reputation for falsely claiming rare minerals, the record must be treated with caution.

POSNJAKITE, $Cu_4(SO_4)(OH)_6.H_2O$

Posnjakite was described from Driggith mine in thin carbonate-bearing veinlets in oxidised sphalerite as minute rounded subhedral crystals with ramsbeckite, schulenbergite, serpierite and linarite (Green *et al.*, 2001). It is widespread at both mines as a component of the crusts of supergene minerals produced by post-mining oxidation. It has also been identified as poorly formed blue platy crystals in ferruginous matrix at Driggith mine.

Pseudomalachite, $Cu_5(PO_4)_2(OH)_4.H_2O$

A number of suspect pseudomalachite specimens were examined by XRD and EDS in this study but they all proved to be other species. The commonest confusion was with rosasite.

Pseudomalachite was noted from the 30-fathom level dumps at Driggith mine by Hartley (1984) presumably on the basis of specimens supplied by Kingsbury. There are three boxes containing broken pseudomalachite fragments in the Kingsbury collection. The first tray, claimed to be from the Sandbed upper dumps contains massive dark green pseudomalachite intergrown with quartz and an unidentified black mineral. The second group of specimens, apparently from Driggith mine contains four fragments of vein quartz with dark green (<1 mm) pseudomalachite crystals forming rich crusts in cavities and fractures. The third tray, apparently from Sandbeds mine contains massive pseudomalachite lining cavities in quartz up to 30 mm in extent. The specimens are an exact match to material from Virneberg in the Rhineland, Germany and the broken pieces in each tray fit together to form larger specimens. This is clearly a fraudulent claim

A final specimen of pseudomalachite, collected in 1950 from the 30-fathom level dumps at Driggith mine, is less easy to discredit. Tiny crystalline pseudomalachite spherules to 1 mm cover a sugary quartz matrix. It too has been broken into fragments, which is often the sign of a Kingsbury fraud and in view of his reputation it must be considered highly suspect.

Psilomelane

The hard manganese oxides which occur commonly in the Caldbeck Fells have been described as psilomelane by a number of authors (*e.g.* Cooper and Stanley, 1990), while softer material has been characterised as pyrolusite or simply manganese soot (*e.g.* Shaw, 1970). The relatively few samples that we have examined have proved to be the barium manganese oxide romanèchite.

PYRITE, FeS_2

Pyrite is uncommon as small cubic and octahedral crystals in cavities in dolomite at Sandbed mine. It occurs as small cubic crystals embedded in quartz matrix at Driggith mine.

Pyrolusite, MnO_2

Pyrolusite is listed from Driggith mine by Davidson and Thomson (1951) and by Stanley (1979). Our analyses of specimens from both the Driggith and Sandbed mine indicate that the dominant mineral is romanèchite, much of which is very poorly crystallised.

PYRRHOTITE, $Fe_{1-x}S$ ($x = 0$ to 0.17)

Pyrrhotite appears to have been a fairly common, paragenetically early phase in the arsenopyrite-rich assemblage found in the opencut above the 60-fathom level at Sandbed mine. It occurs as minute euhedral crystals, enclosed in quartz or arsenopyrite, up to about 0.1 mm long which are commonly replaced by marcasite and pyrite.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$

The outcrop workings above Driggith mine are well known as a source of arsenatian pyromorphite in characteristic green curved crystals on vein quartz (Figs 43 and 44). Specimens to large cabinet size are common in north-of-England collections. The best of these display crystals to about 5 mm richly covering slightly iron stained vein quartz (e.g. Cooper and Stanley, 1990). The site was certainly known to Victorian collectors: pyromorphite is noted by Greg and Lettsom (1858) from "Driggath Mine". Other habits are unusual at this locality, although occasionally barrel shaped green crystals have been found (Fig. 45).

A few extraordinary cauliflower-shaped pyromorphite specimens were collected in the last half of the twentieth century from the northeast end of opencut above Driggith mine. These typically show a central pyromorphite stem with radiating florets up to several centimetres across (George Wilson, *personal communication*). The best specimens of this habit were found at a small outcrop not much more than a metre long at the northeast end of the upper opencut (Norman Thomson, *personal communication*). A superb example of this habit is in the Arthur Kingsbury collection, not all of Kingsbury's good specimens are fraudulent!

In addition to specimens from the outcrop workings, which are typically arsenatian pyromorphite, a large

Figure 43. Green curved 'rice grain' crystals of arsenatian pyromorphite to 3 mm on white vein quartz from the opencut above Driggith mine. Richard Bell collection.

Figure 44. Typical somewhat dirty green curved 'rice grain' aggregates of arsenatian pyromorphite to 2.5 mm from the opencut above Driggith mine.

number of other specimens were analysed by EDS in this study. Most proved to be mimetite. Only two specimens of more than twenty analysed were near to end-member pyromorphite. One had very pale blue groups of radiating crystals up to about 1.5 mm in length from Sandbed mine. The colour is very unusual, although blue pyromorphite has also been identified at Red Gill Mine (Nick Carruth, *personal communication*).

The composition of a few specimens was determined by WDS to assess the extent of calcium substitution. Although calcium was detected in some of the specimens none was sufficiently calcium-rich to fall within the composition field of the newly described species lead-apatite phosphoheyphane. The border between the composition field is 20 atom% substitution of calcium for lead (Anthony Kampf, *personal communication*).

Figure 45. Unusual barrel shaped vibrant green pyromorphite crystals to 3 mm from the opencut above Driggith mine.

QUARTZ, SiO_2

Quartz is the commonest gangue mineral in the Caldbeck Fells and is abundant at both of the mines where it makes up most of the dumps. Cavities lined with stumpy pyramidal crystals are common and 'hacked' quartz, possibly produced by the dissolution of baryte is abundant.

RAMSBECKITE $(Cu,Zn)_{15}(SO_4)_4(OH)_{22}.6H_2O$

Ramsbeckite was reported by Green *et al.* (2001) at both Driggith and Sandbed mines as emerald green pseudo-orthorhombic crystals with schulenbergite and posnjakite in carbonate veins in massive sulphides. In common with other localities in the British Isles these appear to have formed by post-mining oxidation. The crystals from Sandbed mine, which reach 2 mm in length, are among the largest known from the British Isles.

REDGILLITE, $Cu_6(OH)_{10}(SO_4).H_2O$

Acicular crystals of redgillite up to 0.3 mm long of a characteristic light green colour occur rarely in thin fractures in sphalerite-rich veinstone with partly oxidised copper sulphide minerals (Figs 46 and 47). On a number of specimens, the redgillite has been overgrown by black covellite aggregates, which crystallised after the material was collected. On most specimens redgillite is present in thin fractures and cavities without any other supergene species in direct association. Langite is commonly found nearby and linarite and cerussite are sometimes present on the same specimens. Redgillite was identified by comparison of its EDS spectrum with undoubted redgillite from the type locality, this together with its characteristic colour is sufficient to identify it, since it has a unique Cu:S ratio for a green supergene copper sulphate (Pluth *et al.*, 2005).

Figure 46. Pale feathery green redgillite crystals up to about 0.2 mm long with a recent overgrowth of a black copper sulphide from Driggith mine. Neil Hubbard collection.

ROMANÈCHITE

Two specimens from Driggith mine and one from Sandbed mine which had crusts of a black manganese oxide on vein quartz were examined by XRD. The analyses indicated that they were the barium manganese oxide romanèchite. Romanèchite is very common in the lead veins of the northern Caldbeck Fells, almost all of the black manganese oxides examined from the nearby Dry Gill mine in a parallel study proved to be romanèchite.

ROSASITE, $(Cu,Zn)_2(CO_3)(OH)_2$

Rosasite is widespread but uncommon at both Driggith and Sandbed mines, it occurs in zinc-rich veinstone associated with philipsburgite, hemimorphite and adamite (Fig. 48). It was identified in this study by XRD and EDS.

Figure 47. Acicular redgillite crystals up to about 0.1 mm long from Driggith mine.

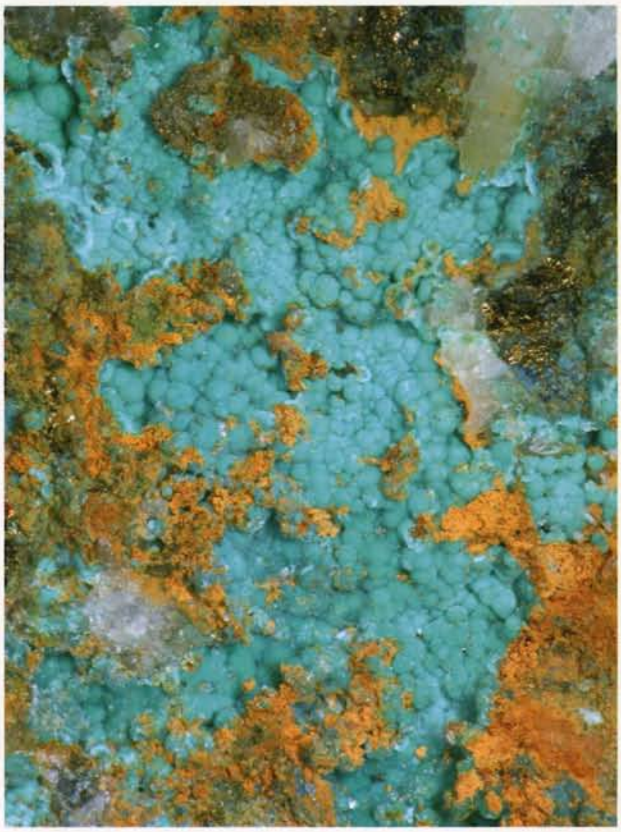


Figure 48. Rosasite balls to 0.4 mm, originally mis-identified as pseudomalachite, from Driggith mine.

Small blue-green wart-like aggregates of rosasite were reported from both the Driggith and Sandbed mines by Kingsbury and Hartley (1957b). This was the first British record of the mineral. Kingsbury donated five specimens of rosasite, supposedly from Driggith mine, to the NHM, but surprisingly, there is no material in his personal collection. On three of the specimens (BM 1958,72, BM 1956,64, BM 19558,71), tiny sub-millimetre rosasite spherules and radiating colourless hemimorphite coat iron stained quartz. These specimens look very like undoubted material from the Caldbeck Fells, although there is always a possibility that they may be from Roughton Gill mine rather than Driggith mine. The fourth specimen, BM 1958,73, supposedly from the 12-fathom level at Driggith mine is a superb rosasite specimen with rich warty crusts on glassy cerussite crystals and massive galena. It is unlike anything otherwise reported from the Caldbeck Fells. The fifth specimen, BM 1958,74, labelled from the Driggith 30-fathom level, is 45 mm across and totally covered in small spherulitic masses of a deep blue rosasite. The individual spherules are sub-millimetre in size but so densely packed that the entire specimen is bright caledonite-blue. It is unlike anything else reliably claimed from Driggith mine and is one of the richest specimens of rosasite in the NHM. It is likely to be fraudulent.

Figure 49. Typical blue-green schulenbergite rosettes up to 0.25 mm across with pale blue linarite from Driggith mine. Mike Leppington collection.

SCHULENBERGITE, $(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}$

Schulenbergite is widespread but uncommon as foliated pale green to pale blue hexagonal crystal aggregates up to about 1 mm across in crusts of supergene minerals produce by the post-mining oxidation of copper and zinc sulphides (Figs 49 and 50) (Green *et al.*, 2001). Analyses by EDS suggest some of the specimens are zinc-dominant and they probably correspond to the as yet un-named zinc analogue of schulenbergite (Livingstone *et al.*, 1992). It is difficult to prepare adequate samples for analysis by WDS, further work on this interesting mineral group is required.

Figure 50. Thin platy schulenbergite crystals a few tens of micrometres across from Driggith mine.

SCORODITE, $FeAsO_4.2H_2O$

Scorodite occurs abundantly as brown to yellow-brown drusy encrustations with barium-pharmacosiderite, beudantite, carminite and minor mimetite on specimens from arsenate-rich outcrop workings on the vein between the Driggith and Sandbed mines (Fig. 51). Epimorphs of scorodite with the characteristic blocky habit of arsenopyrite occur on a few specimens. Scorodite is present at a small trial below the Sandbed 90-fathom level workings and in small area to the west of the Driggith opencut. It has also been found as yellow-brown coatings and encrustations, some pseudomorphing a rhombohedral phase, at a small bell-pit near the Howthwaite trial.

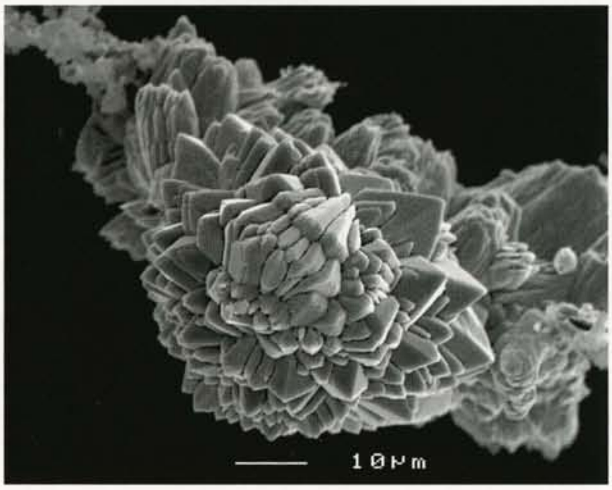


Figure 51. Well formed scorodite crystals up to about 10 µm across from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

SEGNITITE, $PbFe_3H(AsO_4)_2(OH)_6$

A yellow powdery cellular boxwork (Fig. 52) from the arsenate-rich area in the opencut above Sandbed mine produced a good match to segnitite when examined by XRD. Complex substitutions are possible within and between the members of the beudantite and crandallite groups (Mandarino, 1999) and the effects they have on the XRD patterns are not well documented, so XRD alone is not a reliable guide to the particular species that is present. Quantitative chemical analyses by WDS showed that some specimens were sulphate-rich segnitite and others were arsenate-rich beudantite. Beudantite-segnitite commonly encrusts and replaces mimetite and is itself overgrown by carminite in specimens collected from the arsenate gossans exposed in the opencut between the Sandbed and Driggith mines (Fig. 53).

Figure 52. Cellular porous powdery segnitite from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

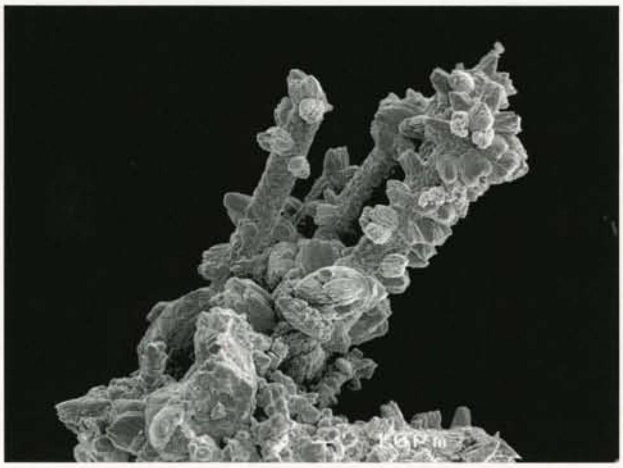


Figure 53. Tubular epimorphs of beudantite-segnitite after mimetite up to about 1 mm long overgrown by carminite from an arsenate-rich gossan in the opencut between the Driggith and Sandbed mines.

SERPIERITE, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6.3H_2O$

Serpierite was reported by Kingsbury and Hartley (1957c) as aggregates of tiny pale blue crystals on altered chalcopyrite-sphalerite matrix. According to Cooper and Stanley (1990), the specimens in the Kingsbury collection are typical of dump-formed serpierite so there is probably no reason to doubt their authenticity. Serpierite has been found recently as pale blue lath-like crystals with brochantite, linarite and langite in crusts surrounding clasts of copper and zinc-rich ore at both Driggith and Sandbed mines.

SILVER, Ag

Minute silver dendrites were found associated with cerussite on a specimen in the David Middleton collection from Driggith mine (Cooper and Stanley, 1990). Some of these have altered to spiky acanthite, after they were collected. Since this alteration occurred subsequent to collecting acanthite cannot be considered as part of the natural mineral assemblage.

SMITHSONITE, $ZnCO_3$

Smithsonite was reported by Cooper and Stanley (1990) at both Driggith and Sandbed mines on the basis of earlier reports including Davidson and Thomson (1951) and Day (1928). They note that some of the early records might be mis-identifications of hemimorphite. White and brown to yellow-brown rice-grain crystal aggregates were identified by EDS in this study at both Driggith and Sandbed mines. Smithsonite was recently identified on a specimen from Sandbed mine as yellow-brown pseudomorphs and epimorphs of minute curved crystals that appear to be replacing dolomite.

Specimens from Kingsbury's personal collection or donated by Kingsbury to the NHM which contain smithsonite have been described previously under aurichalcite and rosasite. They are almost certainly fraudulent.

SPHALERITE, ZnS

Sphalerite is probably the most abundant sulphide mineral present on the dumps at both mine sites and is a major component of the primary assemblage. It occurs rarely as black, dark brown and red-brown crystals with a resinous lustre in cavities in massive sphalerite and quartz veinstone.

STRASHIMIRITE, $Cu_8(AsO_4)_4(OH)_4.5H_2O$

Pale blue to blue-green crusts composed of minute lath-like crystals which contain only copper and arsenic were identified by XRD as strashimirite. Strashimirite appears to be restricted to the 'erythrite-assemblage' found on the 60-fathom level dumps of Sandbed mine.

SULPHUR, S

Sulphur occurs as transparent pale yellow globular crystals to 0.5 mm in fractures in slightly oxidised galena at both Driggith and Sandbed mines.

Susannite, $Pb_4(SO_4)(CO_3)_2(OH)_2$

Pale blue rhombohedral crystals up to about 0.3 mm long, which are probably susannite, are present on a specimen in the Mike Leppington collection. Their small size precludes definite identification.

TETRAHEDRITE, $(Cu,Fe)_{12}Sb_4S_{13}$

Argentian tetrahedrite was recorded as inclusions and grains in quartz and galena at Driggith mine by Stanley and Vaughan (1981). It was identified by XRD at the British Geological Survey on material from the 60-fathom level dumps at Sandbed mine (Mike Leppington, *personal communication*). Tetrahedrite is found at Sandbed mine as inclusion-free masses up to 200 µm across surrounded by chalcopyrite. It also occurs in larger rounded masses up to several millimetres across.

One of the specimens that was examined by reflected light microscopy was analysed by WDS. There are significant chemical substitutions. The chemical formula, determined as an average of six analyses, calculated on the basis of thirteen sulphur atoms per formula unit is:

$$(Cu_{9.62},Fe_{1.07},Zn_{0.87},Ag_{0.51})_{\Sigma=12.07}(Sb_{3.14},As_{0.99})_{\Sigma=4.13}S_{13}.$$

This is in excellent agreement with the idealised tetrahedrite formula, $(Cu,Fe)_{12}Sb_4S_{13}$, if silver and zinc are allowed to substitute for Cu or Fe and As for Sb. These substitutions are well known in natural material where tetrahedrite forms solid solutions with friebergite (silver substitution) and tennantite (arsenic substitution) (e.g. Anthony *et al*., 1990).

Tennantite, $(Cu,Fe)_{12}As_4S_{13}$

Tennantite-tetrahedrite was recorded at the 30-fathom level dump of Driggith mine by Hartley (1984) and from this and the 12-fathom level dump in an unpublished manuscript by Kingsbury according to Cooper and Stanley (1990). Tennantite-tetrahedrite intermediates are not easy to characterise by XRD alone and the record is based on Kingsbury specimens which we have not been able to find. It should be treated with caution.

Turquoise, $CuAl_6(PO_4)_4(OH)_8.4H_2O$

Turquoise was reported by Hartley (1984) from Driggith mine on the basis of a specimen in the Kingsbury collection. In Kingsbury's manuscript notes, a specimen with the analysis code K53/80 is recorded as being identified as turquoise by Jack Hartley in 1953. On Kingsbury's label the name has been altered to the variety 'rashleighite'. The specimen, which Kingsbury claimed to have found on 30-fathom level dumps at Driggith mine in 1953, consists of a pale, apple green, thin coating on massive crystalline quartz. It exactly matches specimen BM 1964R,8735 in the Russell collection from Castle-an-Dinas mine in Cornwall, a locality that would have been well known to Kingsbury. The single specimen represents the only record of turquoise from any locality in the Caldbeck Fells. It is undoubtedly fraudulent. Turquoise should be deleted from the list of species from the Driggith mine.

WROEWOLFEITE, $Cu_4(SO_4)(OH)_6.2H_2O$

Wroewolfeite has been identified by XRD as blue blocky to elongated prismatic crystals up to 0.5 mm long with langite on iron stained quartz veinstone at both Driggith and Sandbed mines. It typically occurs a component of the blue sulphate-rich crusts that are produced by post-mining oxidation.

Wulfenite, $PbMoO_4$

Wulfenite was reported from the outcrop workings between Sandbed and Driggith mine in an unpublished manuscript by Kingsbury and Hartley as "*minute yellow plates (0.5 – 2 mm) ... implanted on yellowish-green pyromorphite and mimetite*" (see also Cooper and Stanley, 1990). Only one specimen from this locality (broken into many fragments) is specifically recorded by Kingsbury as wulfenite. On two of the fragments lemon yellow crystals of wulfenite to 6 mm on edge are almost completely buried in canary yellow pyromorphite-mimetite. The crystals are remarkably large for the Caldbeck Fells (and do not match even with Kingsbury's own description) and the discovery has not been corroborated by other collectors. In spite of the fact that it is relatively widespread in the Caldbeck Fells, Kingsbury's claimed occurrence of wulfenite between Driggith and Sandbed mines must be treated with great caution and is likely fraudulent. The mineral should be deleted from the list of species from the site.

YARROWITE, Cu_9S_{58}

Yarrowite occurs in alteration rims, 5 to 20 µm wide, surrounding chalcopyrite from the 60-fathom level dumps at Sandbed mine. It is associated with digenite and limonite.

ZÁLESÍITE, $CaCu_6[(AsO_4)_2(AsO_3OH)(OH)_6].3H_2O$

Seventeen specimens labelled 'agardite' were examined by EDS in this study. Agardite is a member of the mixite group of minerals and there are a large number of possible substitutions at the A-site (defined by Mandarino, 1999) including calcium, lead and the rare earth elements. If the rare earth elements are dominant the minerals are agardite, if calcium is dominant they are zálesíite and if lead is dominant they are plumboagardite. All three cations were detected by EDS in specimens from Driggith and Sandbed mine.

In a few specimens from both Driggith and Sandbed mine, calcium was the only cation in addition to copper which was detected. These can be identified unequivocally as zálesíite (Figs 54 and 55). Zálesíite occurs as radiating sprays of highly elongated to acicular pale green to apple-green hexagonal prisms up to 0.6 mm long in cavities in iron-stained quartz. It is commonly associated with malachite and sometimes found with partly oxidised ankerite or dolomite and manganese oxides.

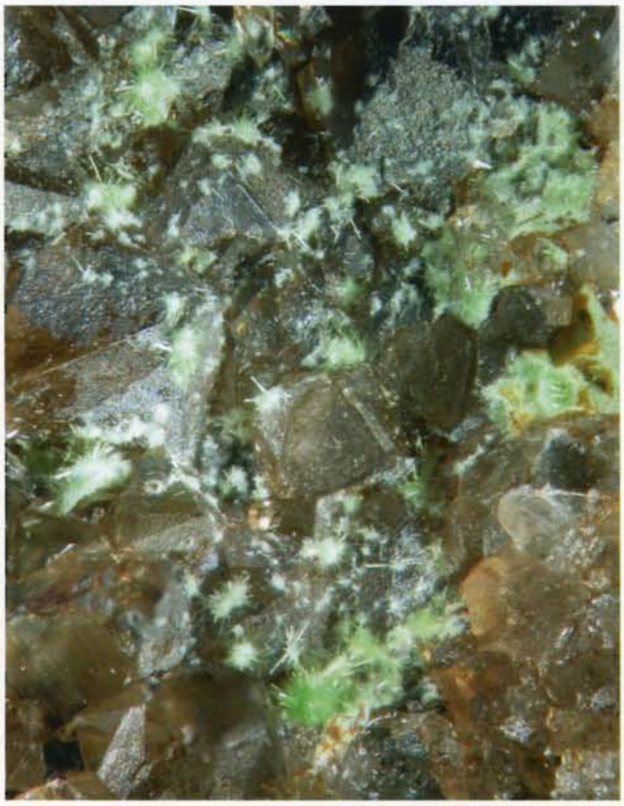


Figure 54. Green radiating feathery sprays of zálesíite up to 0.15 mm long from Sandbed mine. Mike Leppington collection.

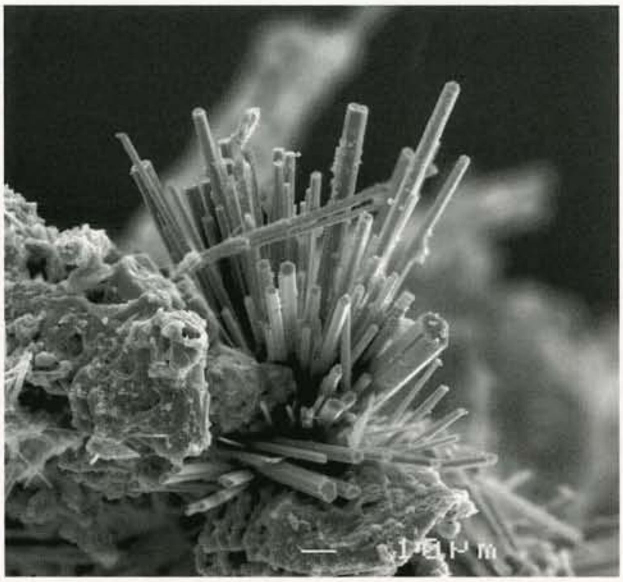


Figure 55. A radiating spray of hexagonal acicular zálesíite crystals 50 µm in length from Driggith mine.

UNIDENTIFIED OR POORLY CHARACTERISED MINERALS

A number of species that could not be characterised came to light during this study. In most cases they were too small or rare for further progress to be made with the techniques available. Some appear to be candidates for new minerals while others may be mixtures or are simply amorphous. It seems worthwhile recording the data as an aid to future research.

Amorphous Cadmium Sulphide

Bright yellow crusts and patches in fractures and cavities in sphalerite-rich matrix are relatively common at both Driggith and Sandbed mines. Analyses by EDS show that these contain cadmium and sulphur. Careful analysis of several specimens by XRD showed that the cadmium sulphide crusts are amorphous. There is no indication of any crystalline structure. The crusts at Driggith and Sandbed mines occur in thin fractures in zinc-rich matrix and appear to have formed by the supergene oxidation of cadmium-rich sphalerite. Amorphous cadmium sulphides, which appear to have formed in a similar way, have been recorded from a number of mines in the northern Pennines (Young *et al.*, 1987).

Copper-dominant Adamite

Although they have similar chemical formulae, adamite has an orthorhombic structure, while olivenite is monoclinic. In the olivenite-adamite solid solution series, crystals only adopt the monoclinic olivenite structure until about 20 atom% Zn is substituted, the structure then changes to the orthorhombic adamite type. This leaves a series of compositions between 20 atom% Zn and 50 atom% Zn where another species name is required. Some of the green copper-rich adamite specimens from Driggith and Sandbed mines have compositions which lie within this range. We have recorded composition up to $Cu_{1.5}Zn_{0.5}(AsO_4)OH$ at Sandbed mine which have an adamite structure.

Potassium-dominant Lavendulan

A sky-blue mineral that forms hemispherical aggregates up to a few tenths of a millimetre across occurs on a few specimens from the 60-fathom level dumps at Sandbed mine. It has an XRD pattern almost identical to lavendulan, $NaCaCu_5(AsO_4)_4Cl.5H_2O$. Examination of a number of fragments by EDS in this study showed that the mineral contained Ca, Cu, As and Cl in the correct ratios for lavendulan, but there was no sodium. Significant potassium was detected in every case so it seems possible that the mineral is a potassium analogue of lavendulan. However, the EDS detector used to collect the spectrum is not particularly Na-sensitive, and it may be that the 3 wt% Na_2O in lavendulan would simply not register. Unfortunately, the size and shape of the individual crystallites (Fig. 56) does not allow further study with techniques currently available to us.

Copper Zinc Sulphate

A mineral with a glaucocerinite-like XRD pattern was identified on a single specimen from the 30-fathom level at Driggith mine as pale blue foliated crudely hexagonal crystal aggregates up to 0.6 mm across associated with anglesite. The perfect cleavage meant that only diffraction peaks of the form {0.0.n} were registered in the powder diffraction pattern. These are similar, but not identical to the peaks produced by glaucocerinite $(Zn,Cu)_{10}Al_6(SO_4)_3(OH)_{32}.18H_2O$.

Analyses of several fragments by EDS only revealed the presence of zinc, copper and sulphur, with no aluminium. The mineral appears to be an unknown zinc copper sulphate with a structure related to glaucocerinite (Fig. 57).

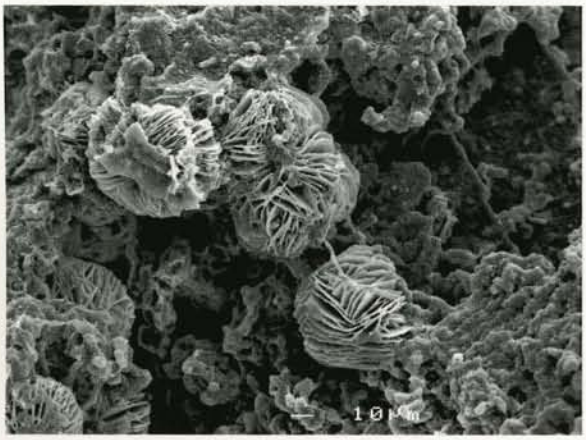


Figure 56. Small spherules of a potassium-rich lavendulan up to about 0.2 mm across from Sandbed mine.

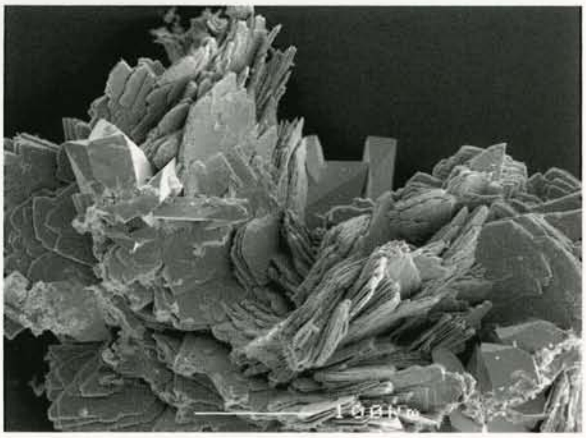


Figure 57. An as yet unidentified zinc copper sulphate with a structure related to glaucocerinite and schulenbergite.

Zinc Arsenate

Rounded white radiating crystal aggregates in the Tim Neall collection, which SEM shows to be composed of minute lath-like crystals, appear to be an as yet unidentified zinc arsenate. Their XRD pattern is distinct from any known mineral and does not match any artificial zinc and arsenic bearing phase in the JCPDS index.

Lead Copper Sulphate

Pale blue feathery masses of a lead copper sulphate mineral were found with elyite, caledonite and chenite on several specimens in the Neil Hubbard collection (Fig. 58). The morphology of the crystals makes analytical studies particularly difficult. Fragments which were embedded and polished for analysis by WDS gave significantly different results, however the data is sufficiently reliable to show that the mineral is an as yet uncharacterised lead copper sulphate.

Figure 58. Pale blue feathery crystals of an undescribed lead-copper sulphate from the 12-fathom level at Driggith mine. Neil Hubbard collection.

Zinc Copper Iron Arsenate Sulphate

A green to yellow green crust in the 'erythrite'-rich matrix appears to be a mixture of a mineral with an erythrite structure and parnauite. When examined by SEM the crust is resolved into minute lath-like crystals much less than a micron in thickness. Analyses by EDS indicate the presence of zinc, copper, iron, arsenic and sulphur. Although the data is consistent with a mixture of parnauite and a parasymplesite-kottigite intermediate, both of which have been reported from Sandbed mine, the SEM images show one distinct phase and spot analyses always show the presence of all of the elements together rather that zinc, iron and arsenic, and copper, arsenic and sulphur, as would be expected if the crust was a mixture.

Copper sulphate

A few specimens from Sandbed mine display eggshell-blue crusts of an unknown copper sulphate. The crust is made up of minute lath-like crystals. As yet insufficient material is available for a full analysis.

DISCUSSION

A significant number of new species have been recorded at the Driggith and Sandbed mines since Cooper and Stanley published their review of the mineralogy in 1990. Minerals discovered as a result of this study include annabergite, aragonite, arsendescloizite, arseniosiderite, brianyoungite, cinnabar, clinochlore, connellite, djurleite, erythrite, gersdorffite, köttigite, lanarkite, lavendulan, olivenite, mawbyite, parnauite, pharmacosiderite, philipsburgite, pyrrhotite, redgillite, segnitite, strashimirite, wroewolfeite and zálesíite. Of these, brianyoungite, gersdorffite, lavendulan, parnauite, segnitite, yarrowite and zálesíite are described for the first time from the Caldbeck Fells and mawbyite for the first time in the British Isles. The first British arsendescloizite, which was recently noted by Neall *et al.* (2006) from Sandbed mine, is another result of our work. The discovery of köttigite at Sandbed mine, the first British locality for which is Hilton mine in Cumbria (see Bridges and Green, 2006) is also noteworthy.

The Kingsbury frauds have seriously compromised previous descriptions of the mineralogy of the Driggith and Sandbed mines. Of the fifty-six species listed by Cooper and Stanley (1990) from Driggith mine, allophane, chalcanthite, chlorargyrite, conichalcite, phosgenite, planchéite, pseudomalachite, turquoise and wulfenite, are almost certainly fraudulent and plumbojarosite and tennantite are in question. Of the thirty-one species listed from Sandbed mine, plumbogummite and pseudomalachite are also likely to be fraudulent. Readers should note that even this seemingly large number of questionable species still seriously underestimates the extent of the fraud since Kingsbury was particularly adept at guessing what ought to occur at a locality. His claimed adamite from Sandbed mine provides a good example: adamite certainly occurs at Sandbed mine and was found there in the 1980s by a number of collectors, but Kingsbury's specimens, which were claimed as the first British in the 1950s, are from Lavrion in Greece. Kingsbury clearly falsified the locality data associated with many of his better examples of more common species. These include fine specimens of aurichalcite, brochantite, cerussite, leadhillite, linarite and malachite, many of which have been unwittingly described by subsequent authors as the best examples from the locality (*e.g.* Cooper and Stanley, 1990). The scale and complexity of the fraud is such that the only reasonable course of action is to quarantine any report either by Kingsbury or based on specimens in the Kingsbury collection. Kingsbury records should be assumed to be fraudulent unless they are proven otherwise.

Several distinct supergene assemblages can be distinguished in the material from the mines. There is a coarsely crystallised supergene assemblage present on most of the dumps, which is dominated by cerussite, hemimorphite, mimetite, malachite, pyromorphite and includes minerals such as adamite, aurichalcite and bayldonite. These are common and thermodynamically stable phases in the conditions encountered at the surface of the earth. This assemblage is similar to many of the evolved supergene assemblages from the Caldbeck Fells (*e.g.* Cooper and Stanley, 1990) and is typical of the weathering of low temperature lead-zinc-copper veins in low carbonate environments. It is produced by supergene oxidation over significant periods of geological time, producing relatively simple, coarsely crystallised assemblages.

Another assemblage is post-mining in origin as it occurs on fracture surfaces on fragments of ore in the dump. It includes the basic copper sulphates langite, wroewolfeite and posnjakite as well as ramsbeckite, schulenbergite, brochantite and linarite, which form as blue to green crusts. The post-mining assemblage records the chemical alteration which takes place in mine dumps over a relatively short time period. Some of the phases may be important as buffers for heavy metals leaching into the environment.

The arsenate gossans characteristically comprise major scorodite, beudantite-segnitite and pharmacosiderite or barium-pharmacosiderite, with minor carminite and arseniosiderite and are closely associated with significant quantities of partly oxidised arsenopyrite. A small collection of arsenate-rich material donated by George Wilson is preserved in the Manchester Museum under accession numbers N14636 to N14641. A diffuse arsenic anomaly (several kilometres square) was identified by Plant *et al.* (1991) at the northern edge of the Caldbeck Fells; it seems likely that this is derived from weathering of the type of deposits we have identified. Arsenopyrite and iron sulphides are present in the volcaniclastic rocks at several localities, some of which appear to be well removed from known veins. These sulphide minerals almost certainly have a different origin to the later hydrothermal lead–zinc–copper veins. Further investigation of this assemblage would be worthwhile.

The much rarer cobalt- and nickel-rich supergene arsenate mineralisation produced by the oxidation of gersdorffite is quite distinct from that produced by the arsenopyrite iron sulphide assemblage. It contains erythrite, annabergite and köttigite with strashimirite and a lavendulan-like phase. Specimens are uncommon and more or less restricted to the 60-fathom level dump at Sandbed mine.

Our research on the mineralogy of the Sandbed and Driggith mines has added a considerable number of species to the minerals known from the sites, it has cast doubt on others and conclusively shown that a significant number, including many Kingsbury frauds, should be deleted from the list. This is worthwhile in any science such as mineralogy which relies on well provenanced specimens with good locality data to make progress. Our research has drawn on many collections, public and private and has greatly benefited from several field visits. We have attempted to be as comprehensive as possible, but as with any similar endeavour, we have only summarised the data available up to a point in time, in this case mid-2006. There is considerable scope for future research and it would be surprising if further interesting discoveries were not made.

ACKNOWLEDGEMENTS

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Hodgson) are thanked for giving permission to examine the sites and collect specimens. Many of the rare species described here were in the collection of Mike Leppington who generously gave access to his extensive holdings of micromount and larger specimens. Thanks are due to Tom Cotterell of the National Museum of Wales for information on specimens in the King collection and also to Alan Hart and Chris Stanley at the Natural History Museum for discussions and information relating to previous work regarding Arthur Kingsbury's collection. Private collections belonging to Richard Bell (also comprising material from the late Mike Rothwell and John Dickinson), Richard Belson, Norman Thomson, George Wilson, Neil Hubbard, David Middleton, Tim Neall, Peter Todhunter and Max Wirth were also examined, and all added to the article. Many of the best specimens we examined were in the collections of the late Mike Rothwell and John Dickinson, it is sad that they did not see the publication of this article.

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A REVIEW OF THE MINERALOGY OF BRAE FELL MINE, CALDBECK FELLS, CUMBRIA

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Brae Fell mine in the Dale Beck valley of the Caldbeck Fells exploited an approximately east-west lead-copper-zinc-quartz vein at two levels. Extensive oxidation has given rise to a wide range of supergene minerals. A detailed examination of well provenanced and recently collected material has been carried out to establish a reliable mineralogy for the site. In the course of this study, it has been concluded that several specimens claimed to have been collected by A.W.G. Kingsbury are probably fraudulent, but all of the reported species except plumbogummite and susannite have been found, albeit in much smaller specimens. In addition, nine previously unreported species have been identified, the most interesting being native silver and mottramite.

INTRODUCTION

Brae Fell Mine is also referred to as Braefell (Shaw 1970; Young 1987) and in the Kingsbury collection in the Natural History Museum (NHM) as Brae-fell. Cooper and Stanley (1990) refer to the site as Brae Fell and for consistency with this major work, that is the name used here. While Brae Fell Mine is not as well known as localities such as Roughton Gill, Dry Gill and Red Gill mines, it has long been a source of interesting mineral species. A.W.G. Kingsbury claimed to have collected numerous specimens from the dumps in the 1950s and Hartley (1984) summarised many of these in a listing of species from the Caldbeck Fells. There are over 20 Brae Fell specimens in the Kingsbury collection in the Natural History Museum (NHM), but it is now an established fact that some of Kingsbury's specimens were fraudulent (Ryback *et al.*, 1998 & 2001). In addition, recent research has identified several species from the site that have not been previously recorded. For these two reasons it has been decided to prepare this review to present an up to-date reliable mineralogy for the site.

LOCATION, GEOLOGY AND HISTORY

Brae Fell Mine is one of a series of mines in the Dale Beck valley in the northern Caldbeck Fells. These include Roughten Gill Mine, Red Gill Mine and several others including the Silver Gill workings. The last is the subject of a paper by Green, *et al*, (2005) and the intention is to describe the mineralogy of the other mines in future work.

Brae Fell Mine sett is situated on the west side of the Dale Beck valley, just above the junction with Hay Gill. Two levels, both long collapsed, have been driven into the hillside at NY 2983 3569 for the upper level and NY 2988 3566 for the lower level. Spoil heaps jut out of the hillside from both levels and below the lower heap there is an extensive area of quartz mineralisation which may have been a sorting area. Below these features is a flat area, which was possibly a dressing floor or small mill. Above the site there is a small dam and prominent hushes extend down the hillside on either side of the spoil heaps. In the hush to the north of the site at NY 2976 3571 is the top of a shaft, which may be how the vein was found or possibly a ventilation shaft (Shaw, 1970).

The two spoil heaps are markedly different. The smaller upper heap consists of quartz vein material in a mass of soft highly degraded sandy clay, typical of the gouge and altered rock associated with many mineral veins. The larger lower heap appears to be a mass of grey-green fine grained lavas of the Eycott Volcanic Group. It is likely, but not proven, that this is a covering on material similar to the upper heap. The whole of the hillside surrounding the site is covered with a thick layer of glacial till and there are no exposures of the underlying rocks nearby.

Little is known about the history of the mine. Shaw (1970) states that no plans are in existence and it is not known when the main period of working occurred, but that the levels were being cleaned out in 1866 by the Red Gill Mining Company. Since no work followed this activity, presumably no worthwhile ore was found.

METHOD

Material in old collections cannot usually be relied upon since locations are often vague or non existent. This study has been made using specimen material, of reliable provenance, collected from the site over the past

30 years. In addition a Russell Society visit to the mine site was made in 2004, with the approval of the Lake District National Park Authority (LDNPA). Comments on the abundance of minerals at the site are made on the basis of this visit.

Specimens were initially inspected using a stereomicroscope. The identification of some common minerals such as quartz and galena was made visually, confirmed in some cases by physical tests. Beyond this, wet chemistry was used to confirm a few species such as linarite. Where further work was merited, minute fragments were detached and mounted on a stub for analysis by EDS. Confirmation of the rarer species was by XRD.

THE MINERALS

Mineral names in italics have not been confirmed in the current study.

ANGLESITE, $PbSO_4$

Greg and Lettsom (1858) reported anglesite from Brae Fell Mine and Hartley (1984) refers to it without description on the basis of material collected by Arthur Kingsbury. Cooper and Stanley (1990) refer to a specimen in the King Collection in the National Museum of Wales (NMW). This specimen consists of a mass of cream to black bladed anglesite sections to 25 mm, with smaller terminated crystals, associated with galena, cerussite, pyromorphite and quartz. It was collected in about 1948 by R.J. King and came from a block situated a little to the south of the upper dump (R.J. King, *personal communication*). The Kingsbury collection in the Natural History Museum (NHM) contains a single specimen from 'Brae-fell mine' collected in 1950 and consisting of 7 mm brownish blades on matrix.

Anglesite is now relatively rare on the dumps, but can still be found as small sword shaped bladed crystals and blocky rhombic tablets, both usually up to about 2 mm across, often associated with cerussite and occasionally bindheimite.

BARYTE, $BaSO_4$

The Kingsbury collection contains a specimen consisting of a slab of quartz with galena, coated on one side with a layer of thin platy crystals resembling one form of cerussite. Other specimens, collected by Kingsbury, have small fragments of massive baryte associated with other minerals. All are typical of the mine and there seems to be no reason to doubt their provenance.

Primary baryte is now relatively rare on the dumps but does occur as white bladed crystals up to 20 mm long and as crystalline masses in quartz. Small (c.1 mm) transparent colourless and white opaque diamond shaped crystals are more common, occurring in cavities in quartz. They are very similar to one form of anglesite, but baryte was confirmed by EDS. At least some of these crystals are supergene in origin since they occur on top of limonite and, in one case, enclose a copper supergene mineral, probably malachite or brochantite.

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Powdery yellow coatings of bindheimite, often associated with cerussite and sometimes with anglesite, are common in cavities in quartz, mainly from the lower dump. Confirmation of the identity was by EDS, the only elements detected being lead and antimony.

BROCHANTITE, $Cu_4(SO_4)(OH)_6$

Brochantite is rare on the spoil heaps, but does occur as bright emerald green crystalline crusts associated with linarite on quartz and as earthy green coatings on oxidising copper suphides. Confirmation was by XRD.

CALCITE, $CaCO_3$

Calcite is uncommon, but occurs as a fissure infilling in blocks of the lava on the lower spoil heap, where it may be derived from alteration of the lavas.

CALEDONITE, $Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$

Listed by Hartley (1984), caledonite is present on a specimen of lanarkite in the Kingsbury collection in the NHM (see later). Cooper and Stanley (1990) record caledonite as small crystals and masses with linarite from the dumps and from the foot of the 'hush' to the north of the lower dump.

Caledonite is rare on the site, but still occurs as small (up to 1 mm) prismatic blue crystals, minute crusts of radiating needles and as small masses in other minerals. It is usually associated with leadhillite and cerussite.

CERUSSITE, $PbCO_3$

Cerussite was first recorded from 'Bray Fell' by Greg and Lettsom (1858) and Cooper and Stanley (1990) record the mineral from both dumps. They note large crystals (<20 mm) from the upper dump. The Kingsbury collection in the NHM contains nine cerussite specimens. These are usually associated with other minerals such as pyromorphite and malachite. Crystals are mostly 'jackstraw' type, but some are small plates or massive pieces in quartz matrix. The colour varies from transparent to pale blue/green, similar to material found in the current study (see below). Several of the specimens are better than those available on the dump surface today, but none are other than typical of the site.

Cerussite remains very common at Brae Fell and occurs on both dumps. Cavities in quartz are often lined with small tabular crystals, but these can reach 10 mm in length. Twinned crystals are common and 'jackstraw' crystals occur. The colour is usually white to nearly transparent, but occasionally is dark grey to black, due to inclusions which are probably residual galena. Pale blue crystals occur and we have shown that the colouration is due to minute inclusions of linarite. Cerussite is frequently associated with pyromorphite. Rarely the cerussite is considered to have pseudomorphed flat plates of hydrocerussite.

CHALCOPYRITE, $CuFeS_2$

Chalcopyrite is recorded from the site by both Hartley (1984) and Cooper and Stanley (1990). It is still fairly common as small masses in quartz.

CHRYSOCOLLA, $(Cu,Al)_2H_2Si_2O_5(OH)_4.nH_2O$

Hartley (1984) lists the mineral from Brae Fell, but the specimen does not seem to be in the Kingsbury collection. Pale turquoise amorphous looking waxy crusts with baryte in the Mike Leppington collection have been shown by EDS to contain Cu, Si and minor Al and are probably chrysocolla.

COVELLINE, CuS

Covelline is fairly common occuring as iridescent purple to black coatings and crusts, which can reach a thickness of 0.3 mm, on quartz, galena and chalcopyrite.

CUPRITE, Cu_2O

Cooper and Stanley (1990) report cuprite in small amounts associated with 'chrysocolla' on a specimen in the M. Leppington collection. This specimen consists of very small bright red masses in cerussite. It remains a very rare mineral on the site with only two other known specimens, consisting of slightly larger red patches in cerussite and quartz.

GALENA, PbS

Galena is common on the dumps, mainly as small masses in quartz, but occasionally as crystals in cavities. It was presumably much more common at one time.

GOETHITE (LIMONITE), FeO(OH)

Brown coatings and powdery crusts of hydrated iron oxides are common on the dumps and are best described as limonite. Occasionally hard botryoidal crusts occur on quartz and these are probably goethite.

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2.H_2O$

The presence of hemimorphite at Brae Fell was noted by Cooper and Stanley (1990). It occurred as a thin, minutely drusy, white coating on quartz. It is very rare, but has been noted as small (0.5 mm) very pale blue balls in a cavity in quartz from the top dump and as small colourless radiating blades in quartz, confirmed by EDS.

HYDROCERUSSITE, $Pb_3(CO_3)_2(OH)_2$

Hartley (1984) listed hydrocerussite from Brae Fell and there are two specimens in the Kingsbury collection, which appear to be from the same piece. One is associated with lanarkite and both are more typical of Leadhills/Wanlockhead than the Caldbeck Fells. Their provenance has to be doubted.

Hydrocerussite is rare, but occurs as small white crystals, usually associated with cerussite on quartz, oxidised galena matrix. The hydrocerussite is invariably partly altered to cerussite and complete pseudomorphs occur. Identification was by XRD (MANCH: XRD1097).

LANARKITE, $Pb_2O(SO_4)$

Listed by Hartley (1984), the Kingsbury collection contains 4 specimens of lanarkite (one as several small fragments), which purport to come from Brae Fell Mine. Kingsbury also gave a specimen to Arthur Russell, which has now been returned to the Kingsbury collection at the NHM. All are far better than anything found anywhere in the Caldbeck Fells in the last 30 years and on some the specimen and matrix are typical of the Leadhills district. (Mattheddleite is associated with most of the specimens). It is probable that these specimens are all fraudulent.

A single specimen has been found in the current study (M. Wirth collection, accession no. 1945). It consists of a 2 mm cavity in oxidised quartz/galena matrix containing 1 to 1.5 mm crystals with the morphology of lanarkite and having the appropriate optical properties. There is too little for XRD analysis without destroying the specimen.

LANGITE, $Cu_4(SO_4)(OH)_6$

A very rare mineral at Brae Fell, langite has only been positively identified on a single specimen in the M. Leppington collection (XRD, Leeds University). The specimen consists of minute (<0.5 mm) complex blocky crystals, associated with covelline.

LEADHILLITE, $Pb_4(SO_4)(CO_3)_2(OH)_2$

Hartley (1984) listed leadhillite from Brae Fell Mine and Cooper and Stanley (1990) report a superb specimen found by R.J. King in about 1948 (R.J. King, *personal communication*) and now in the NMW. This consists of abundant colourless to white thin platy to equant blocky crystals up to 5 mm across on well oxidised quartz veinstone. Mattheddleite is also present. The Kingsbury Collection (NHM) contains two leadhillite specimens, which seem similar to recently collected material. It is fairly rare on the dumps, but still occurs as small (c.1 mm) hexagonal prisms often associated with anglesite, caledonite, cerussite and linarite.

LINARITE, $PbCu(SO_4)(OH)_2$

Linarite is listed by Hartley (1984), but the specimen does not seem to be in the Kingsbury collection. Cooper and Stanley (1990) describe it as occurring as minute crystals and crusts on quartz-sulphide matrix. It is relatively common on the dumps as deep blue anhedral crystals flattened on quartz and occasionally as good small bladed euhedral crystals up to 2 mm long in cavities in quartz. Associated minerals include cerussite, caledonite, leadhillite and brochantite. In one specimen in the Tim Neall collection the linarite is partially replaced by brochantite or possibly caledonite.

MALACHITE, $Cu_2(CO_3)(OH)_2$

Malachite was first reported by Eastwood (1921), it is also noted by Hartley (1984) on the basis of material collected by Kingsbury. There are no specific malachite specimens in the Kingsbury collection although two cerussite specimens include malachite. It is common on the dumps in small amounts as green radiating crystals in cavities in quartz, often associated with chalcopyrite.

MATTHEDDLEITE, $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$

Cooper and Stanley (1990) report matthedleite on the leadhillite specimen in the King Collection (see above) and on the specimens of lanarkite in the Kingsbury Collection. It is a very rare mineral on the dumps, but has been found in the current study as minute (<0.2 mm) colourless lustrous needles associated with caledonite (Mike Leppington collection).

MOTTRAMITE, $PbCu(VO_4)(OH)$

Mottramite is not uncommon on the upper dump. Coatings of minute (<0.1 mm) rice-grain shaped crystals on quartz can cover areas several centimetres across. Colour varies from very dark brown to buff. It is often associated with pyromorphite and limonitic stains and occasionally with cerussite. Two very good specimens of the mineral were found on the top dump on the 2004 visit and it seems likely these had weathered out of the surface fairly recently. Confirmation was by XRD, supported by EDS. Some mottramite is zincian, but not rich enough to be descloizite.

PLUMBOGUMMITE, $PbAl_3(PO_4)_2(OH)_5.H_2O$

Cooper and Stanley (1990) report a specimen of blue-grey plumbogummite, partly epimorphous after pyromorphite, from the upper dump, in the Kingsbury collection in the NHM, but Hartley (1984) does not list it. The specimen seems very similar to some of the material from Dry Gill Mine and is probably fraudulent. The mineral has not been found in the current study and should be removed from the confirmed list of species from Brae Fell Mine.

PYRITE, FeS_2

Pyrite is much less common on the spoil heaps than chalcopyrite, but does occur as small flecks in quartz. The widespread occurrence of limonitic material may indicate much of the original pyrite has been oxidised.

PYROMORPHITE, $Pb_5(PO_4)Cl$ and MIMETITE, $Pb_5(AsO_4)Cl$

These two minerals are considered together, since they are closely related and visually indistinguishable. Pyromorphite has long been reported from Brae Fell Mine and early records are Eastwood (1921) and Shaw (1970). The Kingsbury collection includes one specimen of pyromorphite and two of mimetite all of which are typical of the site. Pyromorphite is also a common accessory mineral on several other Kingsbury specimens.

In this study, 16 specimens, with the morphology of pyromorphite/mimetite and with as wide a range of colour and crystal form as possible, were examined by EDS. One yellow specimen had an intermediate composition between pyromorphite and mimetite, but one yellow specimen and one green specimen appear to be near end member mimetite. In the remaining 13 specimens, arsenic could not be detected by EDS and they are near end member pyromorphite.

Like cerussite, with which it is commonly associated, pyromorphite (and some mimetite) remains very common on both of the dumps, but the specimens are mostly very weathered. The colour varies considerably from dark green to bright golden yellow. Cavities in quartz often contain good sharp euhedral crystals, but these rarely exceed 1 mm in length. Coatings of minute radiating crystals are common and hexagonal barrel shaped crystals and hemispherical crystals also occur.

ROMANÈCHITE, $(Ba,H_2O)_2(Mn^{4+},Mn^{3+})_5O_{10}$, (Wad)

Cooper and Stanley (1990) report 'psilomelane' from Brae Fell Mine, commenting that it is probably coronadite or romanèchite. Black manganiferous coatings on other minerals are common and without analysis are probably best described as wad. However, one example of a hard black coating on quartz has been shown to be romanèchite by XRD (MANCH:XRD1101).

QUARTZ, SiO_2

Quartz is by far the most abundant mineral on the dumps and was obviously the main constituent of the vein. It occurs as crystalline massive blocks with pyramidal crystals in cavities. Most of the other minerals occur on or in a matrix of quartz.

SCOTLANDITE, $PbSO_3$

A single specimen of a cluster of minute (<0.5 mm) chisel shaped crystals associated with corroded galena have the morphology of one form of scotlandite (Tim Neall collection). It is not possible to confirm the identity without destroying the specimen.

SILVER, Ag

Silver has been found as minute (c. 0.2 mm) subhedral masses in a 10 mm cavity in quartz (Mike Leppington collection). The cavity is coated in pale yellow powdery bindheimite. In storage, minute needles of acanthite have grown on the silver.

SPHALERITE, ZnS

Reported by both Hartley (1984) and Cooper and Stanley (1990), sphalerite is much less abundant on the dumps than galena or chalcopyrite. It occurs as small masses in quartz and as small brown euhedral crystals in cavities.

SULPHUR, S

Rare, but sulphur has been found as a crust of minute (0.2 mm) pale yellow crystals in oxidised galena, associated with small crystals of cerussite and anglesite (MANCH:XRD1098).

SUSANNITE, $Pb_4(SO_4)(CO_3)_2(OH)_2$

Cooper and Stanley (1990) note that a Kingsbury specimen in the NHM, collected in 1951, consists of tabular crystals to more than 10 mm, which were originally identified as leadhillite, but were later shown to be susannite. The specimen is an 8 by 6 cm mass of gossan and galena, with a cavity containing tabular crystals with the morphology of a common form of leadhillite up to 10 mm across. Quartz is nearly ubiquitous for specimen material from Brae Fell, but there is no quartz on this specimen. It also has an obvious 'museum patina' and is most unlikely to have been collected as recently as 1951. It is probably a 19th Century specimen from the Leadhills-Wanlockhead mining field.

Susannite has not been positively identified in the current study, but a specimen in the M. Leppington collection consists of a 1 mm pale blue hexagonal prism, with good basal cleavage, and may be susannite. Positive identification is impossible without destroying the specimen.

DISCUSSION & CONCLUSIONS

Based on material of reliable provenance, the mineralisation at the Brae Fell site is typical of the roughly E-W quartz, galena, chalcopyrite, sphalerite veins discussed by Cooper and Stanley (1990, p. 24), though zinc minerals are comparatively rare. Oxidation of the primary minerals has produced a suite of supergene minerals, typical of such vein systems with low carbonate content. Some of these may be post-mining in origin, but it is usually not possible to be sure of this.

Of the specimens in the Kingsbury collection at the NHM, the lanarkite and susannite are far better than anything anyone else has found in the Caldbeck Fells and, based on their appearance, almost certainly originate from the Leadhills-Wanlockhead mining field. This may also be true of the hydrocerussite claimed by Kingsbury. The plumbogummite is probably from Dry Gill Mine. All the other specimens appear typical of Brae Fell mineralisation and, while it is impossible to be certain, may well be genuine. However, with the exception of plumbogummite and susannite, all the species claimed by Kingsbury have been identified in this study, albeit in smaller specimens, so the true mineralogy of the site has not been unduly distorted by his claims.

Pyromorphite is often postulated as forming a series with mimetite. At Brae Fell phosphate is clearly much more abundant than arsenate and if they form a full series, arsenatian pyromorphites would be expected instead of the two near end member mimetites together with a single mid-range specimen found in this study. Similarly at Silver Gill where phosphorus is again dominant, Green *et al.* (2005) noted a single near end member mimetite specimen and no intermediates. This phenomenon is worth following up at other sites.

All the hydrocerussite specimens are at least partly altered to cerussite, a situation which is also common in the Leadhills-Wanlockhead mining field. Williams (1990, p.186) argues that hydrocerussite is the stable lead carbonate phase at atmospheric levels of carbon dioxide, but this seems at variance with these dump collected specimens which have been exposed to the weather. Taylor and Lopata (1984) in a detailed study at 25°C in aqueous media concluded that cerussite was slightly more stable than hydrocerussite in the atmosphere and this does seem to be more consistent with the field evidence.

The British Geological Survey 6 inch geological map of the area shows an approximately NW-SE trending fault line running for approximately 1.5 km across the hillside to the west of the site, mineralised at its SE end and within lavas of the Eycott Volcanic Group. The form and material on the two spoil heaps suggests the original miners worked the mineralised section on two levels until the vein pinched out. It seems that the lower level was then driven along the line of the fault, in the hard lavas, in the hope of finding further ore, but eventually the miners gave up. This would explain the difference in the content of the visible part of the two spoil heaps. It would be of interest to confirm this either by opening up the lower level or more easily by digging a small hole into the top of the lower heap to see if vein material typical of the upper heap is under the surface.

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A REVIEW OF THE MINERALISATION AT ARM O'GRAIN, CALDBECK FELLS, CUMBRIA

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A north-south trending quartz vein is exposed over a strike length of a few metres in scree on the east side of the Arm O'Grain valley in the Caldbeck Fells, Cumbria. The vein is extensively weathered, little remains of the primary mineralisation except quartz. A variety of supergene minerals including mimetite, pyromorphite, vanadinite, mottramite, duftite, plumbogummite and beudantite occur as microscopic crystals. The supergene lead-vanadium mineralisation is relatively rich; it includes the only definite occurrence of vanadinite in the Caldbeck Fells. There is extensive anionic substitution in the lead-bearing members of the apatite group and between mottramite and duftite. There is also considerable substitution of calcium for lead in the lead-bearing members of the apatite group. About 25 m south of the vein exposure, in the west bank of the beck, a rib of quartz-rich rock contains disseminated arsenopyrite and pyrite, which has oxidised on hairline fractures to brown crustose scorodite.

INTRODUCTION

Arm O'Grain beck is a small stream that runs somewhat east of south from boggy headwaters on Great Lingy Hill until it joins Grainsgill beck at NGR NY 317 331. A vein exposure on the east side of the valley about 300 m above the confluence with Grainsgill beck came to the attention of mineralogists in the 1970s when specimens of quartz covered in micro-crystalline mottramite were found. The vein is developed within igneous rocks of the Carrock Fell Complex, but it is difficult to be sure of the precise rock type. The exposure is poor and the wall rocks are weathered to regolith. Felsic and mafic rocks including microgranite, apatite-bearing ferrodiorite and gabbro are marked in the immediate area by the British Geological Survey (1997). Access to Arm O'Grain for collecting and research is currently managed by the Lake District National Park Authority (LDNPA).

A north-south trending manganese vein and an east-west trending lead vein are marked on a geological map of the area, based on the 1:50,000 map published by the British Geological Survey (BGS) in 1957, which is reproduced in Cooper and Stanley (1990, p.16). A vein trending east of south and described simply as "Tree Vein" is recorded on a sketch plan of Carrock Mine in Adams (1988, p.92), but there is no indication of any working on it. The most recent 1:50,000 scale BGS map plots a fault running somewhat east of south approximately parallel to Arm O'Grain at about the same point as the north-south vein marked on the 1957 edition; it does not indicate a western extension of the lead vein beyond Carrock mine (British Geological Survey, 1997).

Manuscript sources quoted by Cooper and Stanley (1990) indicate that a trial was driven in the latter part of the eighteenth century in the Arm O'Grain valley. Little is known of the history of the working, which is not even noted in the standard works on mining in the area (*e.g.* Postlethwaite, 1913; Shaw, 1975; Adams, 1988; Tyler, 2003).

Records of mineralisation in the Arm O'Grain valley are few. Manganese-bearing veins were noted by Day (1928), mottramite was reported on the basis of specimens in the Natural History Museum (London) by Young (1987) and beudantite, mimetite, pyromorphite-mimetite and wulfenite were added by Cooper and Stanley (1990). Arm O'Grain is one of the few localities in the Caldbeck Fells that was not known to Arthur Kingsbury. It does not feature on his annotated maps of the area and consequently the site is not subject to the careful checks that are required to verify the authenticity of records (see Ryback *et al.*, 1998, 2001). Arm O'Grain is not described in the summary of mineralisation in the Caldbeck Fells compiled by Jack Hartley (1984).

SURVEY

Russell Society members conducted a limited field survey in July 2006 with LDNPA permission. There is relatively little to be seen on the ground, which for the most part is covered by dense moorland vegetation. The most obvious mineralisation is developed in a quartz vein that crops out on the valley side about 15 m above Arm O'Grain beck (at NY 3158 3334, determined by GPS). The vein is at least 0.7 m thick, it dips steeply to the west, strikes at about 340° and is exposed over a length of 3 to 4 m. Below it, a few square metres of steep loose scree contain numerous small blocks of broken quartz (Fig. 1). A small flat area beside Arm O'Grain beck, further below the vein exposure, contains a number of large quartz blocks, which were considered to be the remains of a mine dump by Cooper and Stanley (1990). The quartz vein described above corresponds to the manganese-bearing vein marked by Cooper and Stanley (1990), the "Tree Vein" of Adams (1988) and is in the same position as the north-south trending fault marked by the British Geological Survey (1997).

About 25 m south of the vein exposure, a rib of hard brown rock, striking approximately east-west, crops out in the west bank of Arm O'Grain beck. It contains abundant idiomorphic crystals of pyrite and arsenopyrite in a granular quartz-rich groundmass. The extensive sampling that would be required to determine whether or not it is contiguous with the east-west lead vein which is exposed at Carrock mine and in Poddy Gill (see Cooper and Stanley, 1990, p.16) was not possible under the conditions of our field permit. It is in approximately the correct position and has an appropriate strike, but the granular texture of the quartz and the sulphide mineralogy are completely different. On balance, we feel it is likely to be a separate structure.

Figure 1. The main exposure at Arm O'Grain as it stood on a Russell Society survey visit in July 2006. The vein at the top of the scree is concealed in drift and is at least 0.7 m thick. Below it, a few square metres of loose scree contain numerous blocks of broken quartz.

METHOD

As part of a review of the topographic mineralogy of the Caldbeck Fells we have recently investigated material from Arm O'Grain in the collections of David Middleton (DM), Tim Neall (TN) Mike Leppington (ML), Trevor Bridges (TFB), Richard Bell (RB), Peter Todhunter (PT) and the Manchester Museum (MM). The specimens include some of the original material that Cooper and Stanley (1990) investigated in their description of the locality.

The supergene minerals recorded at Arm O'Grain include pyromorphite, mimetite, beudantite and mottramite, all of which present problems in characterisation to species level by X-ray powder diffractometry alone. The complex chemical substitutions that are possible make additional chemical data desirable. An initial reconnaissance survey of specimens using energy dispersive spectrometry (EDS) on a scanning electron microscope (SEM) was made to investigate the chemical variability. Analyses by wavelength dispersive spectrometry (WDS) were then carried out to establish the precise chemical compositions of selected specimens of the lead-bearing apatite group minerals, of the adelite-descloizite group and of the beudantites. Crystallites were hand-picked from the specimens under study, embedded in resin and polished to produce a flat surface. Analyses were made at 20 kV, 20 nA with a 15 μm beam diameter using a Cameca SX100 electron microprobe. Count times of 10 seconds were used to minimise volatilisation and decomposition effects during data collection. The data are reported as wt% oxides in Tables 1-3.

Specimen	CaO	PbO	V_2O_3	P_2O_5	As_2O_5	Cl	Total	O=Cl	Total	Species
R B AOG1A	0.21	72.78	9.09	2.30	7.23	2.80	94.41	0.63	93.78	Vanadinite P- & As-rich
	0.20	70.68	7.86	2.71	7.49	2.74	91.68	0.62	91.06	Vanadinite P- & As-rich
	0.15	70.60	9.13	2.57	6.64	2.76	91.85	0.62	91.23	Vanadinite P- & As-rich
RB AOG2	0.16	71.33	0.00	0.17	21.88	2.66	96.20	0.60	95.60	Mimetite
	0.17	71.55	0.00	0.19	22.14	2.60	96.65	0.59	96.06	Mimetite
	0.19	71.90	0.00	0.24	21.98	2.51	96.82	0.57	96.25	Mimetite
	0.29	71.75	0.00	0.25	22.27	2.51	97.07	0.57	96.50	Mimetite
	0.23	71.22	0.00	0.26	22.21	2.60	96.52	0.59	95.93	Mimetite
DM 10-20	4.41	70.78	0.03	15.80	3.30	3.15	97.47	0.71	96.76	Pyromorphite
	4.07	71.32	0.00	15.19	3.93	3.12	97.63	0.70	96.93	Pyromorphite
	0.20	78.46	0.00	14.38	2.43	2.81	98.28	0.63	97.65	Pyromorphite
	0.18	78.11	0.00	14.16	2.16	2.88	97.49	0.65	96.84	Pyromorphite
	0.29	77.37	0.01	14.09	2.42	2.92	97.10	0.66	96.44	Pyromorphite
DM 10-3	0.33	74.52	0.03	9.18	9.69	2.79	96.54	0.63	95.91	Pyromorphite As-rich
	0.47	74.78	0.02	9.40	9.69	2.75	97.11	0.62	96.49	Pyromorphite As-rich
	0.58	75.24	0.00	11.02	7.15	2.78	96.77	0.63	96.14	Pyromorphite As-rich
	0.51	73.72	0.00	9.29	8.59	2.70	94.81	0.61	94.20	Pyromorphite As-rich
	0.27	74.84	0.04	8.74	9.83	2.83	96.55	0.64	95.91	Pyromorphite As-rich
TN 1795	0.38	73.42	4.24	3.86	11.69	2.62	96.21	0.59	95.62	Mimetite P- & V-rich
	0.25	73.57	4.49	3.91	10.96	2.68	95.86	0.60	95.26	Mimetite P- & V-rich
	0.37	73.42	5.19	3.38	11.50	2.78	96.64	0.63	96.01	Mimetite P- & V-rich
	0.43	72.53	4.69	3.67	11.55	2.64	95.51	0.60	94.91	Mimetite P- & V-rich
	0.33	72.88	4.74	3.93	11.29	2.78	95.95	0.63	95.32	Mimetite P- & V-rich
	0.27	73.48	5.42	3.72	10.65	2.68	96.22	0.60	95.62	Mimetite P- & V-rich
TN 1799	0.22	71.00	0.00	0.04	22.59	2.63	96.48	0.59	95.89	Mimetite
	0.11	71.00	0.00	0.10	22.72	2.59	96.52	0.59	95.93	Mimetite
	0.12	71.39	0.02	0.07	22.86	2.66	97.12	0.60	96.52	Mimetite
	0.28	70.62	0.00	0.15	22.56	2.61	96.22	0.59	95.63	Mimetite
	0.23	71.09	0.00	0.17	22.32	2.62	96.43	0.59	95.84	Mimetite
TN 5983	0.15	76.17	9.73	1.43	7.60	2.68	97.76	0.61	97.15	Vanadinite As-rich
	0.09	76.94	11.58	1.22	5.97	2.77	98.57	0.63	97.94	Vanadinite As-rich
	0.13	76.88	10.62	1.37	6.69	2.59	98.28	0.59	97.69	Vanadinite As-rich
	0.18	76.17	8.78	1.61	9.22	2.65	98.61	0.60	98.01	Vanadinite As-rich
	0.24	76.54	9.22	1.53	8.02	2.74	98.29	0.62	97.67	Vanadinite As-rich
	0.19	76.27	9.39	1.44	7.97	2.70	97.96	0.61	97.35	Vanadinite As-rich

Table 1. Analyses of pyromorphite, mimetite and vanadinite from Arm O'Grain quoted as weight percent oxides. Standards and analysis lines used are: Ca bustamite Kα line; Cu & V metals Kα lines; Pb crocoite Mα; Zn willemite Kα; P fluorapatite Kα; As cobaltite Lα; Ba baryte Lα; Na jadeite Kα. The total column includes a minor amount of oxides not listed in the tabulation and chlorine is subtracted in the usual way. Abbreviations are RB Richard Bell collection, TN Tim Neall collection and DM David Middleton collection.

Specimen	CuO	ZnO	PbO	V_2O_3	P_2O_5	As_2O_5	Total	Species
MM N13843	17.54	0.43	53.76	10.09	1.14	7.07	91.67	Mottramite
	16.94	0.51	54.14	11.12	1.61	6.04	91.30	Mottramite
	18.45	0.05	48.45	8.24	1.03	10.75	88.73	Mottramite
	18.44	0.05	50.83	9.08	1.22	8.35	88.93	Mottramite
	16.35	0.07	52.97	12.92	0.86	3.77	88.21	Mottramite
RB AOG1A	17.34	0.00	46.69	9.84	1.10	8.65	88.28	Mottramite
	17.33	0.14	51.76	9.84	0.58	8.14	88.34	Mottramite
	18.02	0.32	49.71	10.43	0.73	7.80	87.96	Mottramite
	17.58	0.03	50.46	10.59	0.89	8.44	89.00	Mottramite
	17.55	0.19	52.15	12.03	1.33	7.22	91.51	Mottramite
	17.93	0.00	52.36	10.88	1.02	7.80	91.06	Mottramite
DM 10-20	17.99	0.00	50.39	5.41	1.44	14.56	91.22	Duftite
	18.93	0.00	46.57	3.60	0.96	18.93	90.31	Duftite

Table 2. Analyses of mottramite and duftite from Arm O'Grain quoted as weight percent oxides. Standards used are: Pb crocoite Mα; Zn willemite Kα; P fluorapatite Kα; As cobaltite Lα. The total column includes a minor amount of oxides not listed in the tabulation.

Specimen	P_2O_5	As_2O_5	Al_2O_3	FeO	PbO	SO_3	Total	Species
DM 10-13	0.34	9.85	1.66	27.45	31.78	14.05	86.29	Beudantite
	0.45	10.20	1.66	27.36	31.94	13.83	86.60	Beudantite
	0.43	10.32	1.68	27.24	32.04	14.00	87.00	Beudantite
	0.34	10.35	1.65	26.97	31.88	13.86	86.36	Beudantite
	0.07	6.40	1.31	28.38	32.64	16.30	86.95	Beudantite
DM 10-23	0.12	8.95	0.71	28.87	31.92	14.34	85.99	Beudantite
	0.11	9.93	0.77	28.88	31.68	14.25	86.47	Beudantite
	0.06	9.47	0.74	28.88	31.80	14.24	86.07	Beudantite
	0.06	9.52	0.67	28.83	32.02	14.14	86.17	Beudantite
	0.05	10.58	1.04	27.98	31.82	12.84	85.48	Beudantite

Table 3. Analyses of beudantite from Arm O'Grain quoted as weight percent oxides. Standards and analysis lines used are: Pb crocoite Mα; Zn willemite Kα; P fluorapatite Kα; As cobaltite Lα. The total column includes a minor amount of oxides not listed in the tabulation.

Abbreviations are DM David Middleton collection.

MINERALS

The minerals present at Arm O'Grain are described below. Where the identifications are based on modern analytical techniques or sound literature references, the sub-title is capitalised; if there is some uncertainty associated with an identification or further investigation is required the sub-title is written in lower case. The two exposures in the Arm O'Grain valley are mineralogically distinct, so the minerals are described separately.

THE NORTH-SOUTH VEIN

The north-south vein, which is exposed at NY 3158 3334, is the locality which almost all of the literature references appear to be describing when they refer to Arm O'Grain (*e.g.* Young, 1987; Cooper and Stanley, 1990).

BARYTE, $BaSO_4$

Primary baryte occurs rarely as white blades in vein quartz. One specimen from the David Middleton collection displays a partially dissolved baryte blade (identified by EDS) in a planar cavity. The presence of numerous planar voids in the quartz veinstone suggests that baryte may have been more abundant in the geological past.

BEUDANTITE, $PbFe_3[(As,S)O_4]_2(OH,H_2O)_6$

Sharp dark brown to black blocky beudantite crystals up to 0.5 mm on edge, with mirror-bright faces, are present on a number of micromount specimens collected in the 1970s by David Middleton (*e.g.* Fig. 2). An unusual translucent pseudo-cubic zoned beudantite from the DM collection, which was originally identified as pharmacosiderite, is figured in Cooper and Stanley (1990, p.82). Beudantite is rare at Arm O'Grain and very few specimens other than those in the DM collection are known. A large blocky crystal, 2 mm on edge, is present on a single specimen in the Tim Neall collection and red-brown pointed crystals are present on a few specimens in the Mike Leppington collection.

Beudantite is a difficult mineral to characterise by XRD alone. Two DM specimens, with crystals that were large enough to be polished, were analysed by WDS (Table 3). Both crystals are compositionally homogeneous. Sulphate is in excess of arsenate in each case, the molar ratio being approximately 2:1. Average formulae can be calculated from the data of Table 3 with the amount of OH being calculated from charge balance considerations. This produces the formulae $Pb_{1.08}(Fe_{2.87},Al_{0.23})[(AsO_4)_{0.62},(SO_4)_{1.35},(PO_4)_{0.03}](OH)_{6.8}$ and $Pb_{1.10}(Fe_{3.07},Al_{0.11})[(AsO_4)_{0.65},(SO_4)_{1.34}](OH)_{7.1}$, based on two trivalent anions per formula unit. Both compositions fall within the beudantite field.

Figure 2. Dark brown lustrous beudantite crystals, the largest 0.5 mm on edge, on iron stained quartz. David Middleton collection.

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Bindheimite was identified by EDS as inconspicuous yellow powdery crusts in cavities in quartz veinstone.

CERUSSITE, $PbCO_3$

A number of corroded white masses of cerussite up to 5 mm across were discovered in fragments of quartz collected from the vein exposure in July 2006. The cerussite was initially identified by wet chemistry, which showed the presence of both lead and carbonate (complete dissolution in dilute nitric acid with effervescence and a strong positive lead reaction with potassium iodide) and subsequently confirmed by XRD. Cerussite occurs rarely as colourless white and pale blue crystals in quartz veinstone (Mike Leppington, *personal communication*). A specimen containing millimetre-size blocky cerussite crystals on galena in the Peter Todhunter collection was identified by XRD

DUFTITE, $PbCu(AsO_4)(OH)$

An EDS survey of typical black 'mottramite' specimens from Arm O'Grain revealed significant arsenate substitution for vanadate. One specimen from the David Middleton collection, which was subsequently analysed by WDS, had more than 50 mole% arsenate replacing vanadate and is a vanadium-rich duftite (Table 2). It occurs as lustrous black crystals up to 0.3 mm in length on pale green mimetite. Duftite in this form is visually indistinguishable from mottramite.

Grey-green to sage green crusts, which are visually distinct from mottramite, are present as sub-millimetre size botryoidal aggregates and isolated crystals on quartz on a few specimens in the Tim Neall and Mike Leppington collections. These are usually near end-member duftite, there is no vanadate substitution for arsenate, although some crystals show minor substitution of calcium for lead.

GALENA, PbS

Galena is very rare at Arm O'Grain. Residual galena and occasional bright cleavages was visually identified on a few specimens of typical quartz veinstone in the Peter Todhunter and Mike Leppington collections.

GOETHITE, α-FeO(OH)

Goethite is abundant as brown friable limonitic crusts in cavities in vein quartz. It also occurs as hard black encrustations, thin lustrous botryoidal films and very occasionally as minute euhedral crystals in small cavities in the quartz. In some cases, goethite crusts are covered in goethite encrusted filaments. Goethite epimorphs after a curved rhombohedral mineral, probably ankerite, are common. Dark brown compact goethite sometimes replaces a mineral with the morphology of chalcopyrite.

MALACHITE, $Cu_2(CO_3)(OH)_2$

Malachite was identified on a specimen from the David Middleton collection as a spray of bright green acicular crystals up to 2 mm long. It is very rare at Arm O'Grain; only two other specimens, both in the Mike Leppington collection, are known to the authors.

MICROCLINE, $KAlSi_3O_8$

Microcline was identified by XRD as idiomorphic white to colourless crystals up to a few millimetres across in vein quartz (Fig. 3). It is commonly enclosed by late-stage grey chalcedonic quartz, which fills cavities and voids in the vein.

Figure 3. Idiomorphic white microcline crystal sections up to 1.2 mm across are enclosed by late-stage grey chalcedonic quartz. Both minerals occupy planar voids in the quartz vein. They post-date the main stage vein quartz, which is visible as glassy fragments at the bottom of the picture.

MIMETITE, $Pb_5(AsO_4)_3Cl$

Mimetite of near-end member composition occurs as buff, pale brown, yellow, grey-brown and orange-brown resinous barrel-shaped to platy crystals up to about a millimetre across. There are complex substitutions among the lead-bearing members of the apatite group at Arm O'Grain (Table 1) and green and white prismatic hexagonal crystals and golden yellow and orange-brown to pale yellow plates which are mimetite-pyromorphite (*e.g.* Fig. 4) and mimetite-vanadinite (*e.g.* Fig. 5) intermediates also occur. Complex contorted aggregates of pale yellow to grey mimetite with about 50 atom% As and equal amounts of V and P substituting are present on a few specimens.

MOTTRAMITE, $PbCu(VO_4)(OH)$

Mottramite is the commonest lead-bearing supergene mineral at Arm O'Grain. It was found at the locality in the 1970s and first reported by Young (1987). It occurs as black elongated boat shaped crystals up to about 1 mm long, which are typically scattered over white vein quartz (Fig. 6). Occasionally, rich crusts of mottramite occur in planar cavities in the quartz that appear to have been formed by the dissolution of baryte. Mottramite commonly encrusts vanadinite, pyromorphite or mimetite (Fig. 7).

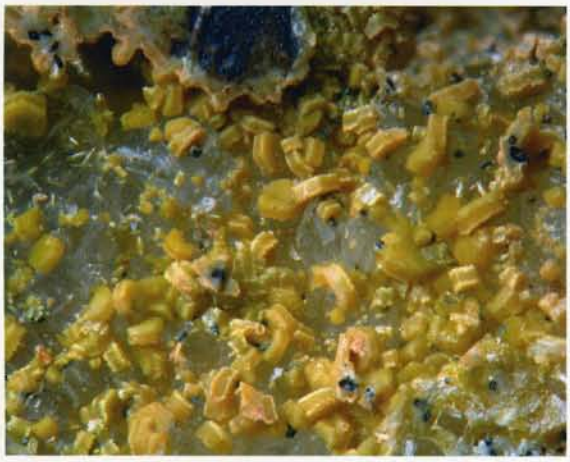

Figure 4. Orange-brown tabular hexagonal phosphatian mimetite crystals up to 0.3 mm across on vein quartz.

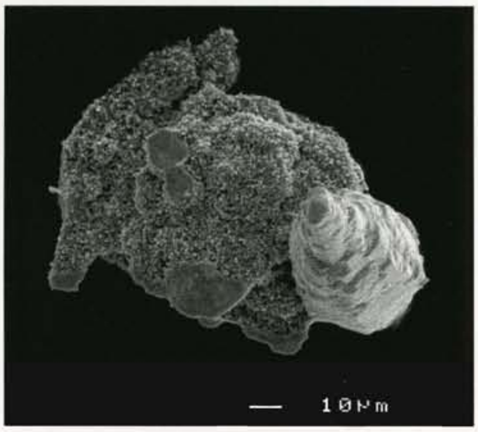

Figure 5. A spindle shaped arsenatian vanadinite crystal on platy phosphatian mimetite, which is covered in minute sharp plumbogummite crystals.

Figure 6. Sharp mottramite crystals in black subparallel aggregates up to 0.6 mm long on white vein quartz.

Mottramite is difficult to characterise by XRD alone. Analyses of a representative group of specimens by EDS showed significant arsenate substitution for vanadate in some cases (Table 2). Although duftite and mottramite cannot be distinguished visually, the WDS analyses supported by extensive EDS indicate that almost all of the black drusy crusts at Arm O'Grain are mottramite.

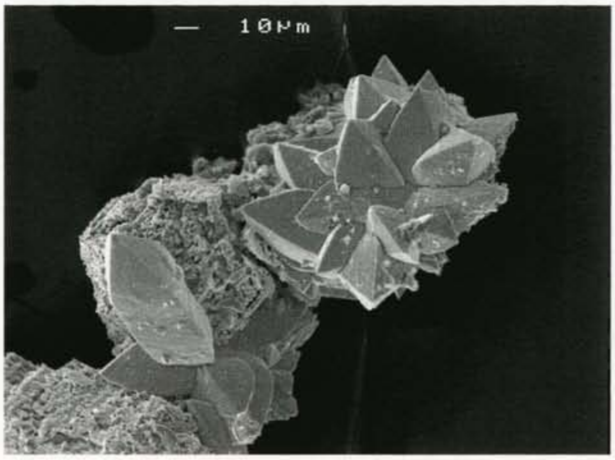

Figure 7. Mottramite as sharp crystals on corroded arsenatian vanadinite.

PLUMBOGUMMITE, $PbAl_3(PO_4)_2(OH, H_2O)_6$

Plumbogummite was identified on a few specimens by comparing its EDS spectrum to a similar spectrum that was generated by an XRD and WDS confirmed plumbogummite specimen from Cornwall. It occurs as scattered colourless to pale brown or rarely pale blue rhombohedral crystals up to a few micrometres in length on pyromorphite or quartz (Fig. 8). The crystals are too small to be resolved under a stereo-microscope, they can sometimes be identified as a thin pale brown crust and in one specimen from the Mike Leppington collection they occurs as pale blue epimorphs after an unknown mineral. The specimens are too small for identification by conventional XRD.

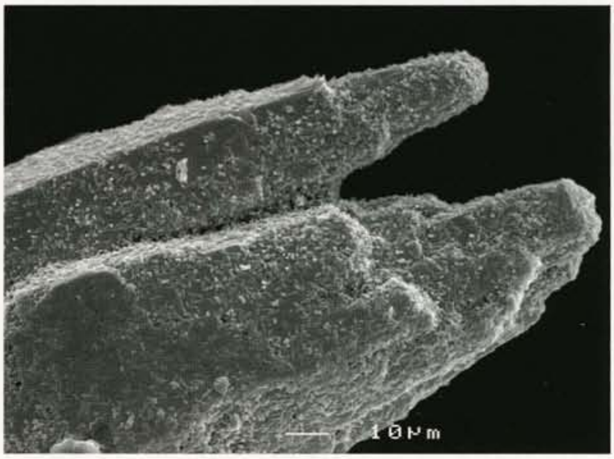

Figure 8. A spindle-shaped crystal of a pyromorphite-mimetite-vanadinite intermediate with about equal amounts of V, P and As coated in minute sharp plumbogummite crystals.

Pyrolusite, MnO_2

Powdery pyrolusite and 'psilomelane' were recorded at Arm O'Grain by Cooper and Stanley (1990) on the basis of a report by F.H. Day (1928). The terms pyrolusite and psilomelane were used loosely by some early workers to describe black manganese oxides. All of the manganese oxide specimens examined by EDS in this study contained significant cobalt and one was almost pure cobalt oxide. Insufficient material was available for identification by XRD, but it seems unlikely that these minerals are pyrolusite.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$

Arsenatian pyromorphite is fairly common as green elongated prismatic to spiky crystals in cavities in vein quartz. Crystalline crusts occasionally cover areas of up to a few square centimetres. Although pyromorphite is probably the commonest of the lead-bearing members of the apatite group at Arm O'Grain, and most of the dark green crystals from the locality are pyromorphite, the lighter green and yellow crystals display complex chemical substitutions and include material that falls within the vanadinite and mimetite composition fields. A few compositions are quoted in Table 1. Pyromorphite occasionally occurs as porous cellular overgrowths on other lead-bearing apatite group minerals (Fig. 9).

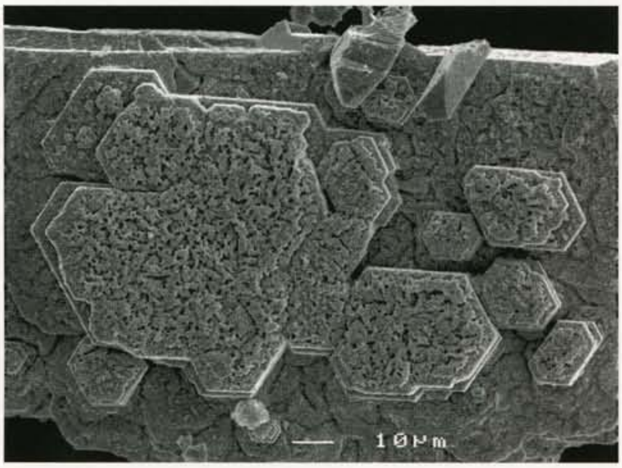

Figure 9. Porous cellular hexagonal arsenatian pyromorphite with two small mottramite crystals.

QUARTZ, SiO_2

Quartz is abundant at Arm O'Grain. A rib at least 0.7 m thick is exposed *in situ* and large blocks are present in the scree and grass below. Cavities lined with stumpy pyramidal crystals up to about 30 mm across are common and 'hacked' and cellular quartz, produced by the dissolution of baryte and carbonates is abundant. Cavities in the cellular quartz which makes up much of the vein are commonly lined with dark brown friable goethite.

Phantoms in some of the quartz crystals indicate episodic crystallisation. Late-stage grey chalcedonic quartz, which is commonly associated with microcline, is present on some specimens. On one specimen a thin drusy quartz crust overgrows a pyromorphite group mineral, while in others mottramite or an as yet uncharacterised green supergene mineral are *enclosed* by quartz (Fig. 10). It therefore seems likely that a small amount of the quartz is supergene.

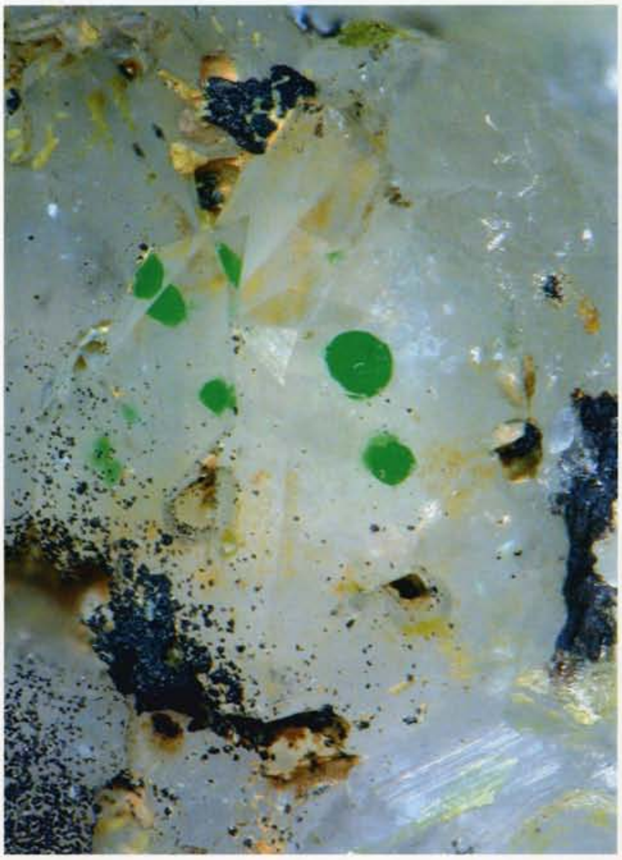

Figure 10. Bright green spheroidal inclusions of an as yet uncharacterised supergene mineral up to 0.8 mm across about 1 mm below the surface of stumpy pyramidal quartz crystals. The supergene mineral is clearly crystallised on a surface within the quartz (visible as a 'phantom') that was subsequently overgrown by quartz in crystallographic continuity.

VANADINITE, $Pb_5(VO_4)_3Cl$

Vanadinite is the rarest of the lead-bearing apatite group minerals at Arm O'Grain. It occurs as thin hexagonal plates, which are often stacked along the c-axis to produce barrel shaped aggregates. The aggregates are usually white and opaque and may be up to a millimetre across. Vanadinite also occurs as porous white shells surrounding pale brown barrel shaped mimetite. In some cases the interior mimetite has dissolved to leave white vanadinite epimorphs. A few green spindle-shaped crystals that look very much like pyromorphite are phosphatian vanadinite.

WULFENITE, $PbMoO_4$

Wulfenite is very rare. It was recorded by Cooper and Stanley (1990) on the basis of an XRD confirmed specimen from the Mike Leppington collection. It occurs as bipyramidal blocky to thin tabular orange crystals associated with yellow mimetite (Mike Leppington, *personal communication*).

THE QUARTZ-ARSENOPYRITE EXPOSURE

The iron and arsenic sulphide rich exposure in the west bank of Arm O'Grain beck about 25 m to the south of the quartz vein exposure does not appear to have been noted by previous workers. It was located on a Russell Society field trip in 2006. This should be regarded as a preliminary description. Further fieldwork to establish its mineralogical and geological affinities is desirable.

ARSENOPYRITE, FeAsS

Arsenopyrite is locally abundant as millimetre-size idiomorphic silver-grey crystals in granular quartz. Occasionally minute blocky crystals and star shaped trillings are present in small cavities in granular quartz.

PYRITE, FeS_2

Pyrite is common as millimetre-size striated cubic crystals in granular quartz. Near thin fractures pyrite is altered to scorodite.

SCORODITE, $FeAsO_4.2H_2O$

Scorodite was identified by XRD as brown to yellow-brown crusts in hairline fractures in the arsenopyrite- and pyrite-rich rock.

DISCUSSION

The only significant description of the mineralisation in the Arm O'Grain valley is by Cooper and Stanley (1990); they note seven species (not including psilomelane) from the north-south quartz vein. Our research has added twelve further species and a substantial amount of quantitative chemical data. Nine of the newly described species, including the first reliably confirmed vanadinite from the Caldbeck Fells, are from the main vein exposure. The other three (arsenopyrite, pyrite and scorodite) are from a rib of quartz rock which crops out in the west bank of the beck about 25 m to the south.

The north-south trend of the main vein at Arm O'Grain is similar to the high-temperature tungsten-bearing quartz veins at the nearby Carrock Mine, but its cellular texture and the absence of primary tungsten-bearing mineralisation mitigate against their being a genetic relationship between the two.

The surface exposure gives the impression of prolonged supergene weathering. The wallrock has been reduced to regolith and baryte and the carbonate minerals calcite and ankerite, which were probably abundant at one time, are now rare or absent. The only primary mineral besides quartz that is present in any quantity is the potassium feldspar microcline. Idiomorphic white microcline appears to have crystallised in open voids in the vein where it is commonly overgrown by grey chalcedonic quartz. Both of these minerals are later than the typical coarse white quartz that makes up most of the rest of the vein (Fig. 3).

A specimen containing a partly dissolved baryte blade in a planar void provides convincing evidence that some of these voids originally contained baryte. The fact that the baryte is in the correct crystallographic orientation with respect to the void shows that the deposition sequence was baryte followed by quartz, with later baryte dissolution. It seems probable that some of the baryte dissolution at localities in the Caldbeck Fells (including Arm O'Grain) is a supergene process, since undoubted *supergene* baryte is present at many localities (*e.g.* Green *et al.*, 2005; authors' unpublished data). Baryte, which is normally regarded as a stable phase at the earth's surface, may be more mobile in the supergene environment than is generally acknowledged.

The presence of grey chalcedonic quartz and microcline in some planar voids (*e.g.* Fig. 3) suggests either that some of the baryte dissolution was a late-stage primary process or that the chalcedonic quartz and microcline are supergene. The inclusion of supergene minerals within late-stage quartz is intriguing in this context (*e.g.* Fig.10) and suggests the latter. Quartz is an exceptionally stable mineral at the earth's surface and it is highly resistant to weathering. It is very unlikely that primary quartz in the vein has been remobilised, especially since bright, unaltered crystals are present in the surface exposure. A alternative source of silica is in the wall-rocks, which are silicate-rich and extensively weathered. The abundance of the silicate mineral hemimorphite in the Caldbeck Fells indicates that silica is commonly present in solution in the supergene environment; in the absence of zinc it may be that silica-rich solutions could deposit both quartz and K-feldspar.

The supergene mineral assemblage can be used to give an indication of the primary minerals that may have been present. Mottramite, duftite, plumbogummite and the lead-bearing apatites were almost certainly produced by oxidising galena, since residual galena is present on a few specimens. Malachite strongly suggests primary chalcopyrite was present and this is further supported by the presence of occasional goethite pseudomorphs with the characteristic sphenoidal morphology of chalcopyrite. In the context of mineralisation in the Caldbeck Fells, the presence of duftite and mimetite suggests the presence of primary arsenopyrite. This mineral is abundant in the sulphide-rich rib of quartz rock on the west side of the beck about 25 m south of the vein and this seems a likely and local source. The main vein exposure probably represents the weathered surface of a low-temperature lead and copper bearing quartz-baryte-carbonate vein, a style of mineralisation that is common in the Caldbeck Fells.

The poor surface exposure means that the precise distribution of minerals *within* the vein is unknown. Careful sampling suggests that the lead minerals are concentrated in a rib of quartz that is bounded by porous cellular goethite-rich quartz veinstone on one side and a pronounced slickenside on the other. The presence of slickensides in the quartz indicates earth movements that

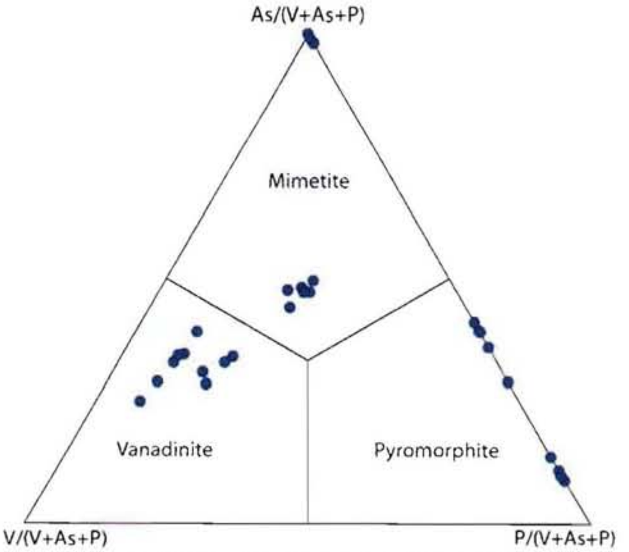

Figure 11. A ternary plot illustrating the variability in the anionic composition the lead bearing apatites, generated from the data in Table 1.

post-date some of the vein mineralisation, there may even be more than one episode of mineralisation. A small excavation across the vein could provide further useful data.

The supergene assemblage contains many minerals that are difficult to characterise without quantitative chemical data. Our analyses have confirmed previous identifications of beudantite, mimetite, mottramite and pyromorphite and added plumbogummite, vanadinite and duftite to the species list (Tables 1–3).

Arm O'Grain is the only locality in the Caldbeck Fells where pyromorphite, mimetite and vanadinite, have been reliably identified. The claimed vanadinite specimens from Carrock Mine, Brandy Gill, Ingray Gill and Potts Gill in the Arthur Kingsbury collection are not reliable (Ryback *et al.*, 1998; 2001; authors' unpublished data). A vanadinite specimen originally in the Trevor Wolloxall collection from upper Brandy Gill, which is described in Cooper and Stanley (1990, p.131) was re-examined in this study and shown to be mimetite. It is now in The Manchester Museum collection (accession number N13839).

The anionic composition of the lead-bearing apatite group minerals is plotted as a ternary diagram in Figure 11. Most specimens from the locality are either pyromorphite or mimetite. The vanadinite and vanadate-rich material that we examined occurs most commonly as squat white hexagonal plates. Green spindle-shaped crystals and platy to squat yellow crystals are also sometimes vanadium-rich, but there is no reliable method of visually distinguishing the species. Surprisingly, none of the lead-bearing apatites that were collected in the 1970s by David Middleton contain much vanadium, although it is quite common in later specimens from a number of different collections. It may be that the early specimens came from a different area of the exposure.

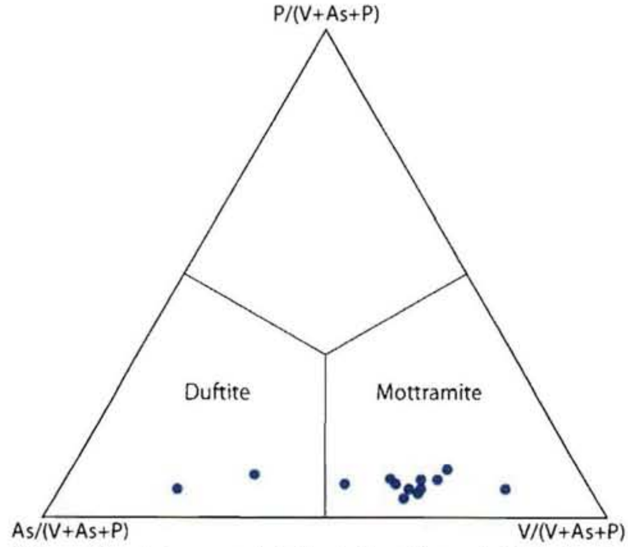

Figure 12. A ternary plot illustrating the variability in the anionic compositions of mottramite and duftite, generated from the data presented in Table 2.

Phosphohedyphane, ideally $Pb_3Ca_2(PO_4)_3Cl$, is a new IMA approved name given to 'pyromorphite' in which between 20 and 40 atom% of lead is replaced by calcium (Anthony Kampf, *personal communication*). The most Ca-rich pyromorphite in the data of Table 1 has a formula that can be written: $Pb_{3.78}Ca_{0.94}(PO_4)_{2.65}(AsO_4)_{0.35}Cl_{1.06}$ when calculated on the basis of three arsenate plus phosphate anions. This is near to the boundary between the pyromorphite and phosphohedyphane composition fields. Qualitative EDS analyses of crystallites from other specimens suggest some compositions are even more Ca-rich. It seems likely that phosphohedyphane is present at Arm O'Grain, but it cannot be claimed with certainty on the basis of the data available. A more extensive quantitative investigation of calcium substitution in pyromorphite at this and other localities seems worthwhile.

Mottramite is much the commonest vanadium-bearing mineral at Arm O'Grain and is abundant on some specimens. It occurs at a number of other localities in the Caldbeck Fells including Driggith mine, Brae Fell mine, Ingray Gill and Roughton Gill (Cooper and Stanley, 1990; Bridges *et al.*, 2006; authors' unpublished data) but it is unusual for it to be so abundant in well-formed crystals. The association between the lead-bearing members of the apatite group and of the adelite-descloizite group is intriguing. In the Caldbeck Fells, the latter commonly form crystalline crusts on the former, as for example at Ingray Gill (mottramite on pyromorphite) and Brae Fell mine (mottramite on pyromorphite). At Arm O'Grain, mottramite and duftite commonly crystallise on pyromorphite and mimetite. At most of the Caldbeck Fells localities that we have data for, mottramite is later in the oxidation sequence than pyromorphite or mimetite. This is generally the case at Arm O'Grain, although some specimens show the reverse sequence, where mimetite or pyromorphite overgrows mottramite. A relatively high vanadate ion activity is likely to be required for this to occur. The source of the vanadate ions that are needed for mottramite and vanadinite to crystallise is uncertain, however, mafic igneous bodies are commonly enriched in vanadium and the rocks in the immediate area include gabbroic lithologies. There are no obvious primary vanadium-bearing minerals in the vein.

A ternary plot of the anionic composition of mottramite (Fig. 12) shows considerable substitution of arsenate for vanadate and includes two compositions that plot in the duftite composition field. Phosphate substitutes for arsenate and vanadate at up to about 10 mol% in the duftite and mottramite from Arm O'Grain. There is a far more extensive substitution of phosphate for arsenate and vanadate in the lead-bearing members of the apatite group from the site but since there are no known phosphate end members in the adelite-descloizite group (Gaines *et al.*, 1997) and it may be that the structure does not incorporate the PO_4 group easily.

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HEAVY METALS AND THEIR WEATHERING PRODUCTS IN RESIDUES FROM CASTLESIDE SMELTING MILL, COUNTY DURHAM, INCLUDING A NEW SLAG MINERAL, COPPER ANTIMONATE

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Originally a lead smelter, Castleside Mill in Co. Durham later processed a wide range of materials including submarine batteries and materials containing antimony and tin. As a result the waste contains antimony, copper and tin as well as lead, and a number of intermetallic phases have been identified in the residues, including cuprostibite and zlatogorite. Oxidative weathering has produced a number of unusual secondary species including possible boleite, caledonite, cervantite, chenite, devilline, elyite, lanarkite, linarite, paralaurionite, schulenbergite, possible valentinite, vivianite, wroewolfeite and copper antimonate. Not previously recorded as a natural or a slag mineral, the copper antimonate, $CuSb_2O_6$, forms pale green thin hexagonal plates with outer zones of cervantite. A simple technique for qualitative microchemical testing is described, by which very small samples can be analysed.

INTRODUCTION

Castleside smelting mill, NGR NZ 078 484, was initially built in 1805 (Atkinson, 1974) to smelt lead ore from the nearby Healeyfield mine. This mine is located in Dene Howl, in the parish of Muggleswick, with an adit at NZ 069 487 and dumps at NZ 071 488. The mine closed in about 1890 (Lee, *ca.* 1979). The lead ore (galena) contained silver at a grade of about 15 oz. per ton (418 ppm) (Dunham, 1948). Other minerals recorded from the mine are quartz, baryte, and probably siderite, with limonitic goethite the most common material on the tips (Dunham, 1948). Young (1985) records pyromorphite on these dumps, and Bridges and Young (1998) report linarite, also covelline coatings on galena.

The later history of the Castleside mill is complex. It was used for smelting ores until about the end of the First World War, not only from Healeyfield, but also from mines at Thornthwaite in Swaledale (Old Gang mines), Arkengarthdale in Teesdale, and from as far away as North Wales (Gill, 1992; A. Roberts, *pers. comm.*). After 1918 the mill also carried out secondary smelting of batteries from submarines, the lead plates of which contained about 1.5 % antimony which was skimmed off the molten lead during refining as oxide (Piddington, 1903; Lee, *ca.* 1979). By 1923 the mill had also started processing "residues" of unrecorded nature, presumably based on litharge and containing antimony and possibly tin (Hoffman, 1970). As a result, the waste at the site may contain compounds of antimony and of an unknown selection of other metals as well as lead.

The mill site is scheduled as an Ancient Monument and was made into a picnic area some years ago. Most of the mill complex was bulldozed and the only visible remains are vestiges of parts of the supposedly-preserved upper flue system, a watercourse entering the field at a point above the mill to drive the waterwheel, and some slag dumps at the base of the bank and in the stream.

TYPES OF SLAG

IRON SLAG

This is characterised by brown iron oxide colouration and contains secondary lead and copper minerals as well as those of iron.

LEAD SLAG

This is heavy, mid to dark grey and appearing crystalline in structure, with some galena, lead metal, and glassy clear yellow material in some vesicles.

COPPER SLAG

This is more colourful than the lead slag, with green and blue-green material. Some of the copper slag is black, red and red-brown coloured, vesicular and vitreous slag, similar to that found at other copper smelting mills, *e.g.* at Middleton Tyas in North Yorkshire. Metallic copper is found as prills within the slags and as fairly large lumps, which have obviously been molten. There are also lumps of white copper alloys containing appreciable antimony as well as iron, lead and minor nickel and arsenic. Samples of some of these materials were analysed by Dr. Richard Smith using energy dispersive X-ray spectroscopic (EDS) microanalysis, and the results (Table I) show a wide variation in compositions. These slags contain oxidised lead, iron and antimony compounds as well as those of copper.

According to Dr. Richard Smith, the results of the analyses suggest that in the refining process the first skimmings rich in Cu, Sb, Pb, Fe *etc.* were re-melted, then cooled slowly to allow lead to separate, the residue giving the material analysed. The separated lead may then have been refined further.

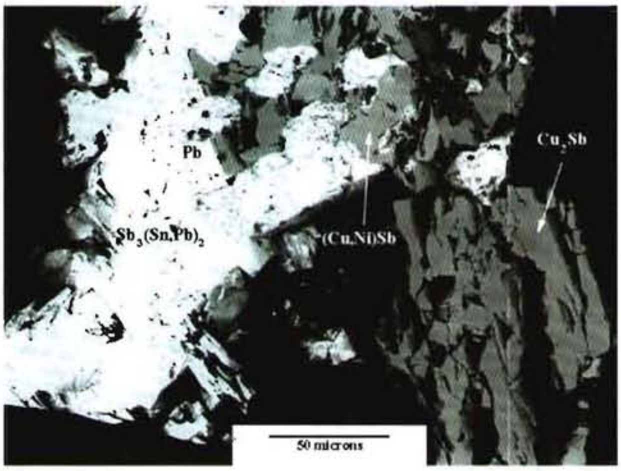

Figure 1. Back scattered electron image of a polished section of a crystallised portion of white metal in specimen RSWB 99-92 showing distribution of intermetallic phases analysed by microprobe (see Table II). D.A. Plant photograph.

MICROCHEMICAL TESTING METHODS

Microchemical tests can only indicate those parts of the chemistry tested for, and will not normally distinguish between polymorphs. The method used was to take small samples, carefully purified by picking under the microscope, and place them on a microscope slide adjacent to a small drop of the relevant reagent, normally initially fairly dilute hydrochloric acid. The particles were then pushed into the reagent drop while observing through the microscope. If the particles contain carbonate they will effervesce, if they contain lead they will turn opaque white. The solution, when treated with a drop of ammonium tetrathiocyanatomercurate(II) solution will reveal the presence of copper by the formation of apple-green ferny crystals; if traces of zinc are also present, a few small purple crystals will appear near the edges of the test drop; if appreciable zinc is present purple ferny crystals will dominate or even replace the green ones. Zinc alone will give white crystals, in which case the test is repeated with a tiny crystal of copper sulphate added, to give the purple crystals. Cobalt gives beautiful blue crystals with this reagent, but was not detected in this study. If iron(III) is present, the background solution turns red.

Sulphate was detected in the absence of lead by pushing the particles into a drop of dilute hydrochloric acid containing barium chloride, in which case the particles turn opaque white; this method is preferable to adding barium chloride solution to a solution of the particles, when the precipitate may be faint and difficult to see, even against a black background, due to excessive dilution; in the presence of lead a solution of barium nitrate in dilute nitric acid is used. Chloride may be detected similarly by using a solution of silver nitrate in dilute nitric acid.

SPECIES IDENTIFIED

ANGLESITE, $PbSO_4$

Identified by infrared spectroscopy, anglesite is found in the lead and copper slags as colourless crystals of prismatic and tabular habits. Small brilliant tabular crystals to 0.2 mm, some perched on the tips of cerussite blades to 1.5 mm are closely associated with rosettes of cervantite in copper slag. Sharp, transparent colourless prismatic crystals of anglesite (associated with caledonite) are mostly about 0.1 mm long, but a few exceptional crystals reach 0.8 mm in length. Anglesite is also present in the iron slag as small colourless to yellowish prismatic striated crystals, which were identified by Dr. David Green using EDS.

ARAGONITE(?), $CaCO_3$

Colourless radiating 0.5 mm long needles in one cavity were soluble in dilute hydrochloric acid with effervescence, giving a brick-red flame test, so are tentatively identified as aragonite.

BOLEITE(?), $KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$ (Cooper and Hawthorne, 2000)

A very few microscopic sky-blue cubes, about 0.07 mm edge-length, one elongated along one axis, have been found on a small specimen of the copper slag (Fig. 2). These crystals resemble boleite in appearance, but could possibly be cumengeite, pseudoboleite or some other phase, such as the rare copper zeolite tschörtnerite, $Ca_4(K,Ca)_3Cu_3(OH)_8(Si_{12}Al_{12}O_{48}).xH_2O$ (Effenberger *et al.*, 1998).

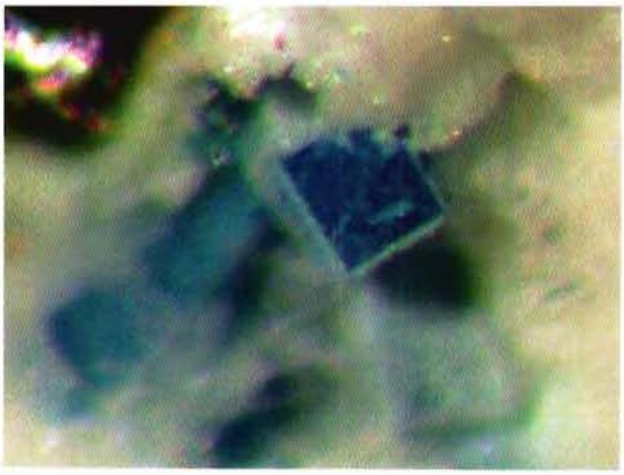

Figure 2. Blue cubes of probable boleite, the largest 0.07 mm along edge. Specimen RSWB 03-117. R.S.W. Braithwaite photomicrograph.

BRASS, (Cu,Zn)

A specimen of golden metallic brass was found in the copper slag, as an irregular lump, spongy in parts. It is encrusted with cuprite, some in crystals and also with small pale green pearly plates of schulenbergite. Microchemical tests on a sample of the brass indicated the presence of copper and zinc, with Cu > Zn.

BROCHANTITE, $Cu_4SO_4(OH)_6$

Identified visually and microchemically, and confirmed by infrared spectroscopy, brochantite is found mainly in the copper slag as crusts of tiny bright green crystals. A few larger individual rectangular plates reach 0.5 mm.

CALCITE, $CaCO_3$

Small opaque white triangular to bipyramidal-looking crystals scattered in a few cavities are of calcite; this was confirmed by infrared spectroscopy.

CALEDONITE, $Pb_5Cu_2CO_3(SO_4)_3(OH)_6$

Caledonite is found in the copper slags as cavity linings of beautiful pale blue-green radiating clusters of long-prismatic crystals to 0.4 mm long, with flat rectangular terminations, appearing darker in colour when viewed through the terminations. Their appearance is very similar to caledonite found in the slag at Glengaber ("Meadowfoot") mill, Wanlockhead, Scotland (Green, 1987). Microchemical tests indicate the presence of lead, copper, carbonate and sulphate. Brilliant colourless anglesite crystals accompany this caledonite, which is also associated with chenite, elyite, hydrocerussite, wroewolfeite and lanarkite.

	1	2	3	4	5	6	7
Cu	79	37	42	96	79	51	8
Sb	20	24	19	1	19	22	10
Pb	-	-	-	-	1	18	2
Fe	-	40	6	2	1	-	80
Ni	-	-	-	-	-	9	-
As	1	-	8	-	-	-	-
S	-	-	24	-	-	-	-

Table I. EDS analyses (weight %) of "white alloys" from the copper slags of Castleside Mill, normalised to sum 100%. Analyst Dr. R. Smith. Analyses 1-4 are different areas on one specimen; analyses 5-7 are different areas on another specimen, also containing oxidised material with Sb, Cl or Pb and some Cu.

Comments on atomic ratios:

1 and **5** are antimonial copper, Cu:Sb ~7.5 or $Cu_{15}Sb_2$.

2 has Cu:Sb:Fe ~3:1:3.5

3 has (Cu+Sb+Fe) : (S+As) ~1:0.92, with Cu:Sb:Fe ~1:0.25:0.17 and S:As ~1:0.15. Near CuS, *cf* covelline.

4 is copper.

6 has Cu:Sb:Ni:Pb ~4:1:0.75:0.45 or Cu:Sb:(Ni+Pb) ~4:1:1.2

7 is iron, Fe:Cu ~ 11

	1	2	3	4	5
Cu	60.0±0.3	49.0±0.3	0	18.9±0.1	12.4
Ni	0.3±0.06	1.0±0.1	0	13.7±0.2	18.6
Sb	12.8±1	46.7±0.2	55.5±0.4	52.0±0.3	54.6
Sn	26.0±1.3	2.7±0.05	29.5±0.1	14.0±0.3	11.4
Pb	0	0.05±0.05	12.9±0.4	0.2±0.05	0
Fe	0	0.08±0.02	0	1.2±0.1	2.0

Table II. Analyses (weight %) of intermetallic phases, normalised to sum 100 %. Elements other than those listed were not detected. Analyses performed by Mr. D.A. Plant at the Department of Earth Sciences, University of Manchester, with a Cameca SX 100 EMPA, using a beam current of 19.9 nA and an accelerating voltage of 20.0 kV. Standards used were chalcopyrite (Cu), nickel (Ni), stibnite (Sb), cassiterite (Sn), galena (Pb) and pyrite (Fe).

1 Orthorhombic $Cu_3(Sn,Sb)$, RSWB 99-97. Average of 6 analyses gave $(Cu_{2.96}Ni_{0.02})_{\Sigma=2.98}(Sn_{0.69}Sb_{0.33})_{\Sigma=1.02}$

2 Cuprostibite, Cu_2Sb, RSWB 99-92. Average of 5 analyses gave $(Cu_{1.94}Ni_{0.04})_{\Sigma=1.98}(Sb_{0.96}Sn_{0.06})_{\Sigma=2.02}$

3 $Sb_3(Sn,Pb)_2$, RSWB 99-92. Average of 3 analyses gave $Sb_{2.97}(Sn_{1.62}Pb_{0.41})_{\Sigma=2.03}$

4 (Cu,Ni)Sb, RSWB 99-92. Average of 2 analyses gave $(Cu_{0.54}Ni_{0.42}Fe_{0.04})_{\Sigma=1.0}(Sb_{0.79}Sn_{0.21})_{\Sigma=1.0}$

5 (Ni,Cu)Sb, RSWB 99-92. One spot analysis gave $(Ni_{0.58}Cu_{0.36}Fe_{0.06})_{\Sigma=1.0}(Sb_{0.82}Sn_{0.18})_{\Sigma=1.0}$

	1a	1b	1c	2	3d	3e	3f	4
Sb	79.3	78.9	79.1	79.2	61.2	59.8	60.5	60.4
Cu	0.2	0.1	0.15	0	15.2	15.7	15.5	15.8

Table III. Electron microprobe analyses (weight %) of cervantite and copper antimonate in pale green "hexagonal crystals" from Castleside smelting mill. Analyses performed by Mr. D.A. Plant at the Department of Earth Sciences, University of Manchester, with a Cameca SX 100 EMPA, using a beam current of 19.9 nA and an accelerating voltage of 20.0 kV. Standards used were chalcopyrite (Cu) and stibnite (Sb).

1. Bulk outer zones, spot analyses (a, b) and average (c).
2. Sb_2O_4, theoretical.
3. Inner zones, spot analyses (d, e) and average (f).
4. $CuSb_2O_6$, theoretical.

CERUSSITE, $PbCO_3$

Colourless needles on pearly hydrocerussite were shown to be cerussite using infrared spectroscopy. It is also prismatic and bladed to 1.5 mm with characteristic pseudohexagonal twinning. Cerussite is found in the lead slags and the copper slags.

CERVANTITE, Sb_2O_4, $(Sb^{3+}Sb^{5+}O_4)$

Colourless to yellow, brownish or pale to bright green plates of hexagonal shape to 0.5 mm (Fig. 3), often clustered in sheafy rosettes, are closely associated with

Figure 3. Pale green "hexagonal platy crystals" of copper antimonate overlain by cervantite, on slag matrix; specimen RSWB 99-95. Field 1.5 mm across. R.S.W. Braithwaite photomicrograph.

anglesite in copper slag. This material is difficult to sample owing to its extreme softness and cleavage, tending to smear when handled. Its infrared spectrum between 400-4000 cm^{-1} shows only a single strong absorption band at 735 cm^{-1}, attributed to an Sb-O stretching vibration, and indicating that no other oxyanions, water or hydroxide are present. Very weak absorptions near 3380 cm^{-1} (O-H stretching) and 1635 cm^{-1} (H-O-H bending) are probably due to traces of moisture, and bands due to anglesite impurity sometimes appear in the spectra. Clinocervantite has strong absorptions at 730, 650 and 425 cm^{-1} (G. Ryback, *pers. comm.*), but no spectrum or authentic specimen of pure cervantite was available for comparison. The powder XRD pattern (provided by Mr. Merfyn Jones) shows a very strong orientation effect, with one extremely strong line at d = 3.082 Å, nearer to strongest line of cervantite at 3.07 Å than to that of clinocervantite at 3.244 Å, and other very weak lines, indicating the presence of a layer-lattice phase. Single-crystal X-ray diffraction (provided by Dr. Robin Pritchard) of a tiny fragment indicated a hexagonal **P**63mc unit cell with dimensions a, 3.8958 and c, 18.3911 Å. It also suggests a layer-lattice structure composed of triple layers of tetrahedra, but the identification is compromised by its mixed nature (*v. infra*).

ED-EMPA analysis by Mr. D.A. Plant on carefully separated 'crystals' showed major Sb only, with variable minor Cu. An element distribution scan (Fig. 4) followed by quantitative analyses of selected areas (Table III) indicate that the 'crystals' contain two platy phases: a minor early green generation of copper antimonate, $CuSb_2O_6$ is overlain by colourless plates of Sb_2O_4 (cervantite).

Copper antimonate has not been recorded as a natural mineral or from slags, but has long been known as a laboratory product. It may be compared with brizziite, $NaSbO_3$ [= $Na_2Sb_2O_6$] and rosiaite, $PbSb_2O_6$, both trigonal, forming hexagonal plates and found in slags, also with bystromite, $MgSb_2O_6$, tetragonal, and partzite, $Cu_2Sb_2(O,OH)_7$(?), probably cubic.

CHENITE, $Pb_4Cu(SO_4)_2(OH)_6$

Chenite occurs as small, transparent, fairly pale blue-green, spear-blade shaped crystals, mostly to 0.2 mm, but exceptionally to 0.4 mm. The crystals are associated with elyite and with caledonite on white pearly crusts of hydrocerussite on copper slag, and appear similar to chenite from Glengaber ("Meadowfoot") mill, Scotland (Green, 1987). Microchemical tests indicate the presence of lead, copper and sulphate, and the absence of carbonate and zinc.

CONNELLITE, $Cu_{19}Cl_4SO_4(OH)_{32}.3H_2O$

Connellite forms characteristic deep blue tiny radiating spherules to 0.1 mm across and needles associated with cuprite. It is found rarely in vesicles in copper slag and on copper metal.

COPPER, Cu

Irregular lumps of copper metal are associated with the copper slag, and occur as prills and blebs in it. The copper contains varying amounts of antimony (Table I, analyses 1, 4 and 5).

COPPER ANTIMONATE, $CuSb_2O_6$

See under CERVANTITE.

CUPRITE, Cu_2O

Small bright red transparent crystals of cuprite, usually cubes typically 0.05 mm across, are found on copper metal. Cuprite also occurs in vesicles in dark vitreous copper slag mostly as octahedra to 0.1 mm, as wire-like pseudomorphs after copper metal, and as small spherical aggregates of needles ("chalcotrichite"). Orange-red fibres, analysed by Dr. David Green using EDS, contained copper with traces of sulphur, and are probably also cuprite.

CUPROSTIBITE, Cu_2Sb

This alloy, of a remarkable violet colour, the "Regulus of Venus" of early chemists, is known naturally as a very rare mineral, containing some thallium, from one vein in Greenland (Sørensen *et al.*, 1969). Broad thin metallic blades of the typical colour to 2.5 x 2 mm associated with lead and Cu-Sb-Sn-Ni-Pb intermetallic phases (*v. infra*) were found on a specimen of white alloy from the copper slag (RSWB 99-92; see Fig. 1 and Table II). Another specimen has a 1-2 mm layer of platy crystals, with a lustrous violet refection when fresh, aligned perpendicularly to the plane of the layer, in a dull grey matrix, with a thin white crust containing small colourless blades of cerussite.

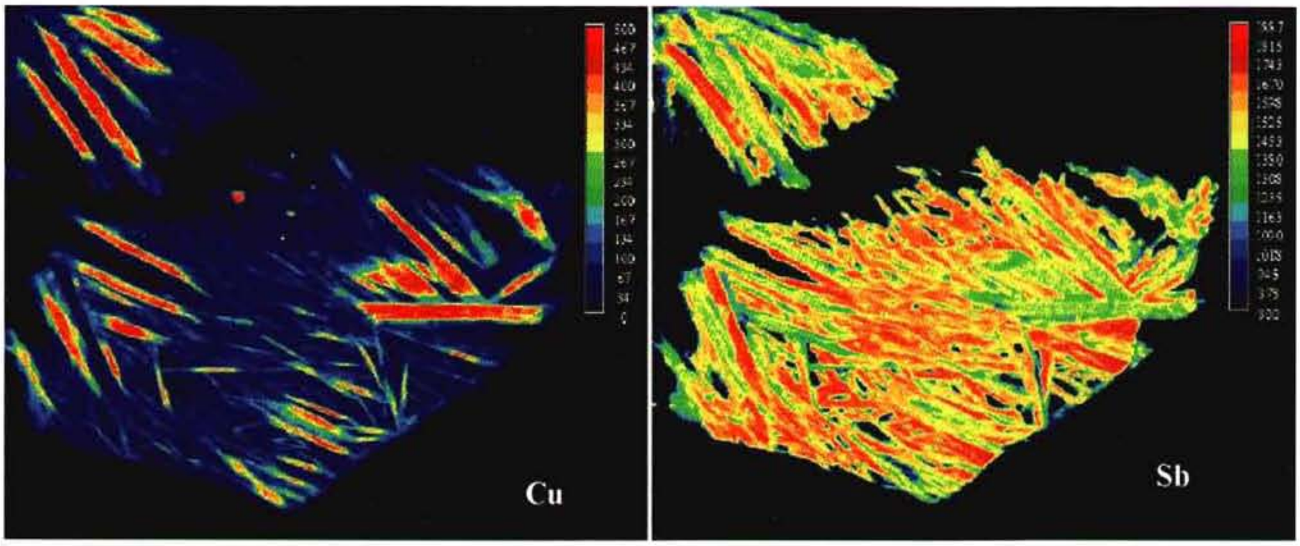

Figure 4. Element distribution maps of (1) copper and (2) antimony in pale green "hexagonal platy crystals" (see Table III). Red = highest % of the element, green = middle % values, blue = low % values. Measured by Mr. D.A. Plant at the Department of Earth Sciences, University of Manchester, using a Cameca SX 100 electron probe microanalyser, utilising a beam current of 19.9 nA and an accelerating voltage of 20.0 kV.

DEVILLINE, $CaCu_4(SO_4)_2(OH)_6.3H_2O$

This was identified by microchemical tests of very thin green laths to 0.4 mm, associated with cerussite on copper slag. The tests indicated the presence of copper and sulphate, and the absence or near-absence of carbonate, lead and zinc.

ELYITE, $Pb_4CuSO_4(OH)_8$

Beautiful clusters of thin violet blades of elyite mostly less than 0.5 mm long are found in vesicles in the copper slag, closely associated with chenite, and normally disposed on pearly white crusts of hydrocerussite. Microchemical tests indicated the presence of lead, copper and sulphate. The largest crystal measured, on a specimen from the Nattrass Collection, is an isolated thin rectangular blade, 0.75 x 0.15 mm, lying flat on hydrocerussite.

GALENA, PbS

Residual galena is found in the lead slag.

GRAPHITE, C

Pieces of graphite containing bright black shiny plates, mostly to 2 mm, some to about 5 mm, have been found with copper slag containing cuprite. The plates have rounded to rounded-hexagonal outlines occasionally with trigonal striations, and are very soft, with a micaceous cleavage. Identification as graphite was confirmed by X-ray powder diffraction. It probably crystallized from pieces of carbon in the slag.

GYPSUM, $CaSO_4.2H_2O$

Gypsum is found as small crystals and crusts on all slags. It was identified visually and by its softness and tendency to bend when poked with a needle.

HYDROCERUSSITE, $Pb_3(CO_3)_2(OH)_2$

Pearly white crusts of hydrocerussite are not uncommon on the lead and copper slags, and underlie caledonite, chenite and elyite. On one specimen the hydrocerussite crust is underlain by white massive lanarkite. These characteristics are very similar to hydrocerussite at Glengaber ("Meadowfoot") mill, Wanlockhead (Green, 1987). Identification was confirmed by infrared spectroscopy (Fig. 5).

IRON, Fe

A sample of white metal analysed by Dr. R Smith (Table I, analysis 7) contained metallic iron with minor Cu and Sb, and traces of Pb.

LANARKITE, $PbSO_4.PbO$

White to colourless needles of lanarkite to 0.6 mm, often in radiating clusters, or tending to become matted, are found in vesicles in copper slag. This phase is often associated with silvery metallic blades of $Cu_3(Sn,Sb)$, described below. Lanarkite is also found as white massive material underlying hydrocerussite and associated with elyite and chenite. Both types were identified by infrared spectroscopy.

LANGITE, $Cu_4SO_4(OH)_6.2H_2O$

Langite occurs rarely in copper slag, associated with cuprite and connellite, as blue-green bladed crystals to 0.5 mm displaying the characteristic pseudohexagonal twinning.

LEAD, Pb

Residual metallic lead is found in the lead slags. Its composition was checked by EMPA (of sample RSWB

99-92; Fig. 1) and found to contain just lead, with only traces of Sn and Sb.

LINARITE, $PbCuSO_4(OH)_2$

Linarite is found rarely in copper slag as tiny royal blue blades in radiating clusters. It was identified visually (Fig. 5).

Figure 5. Linarite, spray of blue crystals on pale green hydrocerussite. Spray about 3 mm across. R.S.W. Braithwaite photomicrograph.

MALACHITE, $Cu_2CO_3(OH)_2$

Small green hemispheres, to about 0.1 mm, radiating thin blades and crusts of malachite are not uncommon. Identification was confirmed by microchemical tests.

PARALAURIONITE(?), PbClOH

Two colourless, transparent, very thin broad blades were visually identified on one specimen of the lead slag. They resemble the paralaurionite crystals in the slags at Glengaber ("Meadowfoot") Mill, Wanlockhead, Scotland (Green, 1987).

SCHULENBERGITE, $(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}.3H_2O$

Small pale green, very thin pearly plates of schulenbergite to 0.2 mm, some in globular clusters to 0.4 mm, were found perched on cuprite coating the lump of brass referred to above. Schulenbergite was identified by infrared spectroscopy and microchemistry; tests with ammonium tetrathiocyanatomercurate(II) in dilute hydrochloric acid solution indicated a Cu:Zn ratio near unity, but with a small excess of Cu.

VALENTINITE(?), Sb_2O_3

A few sheaves of colourless, transparent, extremely thin rectangular blades to about 0.4 x 0.1 mm, with an adamantine lustre, and transverse striations or distortions were found on only one small specimen of the copper slag. These are tentatively identified as valentinite, being strikingly similar to this mineral in habit, fan-like aggregation, lustre and striations. Brandholzite is another less likely possibility.

VIVIANITE, $Fe_3(PO_4)_2.8H_2O$

Vivianite was found on one specimen only of the iron slag, as blue-black tipped near-colourless 1 mm blades in compact radiating masses, appearing to be black until broken open. Its identification was confirmed by infrared spectroscopy.

WROEWOLFEITE, $Cu_4SO_4(OH)_6.2H_2O$

Wroewolfeite is found rarely as deep blue-green, translucent, sharp blocky prismatic crystals to 0.5 mm in length, associated with caledonite in the copper slag. Its identification was confirmed by infrared spectroscopy.

OTHER INTERMETALLIC PHASES

$Cu_3(Sn,Sb)$

Silvery metallic blades with inclined "terminations" (probably fractures), up to about 2 mm long, and often coated with a pearly white material, probably hydrocerussite, are found with the white metal in the copper slag. Single-crystal XRD indicates an orthorhombic *C*2mm phase with unit cell parameters 28.531, 5.506, 4.308 Å. This could not be matched with any published unit cell in the Daresbury database. The crystal used for XRD was analysed by EMPA and found to have the formula $Cu_3(Sn,Sb)$ with Sn:Sb ~2:1. Small variations in composition (up to 1.3 weight %) within the crystal show that when Sb and Ni increase, Sn and Cu decrease (Table II). The sample is intermediate in composition between the well known bronze compound Cu_3Sn and α-Cu_3Sb (β-Cu_3Sb is a high temperature polymorph of Fe_3Si type). A phase with composition Cu_3Sn has recently been reported as a primary phase in smelter slags from north Queensland, Australia (Lottermoser, 2002).

$Sb_3(Sn,Pb)_2$

This phase occurs as a silvery metallic crystalline material with rectangular outlines in the white metal, *e.g.* in RSWB 99-92 (Fig. 1 and Table II).

(Cu,Ni)Sb

This was found in the white metal, *e.g.* in RSWB 99-92 as a silvery metallic phase, associated with the cuprostibite. In one occurrence that was analysed by EMPA, the atomic ratio is Cu:Ni ~1.3:1, close to that of zlatogorite ($CuNiSb_2$), Cu:Ni = 1:1, with some tin replacing antimony (Fig. 1 and Table II analysis 4). Zlatogorite is a silver-white trigonal short-prismatic phase described by Spiridonov *et al.* (1995) from the middle Urals, Russia. Another EMPA analysis (Table II, analysis 5) of a small patch in RSWB 99-92, off the edge of the field visible in Fig. 1, gave an atomic ratio of ~0.62:1 Cu:Ni. This composition lies between that of analysis 4 and zlatogorite. The average of analyses 4 and 5 gives a formula very close to that of stannan zlatogorite, of $(Cu_{0.96},Fe_{0.05})_{\Sigma=1.01}$ $(Ni_{0.95},Fe_{0.05})_{\Sigma=1.00}$ $(Sb_{1.59},Sn_{0.40})_{\Sigma=1.99}$. These results raise the question as to whether zlatogorite (or any polymorph) is a stoichimetric ordered structure as the formula ($CuNiSb_2$) published by Spiridinov *et al.* (1995) implies, or is instead a solid solution (Cu,Ni)Sb with the Cu:Ni atomic ratio near unity. Cu^{2+} and Ni^{2+} have similar ionic radii (72 and 69 pm respectively), charges and electronegativities and are known to substitute for each other. Our analyses (4 and 5 in Table II) suggest that solid solution may well be involved.

UNIDENTIFIED MATERIALS

The complex chemistry of the slags has resulted in a considerable number of phases being present in the weathered material, often in small quantities or in mixtures, and perhaps inevitably, many remain unidentified. A few of these are described below.

(1) Small colourless transparent hexagonal plates and tablets found in the iron slag were analysed by David Green using EDS and found to be a leadhillite group mineral. Its infrared spectrum confirms this, and suggests possible macphersonite, but the small sample size prevents reliable identification within the group as leadhillite, susannite and macphersonite have similar spectra.

(2) Thin opaque brown hexagonal plates to about 0.3 mm across, associated with a white metal, are found sparsely in the iron slags. This could be one of several phases namely plumboferrite, ferrihydrite, ferroxyhite, lepidocrocite or a goethite pseudomorph. They are identical in appearance to material found by the authors at Tindale Fell spelter works, Cumbria (Braithwaite, Lamb and Nattrass, 2006), and to unpublished material found by one of us (RSWB) and J.I. Wilson in slags at Glengaber mill, Wanlockhead, Scotland. Infrared spectroscopy of a small sample was inconclusive, with absorption much weaker than expected, however some carbonate was detected although this probably derives from impurities (as with the Glengaber material).

(3) Small, dull yellow, rounded crystals, reminiscent of sulphur, occur in the iron slag. They are not sulphur as they do not melt when approached with a hot needle.

(4) Tiny red scales, found on one specimen in the lead slag, are probably of litharge.

(5) Dull yellow patches with the probable litharge may be of massicot.

(6) A single, small, very pale green transparent gypsum-like crystal about 0.4 mm long closely resembles that of an unidentified sulphate from the weathered slag of Glengaber mill, Wanlockhead, Scotland, collected by one of us (RSWB) in 1983 (specimen RSWB 83-87). The infrared spectrum of this material indicates a simple but unidentified sulphate, not gypsum, baryte or anglesite.

SUMMARY AND CONCLUSIONS

Weathering processes mobilise heavy metals to varying degrees, depending mainly upon the pH and composition of ground waters, and the initial chemical state of the metals and of their environment, particularly of their direct associates and of the soil or whatever they are surrounded by. The metals may go into solution, in which case they will travel until precipitated as secondary species upon meeting suitable physical-chemical conditions.

A wide range of phases, with a varied chemistry, have been identified at the site of Castleside smelting mill as metallic components of slags and as their weathering products. The varied chemistry is due to the range of materials processed during the working life of the mill. The presence of antimony and copper together has resulted in the formation of some unusual phases, including copper antimonate which is not previously reported from slags or from natural occurrences. However, most of the weathering products are typical of those that have been found in weathered slags from many countries in recent years, indicating a common pattern in the mobilisation of heavy metals from smelting slags into the environment.

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This paper is dedicated to the memory of the late Arthur Roberts (1938 - 2000) whose inspiration was partly responsible for initiating this project.

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SECONDARY SPECIES ASSOCIATED WITH WEATHERING OF INDUSTRIAL RESIDUES AT TINDALE FELL SPELTER WORKS, CUMBRIA

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The site of the Tindale zinc smelter is a wide shallow pit containing a considerable amount of mainly zinc-rich residues. Natural weathering has mobilised and reprecipitated some of the metals, producing a number of secondary products including some unusual phases. Among materials identified are brianyoungite, ettringite, linarite, schulenbergite, dendritic willemite, and a peculiar "flos-ferri"-like vermiform zincite coated with brianyoungite. A number of these phases are strongly fluorescent in UV light, reminiscent of minerals from the zinc mines of Franklin, New Jersey.

INTRODUCTION

The Tindale Fell spelter works, at around NGR NY 617 594, currently consists of a large pit cut into the valley of Tam Beck, bounded on two sides by a former railway, with minimal remains of the works at surface level. In the pit, and particularly at its sides, are piles of variously coloured waste material. This mostly originates from the zinc smelting process in operation from 1845 to 1895, and the fuming process, using rotary kilns, undertaken in the 1930s. The only material with absolute provenance is that from the inside of refractory nozzles from the 19th Century operations. The term "spelter" is an old name for crude zinc metal. Almond (1977) provides a history of the works.

The 19th Century smelting process involved initially roasting in air the crushed zinc ore concentrate, mostly sphalerite. The resulting oxide was then mixed with powdered carbon in the form of coal or coke, and placed in retorts ("pots") of refractory material, these then being heated in furnaces, with the retort nozzles projecting and attached to some means of effecting condensation by cooler air. The carbon reduced the oxide to zinc metal, which being volatile distilled over, was condensed into liquid and collected in vessels for further purification (the process is described by Percy, 1861). Much of the waste at the site probably originates from this process, and consists of slags, unaltered zinc products, carbonaceous residues and materials formed from reaction with the refractory pots, from oxidation of zinc vapour with air, and from impurities in the ore, such as lead, iron, copper and cadmium.

The amounts of zinc, lead and cadmium contamination in the smelter residues, soil, stream sediments and in Tam Beck have recently been studied by Cutter (1998). Wide variations were found, the smelter residues containing up to 16.8 % Zn, 4.2 % Pb and 227 ppm Cd (Cutter, 1998). Residues from the fuming processes, operated in the 1930s to recover zinc and cadmium oxides by volatilisation, may be of more complex composition from its use of differing feedstocks, both local and imported from smelters in SW England.

In addition to visual properties, identification of mineral species was achieved using microchemical techniques (described by Braithwaite, Lamb and Nattrass, 2006), infrared spectroscopy and fluorescence under ultraviolet light.

SPECIES IDENTIFIED

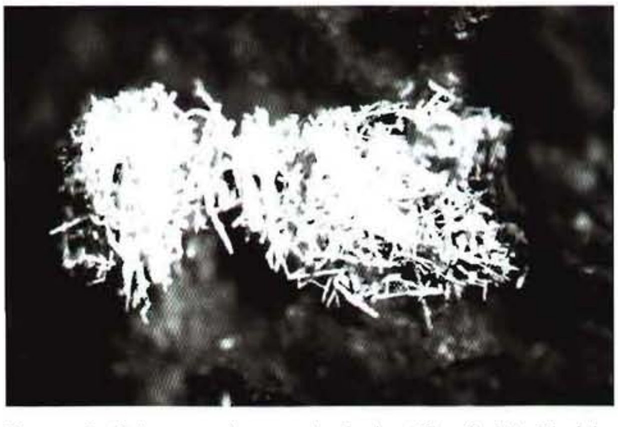

Figure 1. Brianyoungite-coated zincite "flos-ferri", Tindale. Specimen RSWB 99-103. Field of view 3 mm across. R.S.W. Braithwaite photomicrograph.

BRIANYOUNGITE, $Zn_3(CO_3,SO_4)(OH)_4$

Brianyoungite is relatively common, forming crusts of small white needles and white to off-white pearly masses, closely associated with hydrozincite, inside the refractory nozzles, and on a heterogeneous matrix containing black vitreous slag and coke, presumably derived from the pots. Brianyoungite is distinguished from the associated hydrozincite most easily by examination in short-wave UV, in which the hydrozincite normally displays its usual bright sky-blue fluorescence, whereas the brianyoungite shows a bright to weak creamy-yellow fluorescence (weaker or none in long-wave UV). Type brianyoungite is not fluorescent (Livingstone and Champness, 1993). Confusingly, some cream-coloured porcellanous hydrozincite from this site displays a strong cream-yellow fluorescence under long-wave UV (*v. infra*). Brianyoungite is also found, rarely, as white coatings on zincite forming curious growths resembling "flos-ferri" (Fig. 1). The identifications of brianyoungite were confirmed by infrared spectroscopy. It can be confused with the ettringite, which also forms crusts of white needles (*v. infra*).

BROCHANTITE, $Cu_4SO_4(OH)_6$

Crusts of tiny bright green crystals, mostly about 0.1 mm across, and occasional isolated rectangular crystals to about 0.5 mm were shown by microchemical tests and infrared spectroscopy to be brochantite.

CALCITE, $CaCO_3$

Calcite forms indistinct white patches among the hydrozincite-brianyoungite material, and is easily identified by its strong red fluorescence under short-wave UV, weaker under long-wave UV. This fluorescence suggests the presence of manganese impurity. Identification was confirmed by infrared spectroscopy.

DEVILLINE, $CaCu_4(SO_4)_2(OH)_6.3H_2O$

Devilline occurs rarely as tiny green pearly blades to nearly 1 mm long associated with brochantite. Microchemical tests showed that these crystals are a copper-rich sulphate, with no lead or carbonate, and little zinc.

ETTRINGITE, $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$

Rare in the British Isles as a natural mineral, ettringite is found as cavity lining crusts of white needles, superficially resembling natrolite, the fine needles, up to about 1 mm long (considerably longer than those of brianyoungite) in grey slag containing fragments of charcoal. Ettringite was identified by its characteristic infrared spectrum, which also shows some absorption due to carbonate; this may be an impurity or may be substituting for some of the sulphate in the lattice. The crystals are not fluorescent under UV.

GOETHITE, α-FeO(OH)

Goethite is common as rusty-looking lumps and crusts. Its identity was confirmed by infrared spectroscopy.

GYPSUM, $CaSO_4.2H_2O$

Aggregates and crusts of small gypsum crystals are, as expected, not uncommon. A few larger crystals can be found (in the mm range). It was identified visually, by hardness and by ease of bending.

HAEMATITE, Fe_2O_3

Crusts of small black glittering crystals in brown crumbly ferruginous matrix were shown by infrared spectroscopy to be of haematite. It is mixed with an unidentified phase with an absorption maximum at 1035 cm^{-1} extending via a strong shoulder to about 1140 cm^{-1}.

HYDROZINCITE, $Zn_5(CO_3)_2(OH)_6$

Common as white crusts, sometimes scaly or composed of microscopic needles, hydrozincite displays a characteristic brilliant sky-blue fluorescence under short-wave UV only. It is also found as cream-coloured porcellanous crusts and masses with a strong cream-yellow fluorescence under long-wave UV, but giving the characteristic infrared spectrum of hydrozincite.

LEPIDOCROCITE, γ-FeO(OH)

Lepidocrocite forms brown layers of parallel, fairly lustrous fibres, to about 0.5 mm thick, associated with rust-like goethite. Its identity was confirmed by infrared spectroscopy.

LINARITE, $PbCuSO_4(OH)_2$

Linarite is rare at the Tindale site. It forms superb radiating clusters of royal-blue long-prismatic crystals to about 1 mm long (Fig. 2). Its identity was confirmed visually and by microchemical tests, which indicate the absence of carbonate and the presence of lead, copper and sulphate.

SCHULENBERGITE, $(Cu,Zn)_7(SO_4,CO_3)_2(OH)_{10}.3H_2O$

Schulenbergite is rare, forming pale green pearly platy crystals to 0.4 mm, closely associated with the possible leadhillite-group mineral described below under unidentified materials (3) and pearly scaly white hydrozincite. Microchemical tests indicate the presence of sulphate, some carbonate, no lead, but much copper and zinc.

SERPIERITE, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6.3H_2O$

Blue-green pearly laths to 0.5 mm, rich on a few specimens, give positive reactions for copper, zinc and sulphate, but not carbonate or lead. The identification as serpierite was confirmed by infrared spectroscopy.

WILLEMITE, Zn_2SiO_4

Pale brownish dendritic crystallites to about 2mm, projecting from brown crumbly ferruginous matrix, resembling Christmas trees and sometimes coated with white brianyoungite, were shown by infrared spectroscopy to be of willemite. This willemite fluoresces green in short-wave UV, but not very strongly.

ZINC, Zn

Relicts of metallic zinc ("spelter"), the primary product of the plant are, not surprisingly, found in the slag.

ZINCITE, ZnO

White growths resembling "flos-ferri", with thin "worms", some straight but most windingly curved up to 3 mm long and 0.05 mm wide (see Fig. 1), are seen under the microscope to have darkish, translucent cores of crudely hexagonal cross-section, with an adamantine lustre, and a soft white crust. Infrared spectroscopy shows the presence of zincite (presumably the core), with a strong absorption at 444 cm^{-1} with a weaker absorption, almost a shoulder, at 521 cm^{-1} and weaker absorptions characteristic of brianyoungite (presumably the crust). This material is not fluorescent, however, material that probably also contains zincite which shows a strong green fluorescence is described below under unidentified materials (4). The "flos-ferri" zincite was presumably formed by sublimate oxidation and condensation, and the coating by subsequent weathering. Percy (1861, p. 533) notes the formation of "greenish-yellow oxide".

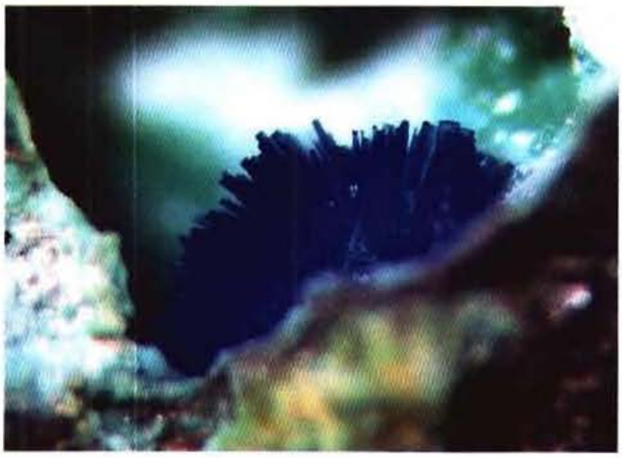

Figure 2. Spray of linarite crystals, Tindale. Field of view 2.5 mm across. R.S.W. Braithwaite photomicrograph.

UNIDENTIFIED MATERIALS

The complex nature of the mix of waste materials at this site inevitably results in a wide range of substances being present, often as mixtures and in small particle size or concentration, rendering identifications difficult. The more distinctive phases present are described below.

(1) A dull sub-metallic dark grey phase in vesicles in dark grey slag, forming tiny tetrahedra with rounded edges and corners to 0.1 mm, and flattened triangular crystals and complexes, some with dull yellow outer zones; one sharp, cleaved part-tetrahedron with a bright yellow outer zone (CdS?) is 0.3 mm across. The sub-metallic phase is probably a primary slag component, not a weathering product.

(2) Thin brown hexagonal plates typically about 0.3 mm across on crumbly goethite-rich matrix. This material is identical in appearance to an unidentified phase found by the authors at Castleside smelting mill, County Durham (Braithwaite, Lamb and Nattrass, 2006) and an unpublished phase found by one of us (RSWB) and J.I. Wilson at Glengaber mill, Wanlockhead, Scotland. A pure sample could not be obtained, impurities including goethite and a black magnetic phase. An infrared spectrum, measured from 4000–400 cm^{-1} of a reasonably strong mull of a sample gave weak absorptions from goethite, and a weak band at ~1118 cm^{-1}, suggesting that the major phase does not absorb in this region, and is free from oxyanions, water and hydroxide. Two samples, with different proportions of matrix impurities, were submitted to X-ray powder diffractometry. The smaller sample, with relatively less matrix, gave no lines distinguishable from noise background. The larger sample gave a pattern with strong lines matching those of ferrokesterite ($Cu_4FeZnSn_2S_8$), the match being distinctly closer than with the spectra of sphalerite or elemental silicon. Weak lines indicate the presence of traces of goethite and magnetite. Lepidocrocite, maghemite, ferroxyhite and haematite are absent. This soft, easily powdered material seems to be largely X-ray amorphous. Ferrokesterite, which is a silver-white mineral, was not visible under the microscope at x 56, so this identification based on XRD must be a finely divided impurity or an error.

(3) Minute colourless crystals of hexagonal tabular habit, which are probably of the leadhillite group. This phase is closely associated with schulenbergite and hydrozincite.

(4) A phase giving a brilliant green fluorescence under long-wave UV, but no fluorescence under short-wave UV, is found with the hydrozincite-brianyoungite material. Under the microscope the green fluorescence is seen to originate from very pale yellow-green to off-white massive to polycrystalline patches. An infrared spectrum of this material shows a very strong, broadish band with maximum at 449 cm^{-1}, a shoulder at about 530 cm^{-1}, a weak but distinct absorption at 599 cm^{-1} and other weak bands suggestive of the presence of brianyoungite impurity. The material may contain zincite, which has a strong absorption near 440 cm^{-1} with a shoulder at 520-550 cm^{-1} but is not normally fluorescent.

(5) A greyish crystalline non-fluorescent material forming the "matrix" of some hydrozincite gives an infrared spectrum indicating a hydrated sulphate, possibly mixed with zinc oxide. Absorptions, in cm^{-1} comprise (a) a strong broad O-H stretching vibration at ~3310, (b) a fairly weak H-O-H "scissor" vibration at ~1630, (c) no carbonate absorptions, (d) strong sulphate absorptions at 1132, 1070, 964 and 604, (e) a shoulder near 1030, (f) a broad medium-strength band with maximum absorption near 730; and (g) possible zincite absorptions forming a strong band at 437 with a weaker one at 514. Similar material underlies brianyoungite, lining a nozzle; being strongly hydrated it must be a weathering rather than a sublimation product.

SUMMARY AND CONCLUSIONS

In addition to unchanged industrial residues including flue linings, a number of secondary species have been identified at Tindale. These have resulted from the natural weathering of the industrial residues, and are mostly similar to those normally found as the weathering products of smelter slags. Zinc species predominate, as the site was mostly used for zinc smelting. Particularly interesting are samples of brianyoungite, serpierite, willemite and zincite, and of the zinc-free species ettringite and linarite. Linarite is rare but forms excellent crystals.

The spectacular fluorescence of much of this material in UV light recalls the fluorescence of the minerals from the famous zinc mines of Franklin, New Jersey.

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HYDRONIUM JAROSITE FROM BRYNYCASTELL MINE, DOLGELLAU, GWYNEDD, WALES

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The uncommon iron sulphate mineral hydronium jarosite has been identified in post-mining efflorescence within a sheltered part of opencast iron ore workings at the Brynycastell mine near Dolgellau in North Wales. Oxidation of pyritic wall-rock has produced the highly acidic conditions required for the formation of hydronium jarosite. This represents the first verified occurrence of hydronium jarosite from Wales.

Hydronium jarosite, $(H_3O)Fe^{3+}_3(SO_4)_2(OH)_6$ is a rare secondary iron sulphate that forms part of a solid-solution series with jarosite, $KFe^{3+}_3(SO_4)_2(OH)_6$ and natrojarosite, $NaFe^{3+}_3(SO_4)_2(OH)_6$ within what has been termed the jarosite family. Hydronium jarosite was the last of the jarosite family to be named in 1960 (Kubisz) following much confusion over the true identity of the species carphosiderite. Detailed analysis by Moss (1957) and Van Tassel (1958) showed that a number of minerals previously described as carphosiderite were in fact jarosite or natrojarosite. Moss doubted the existence of a natural occurring mineral of the composition claimed for carphosiderite, although such a compound $[H_2O.Fe_3(SO_4)_2(OH)_5H_2O]$ had previously been prepared artificially by Posnjak and Merwin (1922). Moss proposed that the name carphosiderite be dropped from usage due to the confusion caused by a rush to name a new species that did not actually exist. However, in 1960, Kubisz demonstrated conclusively that a mineral of this composition exists at Staszic mine, Holy Cross Mt., Poland, naming it hydronium jarosite on the basis of its composition. Typically of supergene origin, hydronium jarosite precipitates under highly acidic conditions brought about through the decay of pyrite, particularly in massive sulphide deposits. Hydronium jarosite is known from a few dozen localities worldwide, but is far less frequent than jarosite and natrojarosite.

In the British Isles hydronium jarosite is extremely rare. Bevins (1988) produced the first record of hydronium jarosite in the British Isles, describing abundant deposits in all underground workings at Parys Mountain, Anglesey, Gwynedd, Wales, based upon a personal communication from D.A. Jenkins in 1986. Identification was believed to have been made by XRD and wet chemical analysis, subsequently however Jenkins *et al.* (2000) recorded hydronium jarosite as 'yet to be confirmed by XRDA' in a provisional list of recorded minerals from Mynydd Parys (Parys Mountain). The first verified account of hydronium jarosite in the British Isles was made by Moreton *et al.* (1995) at Ballybunnion, Co. Kerry, Eire, where dull, earthy, pale yellow encrustations on joint surfaces of pyritic black shales were shown by IR spectrometry and XRD to be hydronium jarosite. A second account, by Moreton *et al.* (1999) describes masses of brown, powdery hydronium jarosite in dumps at Muckross mine, Killarney, Co. Kerry, Ireland with confirmation by XRD and SEM-EDX analysis.

The author can now report the first verified occurrence of hydronium jarosite in Wales, at Brynycastell mine, Cross Foxes, near Dolgellau, Gwynedd (NGR SH 760 164). Brynycastell mine (Mining Journal, 1871 & 1873; London Gazette, 1876 & 1878; Home Office List of Mines, 1908-1910), more commonly, but incorrectly known as Cross Foxes mine, is a small iron mine which worked bedded pisolitic iron ore of Ordovician age by means of a series of narrow NE-SW trending opencuts and adits. A little over 12,000 tons of ore was produced during the last phase of workings, between 1908-10 (Strahan *et al.*, 1920), but no details are known of earlier operations. A large part of the site is now covered by conifer woodland, but the southern end of the site has escaped afforestation and consists of a shallow, partially backfilled, opencut and a collapsed shaft. Exposures around the SE side of the southern-most opencut reveal bedded pisolitic iron ore heavily impregnated with fine-grained to massive pyrite, much of which is heavily decayed, imparting a rusty colour upon the surrounding rock. Of particular interest to the author was a small area (35 cm across) of bright yellow efflorescence underneath a small overhang on the SE side of the opencut (Fig. 1). Closer examination of this sulphur-yellow crust showed it to consist of delicate acicular sprays.

Figure 1. Yellow hydronium jarosite and gypsum efflorescence exposed in the southern opencut at Brynycastell mine. Field of view 40 cm across.

Figure 2. Rusty orange hydronium jarosite pseudomorphs after prismatic gypsum crystals. National Museum Wales specimen no. NMW 2006.11G.M.2. Field of view 6 mm across.

Figure 3. Hydronium jarosite pseudomorphs after prismatic gypsum crystals with colourless gypsum overgrowth. National Museum Wales specimen no. NMW 2006.11G.M.6. Field of view 9 mm across.

Samples were collected and XRD analyses performed. Initial results (XRD no. NMW X-1448) indicated that yellow crusts on specimen no. NMW 2006.11G.M.1, are composed of a mixture of gypsum and hydronium jarosite. Stereo microscopy revealed that the acicular sprays were in fact prismatic gypsum crystals, but with an unusual yellow colour, brought about by inclusions of hydronium jarosite. In order to ascertain whether or not pure hydronium jarosite was present, the author performed further analyses. Hydronium jarosite was found to be present in a number of forms which can be summarized as follows: thin yellow crusts overgrown by prismatic gypsum, in turn coated by thin pale yellow films of hydronium jarosite (XRD no. NMW X-1448); straw-yellow inclusions within slender prismatic gypsum crystals (XRD no. NMW X-1448b); inconspicuous yellow-orange crusts and epimorphs after small flat-lying prismatic gypsum crystals (XRD no. NMW X-1448c) & rusty orange (Fig. 2.) to yellow-orange (Fig. 3) pseudomorphs after delicate prismatic gypsum crystals (XRD no. NMW X-1454 on specimen no. NMW 2006.11G.M.2). Electron probe microanalysis (EPMA) of the same samples, support this identification, indicating the presence of major Fe, S and O with only traces of Ca, Na, Al, Mg, P and Si, no K (jarosite) was detected.

It is clear from all of the specimens studied that hydronium jarosite and gypsum occur in intimate association. Gypsum is however, an extremely common mineral in acidic environments dominated by soluble sulphates (Jambor *et al*., 2000) and therefore its presence in association with hydronium jarosite at Brynycastell mine is of no great surprise. In nature, hydronium jarosite is far rarer than jarosite or natrojarosite. Although all precipitate under highly acidic conditions hydronium jarosite can only form in iron-bearing sulphate solutions poor in alkali ions such as Na^+ and K^+ (Brophy and Sheridan, 1965; Dutrizac and Jambor, 2000). Experiments to synthesise hydronium jarosite have shown that at 140°C, stoichiometric hydronium jarosite forms over the pH range 0.4 to 1.4 and above 160°C precipitation ceases entirely (Dutrizac & Jambor, 2000), but information regarding formation at, or below, room temperature is lacking. Ideal conditions occur in nature only where pyrite or other iron sulphides undergo extremely rapid oxidation (Kubisz, 1961) accompanied by rapid partial neutralization of the solutions by carbonate rocks. This allows hydronium jarosite to precipitate before alkali is released from the country rock, at which point jarosite is more likely to form (Brophy and Sheridan, 1965).

The presence of hydronium jarosite at Brynycastell mine indicates that geological conditions are well suited for precipitation to take place. The pisolitic iron ore occurs within a sequence of beds of fairly uniform dip (between 50-60° SE) and strike (NE-SW) ideal for opencast mining. The resultant open cuts have produced an overhang on the SE side where the beds dip underground. The upper beds of pisolitic ore have been left in place, probably because they contain large quantities of pyrite in lenses parallel to bedding, as witnessed in exposures around the SE side of the southern opencut. Fine-grained pyrite is particularly susceptible to decay, as large surface areas are in contact with groundwater and the atmosphere resulting in rapid oxidation (Jambor *et al*. 2000), a feature clearly evident at Brynycastell mine. The host rock, dominated by the silicate chamosite, is unlikely to have the buffering capacity to override acid production from pyrite oxidation and consequently precipitation of sulphates begins. Quite why hydronium jarosite preferentially forms is unclear, but the only obvious source of alkali at Brynycastell mine is the mineral stilpnomelane $[K(Fe^{2+},Mg,Fe^{3+})_8(Si,Al)_{12}(O,OH)_{27}]$, but this appears not to alter, perhaps because it occurs in veins with the carbonate calcite which appears (from observed specimens) to neutralize the acidic waters. No other iron sulphates have been identified, but many simple hydrated sulphate salts, particularly those of iron (eg. melanterite, siderotil, copiapite and fibroferrite) are soluble in water (Jambor *et al*., 2000; Bigham and Nordstrom, 2000) and would not be expected to form in surface workings exposed to the atmosphere in temperate climes. Hydronium jarosite, in common with other jarosite group minerals, has a relatively low solubility. This, combined with the partial shelter of an overhang within the opencut at Brynycastell mine, allows it to remain unaffected by the damp Welsh climate.

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CLINOPTILOLITE AND HEULANDITE FROM WHEAL HAZARD, ST JUST, CORNWALL

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Quantitative chemical analyses of a number of millimetre-sized crystals detached from specimens labelled 'heulandite' from Wheal Hazard, St Just, Cornwall show that most of their compositions lie within the closely related clinoptilolite series of minerals: specifically, potassium- and magnesium-rich clinoptilolite-Ca. An average of 28 analyses produces the chemical formula: $(Ca_{1.87},K_{1.31},Mg_{0.86},Na_{0.12},Sr_{0.07},Ba_{0.04},)[Al_{7.22}Si_{28.81}O_{72}].nH_2O$. The crystals occur in fine grained metasedimentary rocks of the Mylor Slate Formation, in fractures that post-date the development of the metamorphic fabric. It seems likely that the crystals developed as a result of hydrothermal alteration of the rock during the final stages of the cooling of the Land's End Granite. On the basis of our analyses it is unsafe to label specimens from the well-known 'heulandite' locality at Wheal Hazard as heulandite.

INTRODUCTION

As part of a systematic survey of the chemistry of zeolite group minerals from Britain and Ireland, the composition of a number of 'heulandite' specimens from Cornwall was determined. These included several specimens of grey killas covered in pale yellow blocky crystals up to about 1 mm across from the Wheal Hazard section of Botallack Mine in the parish of St Just, Cornwall (NGR: SW 363 334). Heulandite from this locality is well known and the specimens are characteristic (Fig. 1; Russell, 1910; Golley and Williams, 1995). The material we examined included a specimen collected in the 1970s that was purchased from the mineral dealer Richard Barstow (Manchester Museum accession number N06144) and a number of others supplied by Russell Society members Chris Jewson, Nigel Hoppé, Richard Bell and Neil Hubbard. All are typical of material from Wheal Hazard and there is no doubt of their provenance.

The minerals of the heulandite series share a unique tectosilicate framework structure with those of the clinoptilolite series. Heulandite is defined as the part of the series having an Si:Al ratio of less than four (high aluminium content and high charge on the framework), while in clinoptilolite the ratio is greater than or equal to four (low aluminium content and low charge on the framework) (Coombs *et al.*, 1998).

In the heulandite series, the calcium dominant species heulandite-Ca is very common, heulandite-K and -Na are rarer, and heulandite-Sr and -Ba are known from very few localities worldwide. The clinoptilolite series minerals tend to be dominated by the univalent cations Na and K, but clinoptilolite-Ca is also relatively common (Bish and Boak, 2001; Passaglia and Sheppard, 2001).

Figure 1. A blocky crystal of clinoptilolite-Ca a little over 1 mm across on iron stained matrix from Wheal Hazard, St Just, Cornwall. David Green photograph.

Heulandite commonly occurs in cavities in mafic igneous rocks and is also found in low temperature hydrothermal mineral veins and skarns. Although clinoptilolite is the most abundant zeolite known, it is relatively unfamiliar to collectors. It occurs in 'sedimentary' environments where it forms in hydrologically closed saline alkaline lakes or in open systems from the slow percolation of meteoric waters through tuffs and tuffaceous sediments. It is also commonly formed as a result of burial diagenesis or metamorphism and occurs in deep-sea sediments and those derived from submarine volcanism (Hay and Sheppard, 2001).

METHOD

Initially, specimens were examined by X-ray diffractometry (XRD), which was sufficient to prove that they belonged to the heulandite or clinoptilolite series. For analyses by XRD, the material to be identified was hand-picked with a needle, finely ground and applied in solvent suspension to a glass slide. The thin film produced was mounted in an X-ray diffractometer (CuKα radiation, 40 kV, 20 mA) and its diffraction pattern recorded. Identifications were made using standard pattern matching algorithms.

Initial chemical investigations were made using an SEM with an environmental chamber at the University of Wolverhampton. Quantitative chemical analyses of single crystals were then made by wavelength dispersive spectrometry (WDS) at the Open University. Single crystals were hand picked from the specimens, embedded in resin and polished to produce a flat surface. Analyses were made at 20 kV and 20 mA with a 20 μm beam diameter to minimise volatilisation. Short counting times reduced decomposition under the electron beam.

Back-scattered electron images of the crystal revealed no obvious bulk compositional zoning. The results of 28 spot analyses on crystals from 5 specimens are included in Table 1.

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	SrO	BaO	H_2O*
P112	66.21	14.01	1.25	3.81	0.10	2.44	0.23	0.23	11.72
P112	66.22	14.04	1.23	3.71	0.21	2.70	0.23	0.23	11.45
P112	66.13	14.05	1.28	4.18	0.18	2.12	0.22	0.30	11.53
P112	67.26	14.48	1.46	3.89	0.27	2.24	0.18	0.21	10.02
P112	67.85	13.24	1.14	3.99	0.18	2.03	0.18	0.19	11.21
P113	62.44	15.48	1.87	3.38	0.26	2.91	0.48	0.19	12.98
P113	63.54	14.99	1.60	3.73	0.17	2.50	0.35	0.23	12.89
P113	63.78	14.47	1.62	3.78	0.14	2.23	0.24	0.25	13.48
P113	64.32	14.35	1.47	4.10	0.13	1.80	0.25	0.37	13.23
P113	67.28	13.28	0.98	4.27	0.11	1.76	0.29	0.18	11.86
P114	65.17	13.44	1.18	4.22	0.02	1.49	0.27	0.27	13.95
P114	64.69	13.21	1.17	4.12	0.03	1.68	0.33	0.22	14.55
P114	65.65	13.47	1.19	4.14	0.05	1.76	0.25	0.23	13.25
P114	64.75	13.36	1.17	4.03	0.04	1.81	0.35	0.26	14.22
P114	66.33	12.78	1.24	3.85	0.06	1.57	0.25	0.15	13.78
P115	65.12	13.99	1.26	4.04	0.11	2.17	0.27	0.22	12.82
P115	65.05	14.03	1.30	4.08	0.17	2.12	0.25	0.24	12.76
P115	64.54	14.36	1.47	4.08	0.19	2.13	0.35	0.35	12.54
P115	66.59	13.63	1.25	4.15	0.20	1.99	0.32	0.25	11.63
P115	67.52	13.24	1.31	3.96	0.12	1.42	0.20	0.16	12.06
P116	66.28	14.07	1.18	3.92	0.16	2.46	0.26	0.21	11.45
P116	66.28	13.75	1.34	3.74	0.07	2.34	0.21	0.15	12.13
P116	66.18	13.96	1.23	3.90	0.11	2.17	0.22	0.19	12.05
P116	67.55	14.21	1.16	3.88	0.25	2.60	0.22	0.27	9.86
P116	66.98	13.92	1.17	3.70	0.25	2.66	0.20	0.20	10.93
P116	67.42	14.53	1.26	4.05	0.10	2.37	0.25	0.22	9.81
P116	66.08	15.06	1.51	4.31	0.15	1.83	0.36	0.39	10.30
P116	65.57	14.60	1.53	4.38	0.08	1.44	0.31	0.30	11.79

Table 1. The results of 28 microprobe analyses of crystals of 'heulandite' from Wheal Hazard quoted as weight percent oxides (P116 corresponds to Manchester Museum specimen accession number N06144; the others were supplied by Russell Society members Chris Jewson, Nigel Hoppé, Richard Bell and Neil Hubbard). Analytical standards used are (Si, Al and K = K-feldspar, Ca = bustamite, Na = jadeite, Sr = synthetic $SrTiO_3$, Ba = baryte). Water is calculated by difference. In addition to the elements tabulated, S, Cl, Zn, Ti, Mn, P and F were measured, but all were at or below the detection threshold of the spectrometer.

	Si	Al	Mg	Ca	Na	K	Sr	Ba	Si/Al	E value	Conclusion
P112	28.86	7.20	0.81	1.78	0.08	1.52	0.06	0.04	4.01	3.20	Clinoptilolite-Ca
P112	28.83	7.20	0.80	1.73	0.18	1.68	0.06	0.04	4.00	1.46	Clinoptilolite-Ca
P112	28.78	7.21	0.83	1.95	0.16	1.32	0.06	0.05	3.99	-0.54	Heulandite-Ca
P112	28.74	7.29	0.93	1.78	0.22	1.36	0.04	0.03	3.94	1.84	Heulandite-Ca
P112	29.27	6.73	0.73	1.84	0.15	1.25	0.04	0.03	4.35	0.36	Clinoptilolite-Ca
P113	27.86	8.14	1.24	1.62	0.23	1.85	0.13	0.03	3.42	0.32	Heulandite-K
P113	28.21	7.84	1.06	1.77	0.14	1.58	0.09	0.04	3.60	2.38	Heulandite-Ca
P113	28.42	7.60	1.08	1.81	0.12	1.42	0.06	0.04	3.74	1.14	Heulandite-Ca
P113	28.54	7.50	0.97	1.95	0.11	1.14	0.06	0.06	3.80	2.31	Heulandite-Ca
P113	29.24	6.80	0.63	1.99	0.09	1.09	0.07	0.03	4.30	2.57	Clinoptilolite-Ca
P114	29.01	7.05	0.78	2.01	0.02	0.95	0.07	0.05	4.11	3.86	Clinoptilolite-Ca
P114	29.04	6.99	0.78	1.98	0.03	1.08	0.09	0.04	4.16	1.36	Clinoptilolite-Ca
P114	29.02	7.02	0.79	1.96	0.04	1.11	0.06	0.04	4.14	2.43	Clinoptilolite-Ca
P114	28.99	7.05	0.78	1.93	0.04	1.15	0.09	0.05	4.11	2.24	Clinoptilolite-Ca
P114	29.37	6.67	0.82	1.82	0.05	0.99	0.06	0.03	4.40	2.56	Clinoptilolite-Ca
P115	28.75	7.28	0.83	1.91	0.10	1.36	0.07	0.04	3.95	1.70	Heulandite-Ca
P115	28.71	7.30	0.86	1.93	0.15	1.34	0.06	0.04	3.93	0.45	Heulandite-Ca
P115	28.50	7.47	0.97	1.93	0.17	1.34	0.09	0.06	3.81	-1.68	Heulandite-Ca
P115	28.97	6.99	0.81	1.93	0.17	1.23	0.08	0.04	4.14	-1.98	Clinoptilolite-Ca
P115	29.29	6.77	0.85	1.84	0.10	0.88	0.05	0.03	4.33	3.89	Clinoptilolite-Ca
P116	28.83	7.21	0.77	1.83	0.14	1.53	0.07	0.04	4.00	2.22	Clinoptilolite-Ca
P116	28.96	7.08	0.87	1.75	0.06	1.46	0.05	0.03	4.09	2.43	Clinoptilolite-Ca
P116	28.90	7.18	0.80	1.82	0.09	1.35	0.06	0.03	4.02	4.50	Clinoptilolite-Ca
P116	28.88	7.16	0.74	1.78	0.20	1.59	0.05	0.05	4.03	1.85	Clinoptilolite-Ca
P116	28.95	7.09	0.76	1.71	0.21	1.64	0.05	0.03	4.08	1.97	Clinoptilolite-Ca
P116	28.76	7.31	0.80	1.85	0.09	1.44	0.06	0.04	3.94	4.00	Heulandite-Ca
P116	28.41	7.63	0.97	1.98	0.12	1.12	0.09	0.07	3.72	2.20	Heulandite-Ca
P116	28.56	7.49	1.00	2.04	0.07	0.89	0.08	0.05	3.81	2.75	Heulandite-Ca

Table 2. Formulae calculated from the data in Table 1 on the basis of 72 structural oxygen atoms. The first column is the analysis number. The next eight columns contain the formula amounts of silicon, aluminium, magnesium, calcium, sodium potassium, strontium and barium so the formula in the first row is: $(Ca_{1.78},K_{1.52},Mg_{0.81},Na_{0.08},Sr_{0.06},Ba_{0.04},)[Al_{7.2}Si_{28.86}O_{72}].nH_2O$. The ratio of Si/Al is obtained by dividing the value in column three by column two. The E-value, which is an indication of the quality of the analysis, is ((Na+K)+2(Ba+Sr+Ca)-(Al))/((Na+K)+2(Ba+Sr+Ca))x100 (see Passaglia and Sheppard, 2001). The final column gives the species name.

DISCUSSION

Clinoptilolite and heulandite series minerals require XRD and full chemical analyses if they are to be identified to species level. Minerals of the heulandite series tend to be found as macroscopic crystals in cavities in mafic igneous rocks whereas clinoptilolite series minerals occur as microscopic crystals, which form diagenetically in a variety of 'sedimentary' environments. There is a tendency to label specimens as either heulandite or clinoptilolite on the basis of the environments in which they formed. One of the objectives of this study was to test whether this is reasonable.

In Britain, heulandite is well known from the basalts of Devonian age that crop out around Glasgow and from the Tertiary basalts of western Scotland and Northern Ireland (Heddle, 1901; Tindle, 2006). We have examined specimens, labelled as heulandite, from fourteen different localities in the British Isles. They are representative of a variety of geological environments including cavities in basalt, skarns and low temperature hydrothermal veins. All fell within the heulandite composition field, with Si/Al < 4 with the exception of the specimens from Wheal Hazard described here. The data support the general observation that macroscopic crystals and especially those in mafic igneous rocks, tend to be heulandite.

In comparison to heulandite, clinoptilolite is uncommon as macroscopic crystals in veins and vesicles in volcanic rocks (*e.g.* Gottardi and Galli, 1985). There are a few reports of this type of occurrence in the British Isles, the most recent of which is due to Robert (2001) who provided analyses of samples from the tholeiitic Middle Basalts at Criagahulliar Quarry, Co. Antrim, Ireland: XRD and microprobe analyses confirmed the identity of this mineral, with measured Si/Al ratios of four specimens falling within the accepted range for clinoptilolite (4.2-4.72). Earlier, Evans (1987) had described clinoptilolite from Clyde Plateau Lava localities near Jock's Craig, Clachen, near Kilmalcolm and at Lang Craig, near Dumbarton. Identification was based upon XRD coupled with optical observations, but without elemental analyses. Our own quantitative analyses of specimens from the last of these localities indicate that at least some of the material from Lang Craig is heulandite-Ca.

Several authors have reported XRD identifications of undifferentiated clinoptilolite-heulandite in sedimentary environments in Britain. It was first noted in this type of environment in Upper Greensand of Cretaceous age (at Halton, Buckinghamshire in the Harwell Series soils) and from Jurassic and Palaeocene sediments (the Thanet Beds at Upnor, Kent) by Brown *et al.* (1969). Jeans *et al.* (1977) noted similar occurrences in the Lower Cretaceous Fuller's Earth in Surrey and Bedford, and later (1982) in the Cretaceous (Cenomanian) Hiberian Greensand Formation at Cloghfin Port, Co. Antrim. Estéoule and Estéoule-Choux (1972) found marine clinoptilolite in the Cretaceous chalks of the English Channel and Milodowski and Wilmot (1984) comment on clinoptilolite-heulandite in borehole sediments from the Corallian Beds of Upper Jurassic age beneath the Harwell research site in Oxfordshire.

Formulae based on the data of Table 1 are calculated on the basis of 72 structural oxygen atoms in Table 2. Zeolites can be problematic to analyse using microprobe techniques because of their instability under the electron beam. Fortunately, the quality of the analytical data can be checked. The charge balance error (the e-value in Table 2) should be less than ten percent (Passaglia and Sheppard, 2001). The data of Table 2 indicate that our analyses are reliable, the largest charge balance error is less than five percent.

Calcium is the dominant extra-framework cation in all but one of the analyses, varying between 2.04 and 1.62 atoms per formula unit. Significant potassium (1.85 – 0.88 atoms per formula unit) and magnesium (1.24 – 0.73 atoms per formula unit) are present in every case. There is sufficient potassium in one analysis for the species to be heulandite-K. The highest Mg-value (1.24 atoms per formula unit) is close to the highest recorded for the heulandite-clinoptilolite group (1.46 in a specimen from Victoria, Australia analysed by Birch, 1989). The sodium content is relatively low, varying between 0.23 and 0.02 atoms per formula unit and the heavier group two elements, strontium and barium, are present in even smaller amounts. The Na/K ratio averages about 0.09 which is at the lower end of recorded values (see Passaglia and Sheppard, 2001). It is lower than the molar ratio of these elements in bulk samples of typical Cornish granite, which are typically a little less than 1 (Manning, 1998, p.128) and very much lower than in seawater, which is about 50 (Krauskopf, 1982, p.262). Taking an average of the analyses in Table 1 produces the formula $(Ca_{1.87},K_{1.31},Mg_{0.86},Na_{0.12},Sr_{0.07},Ba_{0.04},)[Al_{7.22}Si_{28.81}O_{72}].n H_2O$. Although this disguises the variability in chemistry it is useful as it gives an idea of a typical composition. Most of the silicon to aluminium ratios are greater than four (the average value is 4.00 with a maximum of 4.40 and minimum of 3.42) so the analyses fall largely within the clinoptilolite composition field; specifically, they are a potassium and magnesium-rich clinoptilolite-Ca (Table 2).

The geological environment at Wheal Hazard is different to most heulandite or clinoptilolite occurrences. Crystals occur in late-stage fractures in fine-grained metasomatised sediments belonging to the Mylor Slate Formation. The fractures post-date the development of the metamorphic fabric of the rock and since they are well within the aureole of the Land's End Granite it seems likely that the crystals formed from hydrothermal solutions during the later stages of the cooling of the granite. This is a subtly different mechanism to those outlined above since the zeolites formed as a result of *external* heat from the cooling granite causing zeolitisation within fractures in the fine grained metasediment. No precisely similar genesis of clinoptilolite has been reported elsewhere.

The composition of the specimen from Wheal Hazard lies in an interesting region outside the main heulandite and clinoptilolite trends (this region is defined by Bish and Boak, 2001 as Si/Al of 4 ± 0.5 with divalent cations exceeding univalent cations). There is doubt as to whether material within this region represents mixtures or overgrowths of clinoptilolite and heulandite from the main trends or whether it is genuinely homogeneous. Material with intermediate thermal behaviour, which is typical of neither clinoptilolite nor heulandite also lies within this region. Our specimens appear homogeneous at a micrometre scale and appear to genuinely represent macroscopic crystals with intermediate properties.

Specimens from Wheal Hazard are still commonly available and would certainly be able to provide sufficient material to characterise the behaviour in this composition range. Further analyses work is certainly desirable. On the basis of our analyses it is unsafe to label any specimen from Wheal Hazard as heulandite. Using the modern IMA definitions most of the material is clinoptilolite-Ca.

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BARYTE REPLACEMENT BY BARIUM CARBONATE MINERALS

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While replacement of baryte by witherite has been known for nearly 100 years and from several localities, replacement by barytocalcite has only been reported from two minor localities. However, recent research in Nentsberry Haggs and Rampgill Mines, Nenthead, Cumbria has established replacement of baryte by both barytocalcite and witherite on a significant scale. Further, in Rampgill Mine it is virtually certain calcite has then replaced barytocalcite, indicating the importance of calcium in the replacement process. In this paper, the geochemistry of the replacement process is discussed and it is suggested that the most likely mechanism is solubilisation of barium from baryte by bacteriogenic reduction of the sulphate, involving solutions of relatively low salinity. However, there is no evidence to confirm this hypothesis, which must await evaluation of fluid inclusions in witherite and barytocalcite.

INTRODUCTION

Baryte, $BaSO_4$, is an extremely stable mineral and is by far the most common sink for barium in the environment. Under surface and near surface conditions it is far less soluble in aqueous media than the barium carbonate minerals, witherite, $BaCO_3$, barytocalcite, $BaCa(CO_3)_2$ and alstonite, $BaCa(CO_3)_2$, a fact well evidenced by the numerous pseudomorphs and partial pseudomorphs of baryte after the barium carbonate minerals that can be found on many Northern Pennine mine spoil heaps. It is clear that these form readily in spoil heaps by the oxidation of mixed sulphide and barium carbonate material. In addition, the sharp pointed crystals of baryte that occurred in many of the Northern Pennine mines, particularly where witherite is also present, are considered to be secondary in nature, forming from witherite under hydrothermal conditions (Dunham, 1990, p. 77). Nevertheless, it has long been known that the barium carbonates, particularly witherite, can replace baryte. Spencer (1910) noted that at New Brancepeth Colliery, Co. Durham, 'small colourless crystals [of witherite] encrust the cavities of corroded baryte'. Brown (1919) reported that in a large cavity (which was partly filled with calcite, quartz and baryte), in the 'west branch of the new Glencrieff Mine', near the bottom of the cavity witherite was clearly pseudomorphing baryte and that in addition there were two large globular masses that 'gave you the impression that you were looking at two large fungi'.

Hancox (1934) inspected witherite veins in several working mines in the Northern Pennines and the associated eastern coalfield and in addition examined specimen material from localities in the collections of the Natural History Museum. In all he summarised material from nine localities, many of which showed clearly that baryte had been replaced by barium carbonate minerals. In general, he concluded that baryte was replaced by witherite by the action of 'carbonating solutions' and that, later, calcium in the solutions resulted in the formation of barytocalcite and alstonite with calcite and 'dolomite' [ankerite]. In addition he noted that several veins consisted entirely of witherite and that in these the witherite was usually granular as distinct from botryoidal and that the veins carried large amounts of brecciated country rocks, which is unusual for barytic veins. He concluded these veins were not formed by replacement of baryte. Hancox also points out that in some veins, the witherite was later partially replaced by 'coral-like' masses of baryte and that the alteration from baryte to witherite to baryte could be episodic.

Young (1993) noted the occurrence of barytocalcite apparently with the morphology of baryte from Ouston Mine and Blagill Mine in the Northern Pennines. Without the presence of some of the original mineral, it is always difficult to be certain about pseudomorphism, but that at Blagill Mine is most convincing and is discussed further in the text that follows.

To the above, we can now add observations from other localities, some of which are potentially quite important because they conflict to some extent with Hancox's findings.

THE LOCALITIES

Mineralisation at four localities is considered below. All are within 4 km of the village of Nenthead, Cumbria and all are disused lead mines, although one (Blagill Mine) was also worked for barytocalcite. The National Grid References for the entrances are given in Table 1 and the localities are then discussed in turn.

Admiralty Concession Flat, Nentsberry Haggs Mine

The Admiralty Concession Flat is situated on the Second Sun Vein in what is now usually called

Admiralty Concession Flat, Nentsberry Haggs Mine, Nenthead, Cumbria	NGR NY 766 450
Rampgill Mine, Nenthead, Cumbria	NGR NY 782 435
Scraithole Mine, West Allendale	NGR NY 803 469
Blagill Mine, Nenthead, Cumbria	NGR NY 741 474

Table 1: National Grid References for the localities under consideration.

Nentsberry Haggs Mine, although at the time of Hancox's research it was known as Nentsbury Mine. Hancox visited the First Sun Vein but, it would seem, not the Second Sun Vein and the Admiralty Concession Flat. The flat is well known for excellent specimens of relatively large complex almost 'wave shaped' crystals of barytocalcite coated with a crust of minute white calcite crystals and some baryte (Fig. 1). In addition museum quality specimens of sphalerite have been found here and also good specimens of witherite, alstonite, ankerite, quartz, galena and interesting small specimens of harmotome.

Figure 1. Barytocalcite, coated with calcite and baryte. Admiralty Concession Flat, 2nd Sun Vein, Nentsberry Haggs Mine, Nenthead, Cumbria. Specimen width 7 cm.

The flat, which is situated in the Great Limestone (Namurian), was worked on two levels. The highest of these is at the High Flat Horizon, directly under the Tumbler Beds, which are in a considerable state of collapse in parts of the flat. The lower working is probably at the Middle Flat Horizon, but this is not certain. Movement along the Second Sun Vein fault has created extensive horizontal slickensides on the north wall of the working and the development of the flat deposits was mainly on the south side of the fault. The host limestone of the flat is altered to a hard quartz-ankeritic rock, which contains numerous cavities and fissures, mostly fairly small, but with some cavities up to several metres across. Cavities are commonly lined with combinations of drusy quartz, ankerite and sphalerite crystals. Galena is not as common as sphalerite, though presumably it was once much more abundant. It occurs as good cubo-octahedral crystals, usually with sphalerite, probably having formed later than that mineral. The barium minerals, which include baryte, witherite, barytocalcite and minor alstonite and harmotome are invariably the last primary minerals to have formed in the cavities and fissures, except that these are often coated with mainly small calcite crystals, with some small diamond shaped baryte crystals.

Witherite is the dominant barium mineral in the upper working, where it is abundant at the north east end. It forms radiating masses, often with a rudimentary pseudo-hexagonal structure and usually with a coarse etched appearance and coated with a mixture of white minute calcite and baryte crystals (Fig. 2). However, good euhedral pseudo-hexagonal crystals do occur. Barytocalcite is uncommon, but occurs as honey brown relatively small crystals with monoclinic symmetry, usually on witherite. Apart from the encrustations on witherite, baryte is rare in the upper flat, but does occur as masses of small spear shaped crystals, which are probably secondary. Harmotome is very rare, but has been found as small elongated needles (up to 1 mm), with cruciform cross-section, on sphalerite.

Figure 2. Witherite, coated with calcite and baryte. Note the rudimentary pseudo-hexagonal form. Admiralty Concession Flat, 2nd Sun Vein, Nentsberry Haggs Mine, Nenthead, Cumbria. Specimen width 7 cm.

The mineralisation in the lower working shows to best advantage the replacement of baryte by the barium carbonates. Early formation of baryte crystals, which reached at least 15 cm on edge, in the cavities was followed by significant fracturing of the baryte, ankerite, sphalerite and the wall rock of the cavities. The clasts are then often cemented together by later barium minerals. There are numerous examples where cavities contain cracked baryte crystals which have been cemented with small crystals of witherite and alstonite, the baryte usually being highly corroded (Figs. 3 & 4). The witherite and alstonite are then mostly coated with or completely altered to a fine white crust of minute calcite and/or baryte, similar to that on the witherite of the upper working. Other cavities are lined with crystals of the classic barytocalcite of this locality (Fig. 1). However in some cases, after being overgrown with barytocalcite, the original baryte has been completely

Figure 3. Baryte crystal, fractured and re-cemented with alstonite and witherite. Admiralty Concession Flat, 2nd Sun Vein, Nentsberry Haggs Mine, Nenthead, Cumbria. Specimen width 15 cm.

Figure 4. The bottom left hand side of Fig. 3, showing the deep corrosion of the baryte.

Figure 5. Barytocalcite, epimorphic after baryte. Admiralty Concession Flat, 2nd Sun Vein, Nentsberry Haggs Mine, Nenthead, Cumbria. Specimen width 20 cm.

dissolved leaving barytocalcite epimorphous after baryte, the casts having the morphology of baryte on the underside (Fig. 5). Casts of baryte crystals in material with the appearance of a highly silicified silt also occur. Most convincing are examples of partly dissolved baryte crystals with crystals of barytocalcite and witherite in the resulting cavities in the original matrix (M. Woodward collection). These specimens clearly show that original baryte is being replaced by both barytocalcite and witherite and unlike Hancox's observations, much of the barytocalcite is at least as early as the witherite.

Rampgill Mine

This mine is accessed by the Rampgill Horse Level [NY 782 435], which leads to the Scaleburn Vein and the Rampgill Vein, the latter becoming Whitewood Vein when it crosses the county boundary into Northumberland. An occurrence of witherite in the Scaleburn Vein was described by Bunting (1994), but it was not possible to access the locality as part of this study. However, examination of specimens from the locality (R. Bunting collection) reveals no evidence of replacement of baryte by witherite. The witherite is extensively replaced by and overcoated with minute baryte crystals (up to 2 mm long) combined with some calcite. Rarely the witherite occurs as small (5 mm) pseudohexagonal prismatic crystals with pyramidal terminations, similar to some of the material from the Bounder End Cross Vein (see later).

Two further barium localities have now been found in the Rampgill Mine system: the Bounder End Cross Vein and the High Flat Horizon.

Rampgill Mine - Bounder End Cross Vein

After complete closure for many decades due to collapses in the horse level, it has recently become possible to access the Bounder End Cross Vein (also known as the Boundary Cross Vein). There are extensive flats associated with the vein at the High Flat Horizon of the Great Limestone (Namurian). Bridges and Wilkinson (2003 and 2005) described interesting epimorphs of quartz after fluorite from the North String extension of the Bounder End Cross Vein and the vein itself to the south of the horse level. They also corrected the records on the precise location of the Cross Vein with respect to the vertical shaft sunk by the Vieille Montagne Zinc Co. and called Rampgill Shaft on the 1922 abandonment plan.

The flats at the High Flat Horizon have been largely back filled with waste rock by the old miners, rendering most of their workings inaccessible. At a point about half way between the position of the Horse Level and the North String, adjacent to a vertical rise, a large quantity of barium minerals was found in the front of a backfilled section of the workings. There is very little wall rock directly associated with the barium minerals, inferring that somewhere there might be barium mineralisation *in situ*. However, it has not been possible to find this, possibly because the site has been completely back filled with waste rock or completely worked out. Nevertheless,

Figure 6. Witherite crystal, with rudimentary pseudo-hexagonal cross section. The crystal is coated with a crust of minute calcite and baryte crystals. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 12 cm

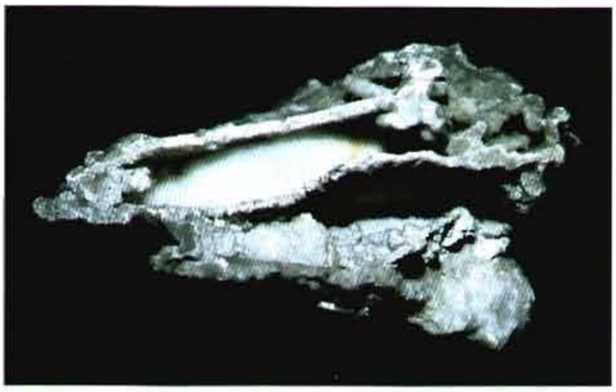

Figure 7. Skeletal calcite, epimorphous after baryte. The white mass in the upper cavity is a crystal of witherite, coated with calcite. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 12 cm.

the minerals that are accessible throw considerable light on the replacement of baryte by barium carbonate minerals.

The small amount of wall rock associated with the barium minerals indicates the site to be limestone recrystallised and metasomatised to a quartz-ankeritic rock with small clasts of sphalerite and pyrite. Presumably cavities formed during this mineralisation episode. At least some of the cavities were then lined with more quartz and sphalerite crystals followed by deposition of fluorite. Galena formed at this time, but the relationship to the fluorite and sphalerite is not clear. These minerals are paragenetically earlier than the barium mineralisation episode that followed, which comprised:

1. **Baryte**. Quite large slabs (> 10 cm) of irregularly layered crystalline primary baryte were common in the pile of waste rock and also occurred with other minerals. Crusts of earthy baryte are present on earlier minerals as are encrustations of minute diamond shaped crystals, which are typical of the supergene baryte common as dump alteration of barium carbonates in the orefield.
2. **Barytocalcite**. Major masses of buff coloured granular crystalline barytocalcite are abundant, with crusts of small euhedral to anhedral monoclinic crystals in cavities.
3. **Witherite**. Probably the most abundant barium mineral. Mostly massive, colourless to brown, good crystals have been found in cavities. Large (up to at least 15 cm) barrel shaped masses, often with a rudimentary hexagonal cross-section, of radiating witherite formed in what must have been quite large cavities in the deposit (Fig. 6). These are always covered in a crust of minute calcite and/or baryte crystals and most are dirty, probably due to mining, transport and ageing in an open mine environment.
4. **Chalcopyrite** is present as a very minor phase, small irregular crystals occurring in all of the barium minerals. Much more important is:
5. **Calcite**. Calcite played a much more significant role than that described in all the other localities by Hancox and Young and in our observations in Nentsberry Haggs Mine. It is present as quite large masses and crusts of a granular nature as well as forming skeletal frameworks (Fig. 7) epimorphous after baryte. Crusts of minute scalenohedral crystals often associated with minute baryte crystals are common on other minerals.

Establishing the relationships of the minerals is difficult due to the fragmented nature of the material available for study. The following observations are based on the study of over 40 different specimens. Energy dispersive X-ray spectrometry (EDS) was used extensively to be sure of the identity of the various mineral phases on the specimens. Many of the specimens show signs of brecciation during the barium mineralisation period, with small clasts of galena and fluorite in the barium minerals.

Only two specimens have been found where primary crystalline bladed baryte has grown directly on fluorite or galena, but it must be noted that there are very few specimens where the barium minerals are associated with earlier minerals. However, the evidence indicates that, as elsewhere in the Northern Pennines, baryte was the first barium mineral to form.

Both barytocalcite and witherite have crystallised directly on fluorite and galena, probably with barytocalcite dominating. In particular, several of the fluorite specimens have a coating of about 5 mm of barytocalcite, which is often altering to baryte, followed by witherite (Fig 8).

Several specimens have been found where blades of crystalline baryte have apparently been partially altered to other minerals and some of these have been sliced to reveal internal structures. While occasionally barytocalcite has grown on baryte, with no more than pitting of the latter's surface (Fig. 9), there is good evidence that barytocalcite, as well as witherite, has replaced baryte. In addition there is material where relict baryte structure appears to have been retained in witherite and even calcite. On several specimens the residual blades of baryte appear to have been partially replaced with calcite, but sectioning of one of these shows there are small patches of barytocalcite in the calcite adjacent to the baryte (Fig. 10). The evidence indicates that the major calcite episode has resulted in the replacement of some of the barytocalcite by calcite. This has a bearing on the skeletal calcite, which is abundant in the deposit.

The gaps between the ribs of calcite in the skeletal specimens often have the morphology of blades of baryte and residual baryte is present on some specimens (Fig. 11). The ribs are broadly symmetrical across their width and rarely there is a thin layer of barytocalcite in the middle of the rib (Fig. 12).

Material formed before the main calcite episode has examples where witherite has clearly grown on barytocalcite (Fig. 13), but on occasion the witherite has formed first. This phase of deposition may well have been episodic.

Following the major calcite deposition, there was another major witherite episode, with small to large usually roughly barrel shaped crystals, often with an obvious hexagonal section, forming on and entirely supported by the calcite (Fig. 14). Small prismatic crystals of witherite, similar to those from the Scaleburn Vein (see above) also formed in cavities during this episode.

Finally the outside of much of the witherite and some barytocalcite shows signs of corrosion and an encrustation of calcite crystals, usually with some small baryte crystals. This stage has a supergene appearance and could be postmining in the case of some of the baryte.

Rampgill Mine - High Flat Horizon

Approximately 260 m along the horse level, beyond the Bounder End Cross Vein, in flat workings at the High Flat Horizon, to the south east of Whitewood Vein a small deposit of barytocalcite has been located. The wall rock has been replaced by ankerite and quartz and is extensively fractured and cavities are common. Galena is abundant as a fissure infilling. Quartz lined cavities are common and many are then further infilled with galena and sphalerite often with a coating of small fluorite crystals. On the north-east side of the flat a small area of galena, sphalerite and fluorite lined cavities was coated with a layer of about 15 mm of barytocalcite, which appears to have been partly pseudomorphed by calcite. On several specimens, the mineral surface has the morphology of barytocalcite showing this is a pseudomorphous alteration and not a coating. Some attack of the barytocalcite at its junction with the underlying minerals is also obvious. There is no evidence of baryte replacement here, but the deposit is very similar to the calcite phase of the Bounder End Cross Vein deposit.

Figure 8. Fluorite coated with barytocalcite (lower arrow) followed by witherite (upper arrow)

Figure 9. Baryte crystal with overgrowth of barytocalcite and more baryte on the left hand side. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 5 cm.

Figure 10. Pale brown barytocalcite (arrowed) on baryte and apparently largely replaced by calcite. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 9 cm.

Figure 11. Skeletal calcite, with calcite and partially replaced baryte in the cavities. The specular reflectance is baryte. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen height 11 cm.

Figure 12. Skeletal calcite. The arrow marks a thin layer of barytocalcite in the calcite. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 6 cm.

Scraithole Mine

A witherite vein of the brecciated granular form described by Hancox was inspected by one of us (TFB) in 1982. Dunham's classic work on the Northern Pennines (Dunham, 1990, p. 157) includes a photograph of this vein. The vein is in the Great Limestone and consists of large clasts of wallrock cemented together by witherite. Honey coloured crystals of barytocalcite occur in small cavities in the witherite, but are a very minor part of the assemblage. No pseudomorphism of baryte was evident in the exposure.

Figure 13. Witherite crystals in a cavity in barytocalcite. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 25 cm. (F Bouweraerts specimen).

Figure 14. Barrel shaped crystals of witherite, with hexagonal cross section, growing on calcite. Bounder End Cross Vein, Rampgill Mine, Nenthead, Cumbria. Specimen width 10 cm.

Blagill Mine

Blagill Mine, Nenthead, Cumbria has long been known for excellent specimens of crystalline barytocalcite and examples are to be found in museum collections around the world. As Young (1993) points out, the site is probably the type locality for the mineral. The spoil heaps of the mine on the east side of the B6294 at NY 741 474 contain abundant blocks of massive barytocalcite, often with good monoclinic crystals in small cavities. Witherite and baryte also occur on the heaps, much of the latter being dump alteration in origin. Young (1993) reported barytocalcite with the morphology of the common bladed form of baryte from the site and a typical specimen has been placed in the collections of the Hancock Museum, Newcastle upon Tyne. A further even more convincing but smaller pseudomorph specimen of barytocalcite (Fig. 15) has the typical form of blades of baryte embedded in a matrix of partially oxidised ankerite. However, the material, which has been shown to be barytocalcite, has a structure which in places is radiating across the width of the blades (Fig. 16). It is considered that the barytocalcite could not have grown in this way other than by replacing original baryte.

Figure 15. Barytocalcite, pseudomorphous after blades of baryte in a matrix of limonite. Blagill Mine, Nenthead, Cumbria. Specimen width 9 cm.

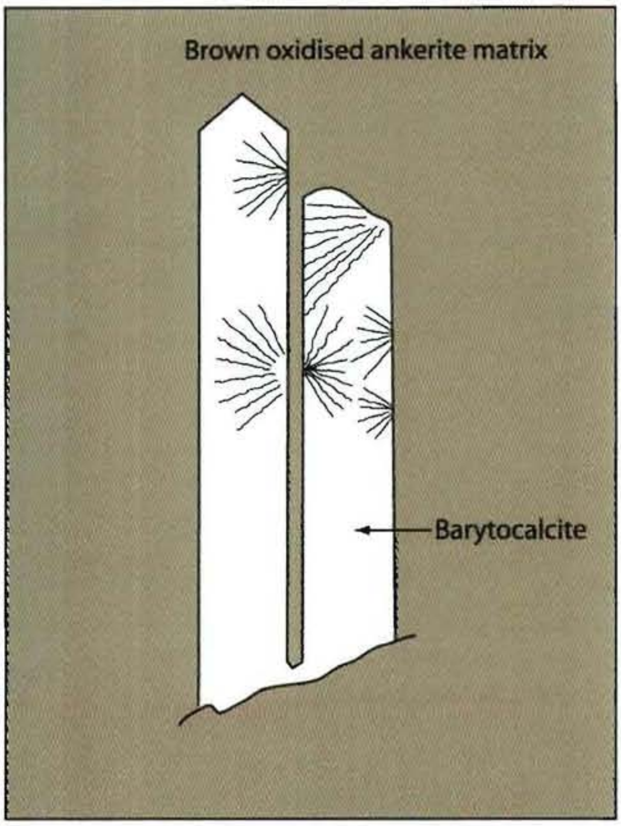

Figure 16. Sketch showing the radiating structure of the barytocalcite in the blades of Fig. 15.

For the record, alstonite has now been found at Blagill Mine. It consists of minute (c. 0.1 mm) crystals in grey sandy material cemented with barytocalcite and in a mass of barytocalcite (N. Hubbard specimen). Identification was by crystal morphology and EDS.

DISCUSSION

At all of the underground sites investigated here, the limestone wall rock has been metasomatised to a hard quartz-ankerite rock, with cavity formation. Cavities and fissures are coated with quartz, galena, sphalerite and ankerite in varying amounts, with fluorite as well in the Rampgill locations. The rock is invariably heavily fractured, leaving unstable ground. At the Admiralty Concession Flat (ACF) and the Bounder End Cross Vein (BECV) there followed deposition of crystalline baryte, which was also fractured in the case of the ACF and possibly the BECV. At both localities baryte was replaced in part by witherite in keeping with earlier observations. However, at both localities there is clear evidence that barytocalcite also replaced baryte and it is virtually certain the same is true of Blagill Mine. Thus calcium plays a more important role here than Hancox observed in his work. In addition at the BECV locality there was a major calcite event followed by further deposition of witherite. There is good evidence that the calcite in part actually replaced barytocalcite in the BECV and this also seems to have occurred at the minor barytocalcite site deeper in Rampgill Mine. The mechanism by which baryte, a very stable mineral, is being replaced by apparently less stable carbonate minerals is clearly of considerable interest.

The Alston Block of the Northern Pennine orefield is a Mississippi Valley type deposit. A great deal of work has been carried out over several decades in order to gain an understanding of the geochemistry of such deposits. Much of the work has been done in continental North America, where many of the basins around such deposits contain oil reservoirs, but there have been important studies in the Northern Pennines as well. Baryte is widespread across the Pennines, occurring in commercial quantities in many places. In the Alston Block of the Northern Pennine orefield, it is mainly restricted to an outer zone as defined by Dunham (1990). Reasonable models now exist for the formation of baryte in the Northern Pennines. Based on the analysis of brines from coal mines in the north-east coalfield (Edmunds, 1975), numerous fluid inclusion studies, *e.g.* Sawkins (1966), Shepherd, *et al.* (1982), Cann and Banks (2001), analysis of a brine spring in Cambokeels Mine, Weardale (Manning and Strutt, 1990) and waters from a geothermal energy exploratory borehole in Eastgate, Weardale (David Manning, *personal communication*) barium and the other heavy metals seem to have been transported in highly saline Na-Ca-Cl brines as their chlorides. Many of the brines have a total salinity in excess of 20 wt% NaCl (eq) and concentrations of Ca^{2+} range up to about 50,000 mg/l. Based on sulphur isotopic analysis, precipitation of baryte ensued by mixing of barium containing brines with similar, but sulphate-rich brines derived mainly from the Lower Carboniferous evaporite facies of the basins to the north and south in the case of most of the orefield (Crowley *et al.*, 1997), but at least partly from Permian evaporites in the case of the deposits in the north-east coal mines. In the latter, the process could actually be observed in several of the coal mines, necessitating trying to keep different aqueous streams separate in the mines to avoid rapid blocking up of pumping pipework by baryte. Such deposits in pipework were called 'Sunday Stones' by the miners and good examples are preserved in the Hancock Museum, Newcastle upon Tyne. Very substantial quantities of the barium sulphate pigment 'blanc fixe' were made at Eccles Colliery, Backworth, Northumberland over a period of 33 years (Gray and Judd, 2003) indicating a substantial and continuous source of barium containing hypersaline brine, but similar smaller springs seem to have occurred in most of the north-east coal mines (Edmunds, 1975).

Barium carbonate minerals are also common in the Northern Pennines. Young (1985, 1991 and 1993) lists a total of 45 localities in the Alston Block where barium carbonates have occurred. This area is the only place in the world where commercial quantities of witherite and to a lesser extent barytocalcite occurred and have been worked. Replacement of baryte by barium carbonates is much more difficult to explain than the mineral's original deposition and it is still not possible to propose a completely satisfactory mechanism. Indeed this problem extends to the deposition of large deposits of witherite as well, which is very surprising. Hancox favoured the action of alkali metal carbonates, such as potassium carbonate and other authors refer to 'carbonating' solutions. However, current knowledge of the nature of the hydrothermal fluids, evaluated since Hancox carried out his investigation, dismisses this mechanism.

There now seems to be two potential processes for de-stabilising baryte relative to the barium carbonate minerals:-

1. The carbonates have an inverse temperature-solubility relationship, whereas baryte solubility is only slightly affected by temperature over the likely range of the pseudomorphic process. At higher temperatures witherite becomes more stable than baryte.

2. Reduction of baryte to the far more soluble barium sulphide could greatly increase the concentration of Ba^{2+} in solution, possibly to the point where carbonates could form. This latter mechanism is plausibly argued by Chamberlain *et al.* (1986) for conversion of baryte to witherite in septarian nodules from Devonian shales near Syracuse, New York.

Discussing these mechanisms in turn in the context of the Northern Pennine orefield:-

1. There is great variability in the literature on solubility data for the carbonate minerals. However, good data for calcite, strontianite and witherite up to c.100°C have been determined by Busenberg and co-workers using the same technique throughout (Busenberg, Plummer and Parker, 1984; Busenberg and Plummer, 1986; and Plummer and Busenberg, 1982). Since magnesite is more soluble than any of the above minerals, the above work shows the solubility of magnesite, calcite and strontianite decreases progressively as might be expected for the elements of Group II of the Periodic Table. Surprisingly, they found the solubility of witherite to be slightly greater than calcite a phenomenon confirmed by other independent workers. Fig. 17 shows solubility products versus temperature, from the above work, for calcite and witherite up to 100°C combined with data for baryte, witherite and calcite above 100°C taken from the compilation of Barner and Scheuerman (1978). Witherite consistently has a slightly higher solubility than calcite at all but the lowest temperatures. Considering the optimum conditions for the pseudomorphic process (all the sulphate in solution derived from baryte and all the calcium present as carbonates) temperatures over 125°C would be needed for witherite to become sufficiently stable to replace baryte. The reality is that much of the calcium will be present as the chloride which would result in the need for much higher temperatures. Generally fluid inclusions in baryte are overwhelmingly monophase, indicating relatively cool conditions during crystallisation (<50°C) (Sawkins, 1966; Jon Naden, *personal communication*). The rare high temperatures observed (maximum 128°C at 'Nentsbury' Mine by Sawkins, 1966) may well be elevated by 'stretching' of the inclusions, a phenomenon to which baryte is particularly prone (Jon Naden, *personal communication*). It seems reasonable to assume the pseudomorphism is not likely to have occurred at significantly higher temperatures than the original baryte deposition and so it has to be concluded it is improbable this mechanism accounts for the baryte replacement.

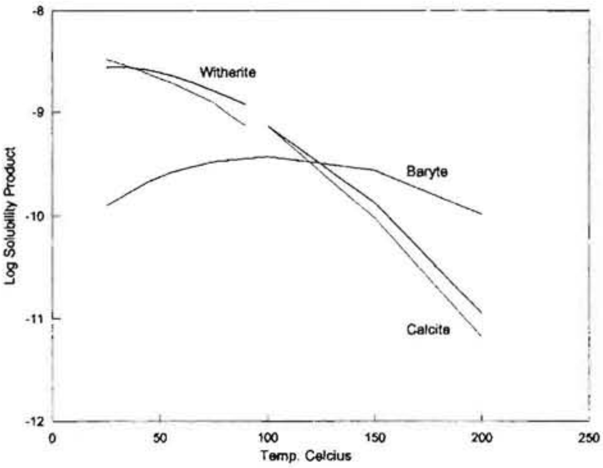

Figure 17. Thermochemical data for witherite, barite and calcite. Low temperature data from Plummer and Busenberg (and Parker), 1982 to 1986. High temperature data from Barner and Scheuerman (1978).

2. Reduction of baryte to the far more soluble barium sulphide can occur thermochemically (TSR) or bacteriogenically (BSR). Much work has been done on these mechanisms in the context of oil field reservoirs, where the oil can be 'soured' by hydrogen sulphide (H_2S) as a result of both processes. There are numerous references on this subject, but particularly useful is a recent review by Machel (2001). Both mechanisms require a source of suitable organic matter, preferably partially oxidised (*e.g.* carboxylic acids), though it is possible methane can support BSR. TSR requires a source of reduced sulphur, preferably sulphur itself, as a catalyst. None of these materials has been demonstrated to be present in solutions in the Northern Pennine orefield, although, with the exception of sulphur, it is likely they would be present in sufficient quantities in geological timescale terms. Theoretically TSR can commence at temperatures above 100°C (Cross *et al*,

2004), but it has not been clearly demonstrated below a temperature of 127°C (Machel, 2001), which again is high for the barium zone of the orefield. BSR appears to commence at temperatures below 80°C, which is more in keeping with known temperatures in the barium zone. That BSR can reduce baryte has been shown in a landfill leachate situation by Ulrich *et al.* (2003). Baryte grains corroded in a few days and while concentrations of Ba^{2+} in solution remained low (<100 mg/l) the potential for high concentrations is clearly there if not demonstrated. Both BSR and TSR will raise the pH of the solutions in which they occur, increasing carbonate ion activity (aCO_3^{2+}), which will assist precipitation of carbonates, particularly if CO_2 is also present.

While BSR would seem to be the most likely of the above three mechanisms, the nature of the mineralising brines presents problems for all of them. As stated previously many of the brines contain high concentrations of calcium and this will hold aCO_3^{2+} to a very low level due to the low solubility of $CaCO_3$ and it is high aCO_3^{2+} that is needed to favour baryte replacement. In addition, due to the difference in atomic weights between calcium and barium, concentrations of the latter would have to rise to over three times the calcium concentration before witherite could crystallise from solution in preference to calcite, unless the complexation chemistry of the two elements is markedly different, which seems unlikely. Clearly low salinity brines with a low calcium concentration would favour baryte pseudomorphism by barium carbonates and in this context there is evidence that such solutions were involved in baryte formation at some localities and may therefore also be applicable to the barium carbonate pseudomorphic process.

At Hilton Mine, Scordale, Cumbria, fluid inclusions with a salinity of 5 wt% NaCl (eq) have been found in baryte (Jon Naden, *personal communication*) and Cann and Banks (2001) found fluid inclusions in baryte from Settlingstones Mine, Haydon Bridge, Northumberland, to have salinities of 0.5-2 wt% NaCl (eq). Settlingstones Mine was a major witherite producer. If such solutions or preferably even more dilute streams were available in the pseudomorphic episode, the solutions could contain low enough calcium concentrations to permit replacement of baryte by witherite and possibly barytocalcite by BSR. In the context of formation of the barytocalcite, it should be noted that the formation of double carbonates often requires quite specific conditions of temperature and pressure, which might account for the prevalence of replacement by witherite.

The formation of the 'brecciated' veins discussed by Hancox (1934) is highly problematic. It is possible these formed in the same way as the pseudomorphic process, but with no preservation of the original baryte structure. In this respect it should be noted that Hancox included the main vein of Settlingstones Mine in this category, but Dunham (1990, p.96) notes that in this mine in 1954, near the Grindon Cross Vein, he observed clear evidence of baryte replacement by witherite. Certainly it is difficult to see how carbonate ion activity could become high enough to form witherite from the type of barium chloride containing brines found in the north-east coalfield.

Resolution of the above problems requires work on fluid inclusions in witherite and barytocalcite, which is lacking at present.

Typical specimens from the underground localities have been placed in the collections of the Manchester Museum and the Hancock Museum, Newcastle upon Tyne.

CONCLUSIONS

While baryte replacement by witherite has been known for many years and is supported by our recent work, it is also clearly established that barytocalcite can replace baryte and it is highly probable that calcite has replaced barytocalcite in Rampgill Mine.

With the data available at present it is not possible to suggest a satisfactory mechanism for the replacement of baryte. The best hypothesis would seem to be bacteriogenic sulphate reduction of baryte by a low salinity fluid, similar or preferably more dilute than those recently found in baryte from the Northern Pennine orefield. Low sulphate ion activity would also be essential. Studies on fluid inclusions in witherite and barytocalcite are required and in this context the authors could make well crystallised material available for study on request.

ACKNOWLEDGEMENTS

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SCOTLANDITE IN THE BRITISH ISLES: ITS OCCURRENCE, MORPHOLOGY AND PARAGENESIS

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The rare lead sulphite mineral scotlandite has been identified at localities in the Caldbeck Fells, Cumbria, the Leadhills-Wanlockhead mining district, southern Scotland, and at Whitwell quarry in Derbyshire. It occurs in several distinct and characteristic morphological variants. Scotlandite crystallises at an early stage in the supergene oxidation process, often in direct contact with partly oxidised galena, in fractures and cavities that are relatively well sealed from the atmosphere. It is commonly associated with lanarkite, mattheddleite and leadhillite. Careful examination of the mineral assemblages suggests that scotlandite crystallises in alkaline environments where the carbonate and copper ion activity is very low. It requires a narrow range of relatively low Eh conditions, to stabilise sulphite ions in solution. More oxidising conditions favour anglesite at low pH while leadhillite, hydrocerussite and cerussite are the stable phases if more than a trace of carbonate is present at higher pH.

INTRODUCTION

Scotlandite, $PbSO_3$, is a rare supergene sulphite mineral that has been reported from very few localities worldwide. It was first described on an old museum specimen from the Susanna vein, Leadhills, South Lanarkshire, Scotland (Paar *et al.*, 1984). The same authors reported a second occurrence at the Argentoille mine, Soane et Loire, France. Scotlandite has since been recorded from an exposure of the Roughton Gill South Lode in higher Roughton Gill, Caldbeck Fells, Cumbria (Green, 1989) and from two localities in Germany. We describe five further localities in the Leadhills-Wanlockhead mining district, three in the Caldbeck Fells and one at Whitwell quarry in Derbyshire.

SCOTLANDITE MORPHOLOGY

Most scotlandite crystals on the specimens we have examined are variants of two distinct habits labelled here as types 1 and 2. Both of these habits were described by Paar *et al.* (1984). Type 1 crystals comprise elongated needles bounded by four gently curved faces that terminate at a point, they often occur in radiating clusters. Type 2 crystals are made up of elongated prismatic {100} and {010} forms terminated by various pinacoids to produce acute chisel-shaped crystals. Some Type 2 crystals from the Caldbeck Fells and Leadhills occurrences differ from the type material in that they are repeatedly twinned on [100]. This twinning causes a series of parallel grooves to form on the (010), (011), (013) faces (Figs 1 and 2).

A few rich specimens from Short Grain Low Level comprise fracture surfaces in quartz-galena vein material coated with flat lying bundles of parallel double terminated boat-shaped crystals. These are described as Type 3. Crystals with this morphology are present on some of the richest specimens from Short Grain Low Level where they can cover 4 cm^2 or more. They are otherwise rare.

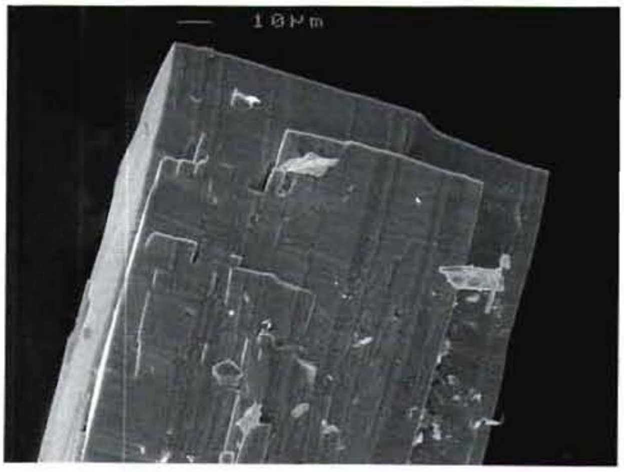

Figure 1. Furrows on the (011), (012) and (013) faces caused by polysynthetic twinning in Type 2 scotlandite. Short Grain specimen. Tim Neall collection.

In the Type 1 to 3 morphological variants, the scotlandite crystals are elongated parallel to the c-axis. There is another morphology, described here as Type 4, in which the crystals are elongated parallel to the a-axis. Type 4 crystals occur as blades or tablets which are morphologically similar to Type 2 crystals but elongated along the a-axis. A single untwinned specimen with this

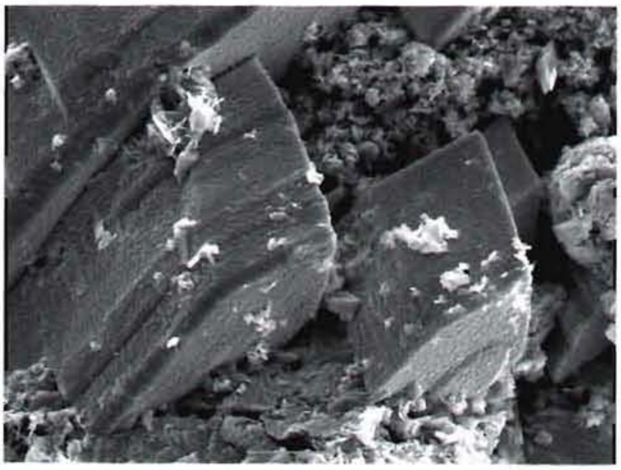

Figure 2. Twinning induced furrows in Type 2 scotlandite accentuated by corrosion. Short Grain specimen. Tim Neall collection.

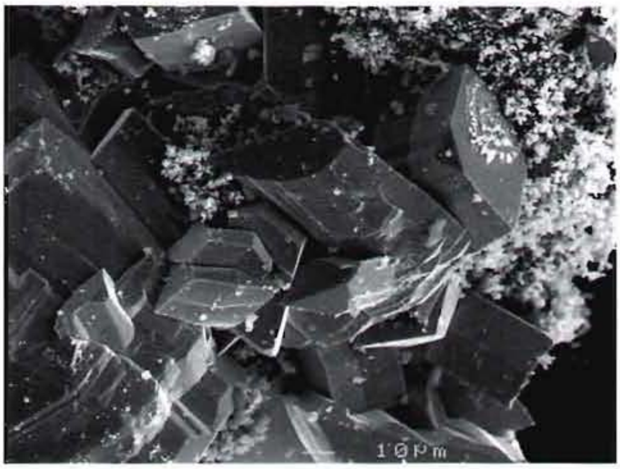

Figure 3. Type 4 scotlandite. Note the elongated crystal's (100) terminal face in the upper part of the image and the simple contact twins in the lower part of the image. Dry Smale Gill specimen. Tim Neall collection.

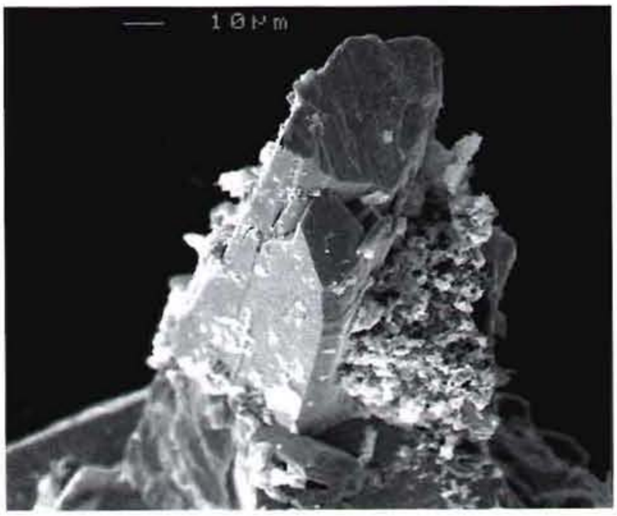

Figure 4. A broken prism of scotlandite terminated by cleavage on (100), a Type 4 crystal. Dry Smale Gill specimen. Tim Neall collection.

morphology was found at Short Grain Low Level. It has a well-developed (100) terminal face truncated by a second smaller face, possibly (210). At Dry Smale Gill, the Type 4 morphology is relatively common and the crystals are often twinned, sometimes repeatedly, producing low angle V-shaped or W-shaped crystals. In some scotlandite from Dry Smale Gill, prisms which are highly elongated parallel to the a-axis are terminated by a small rhomb or canoe shaped {100} pinacoid (Figs 3 and 4). These crystals are generally not polysynthetically twinned. The Type 4 morphology is rare at Leadhills-Wanlockhead having only been found at the Lady Anne Hopetoun Shaft dump.

LOCALITIES

Using a stereomicroscope it is relatively easy to recognise scotlandite and we have found potential specimens at a significant number of locations. The crystals are mostly minute and inconspicuous. Only those locations where specimens have been identified by XRD are described below. The XRD pattern of scotlandite is characteristic and cannot easily be confused with any other species.

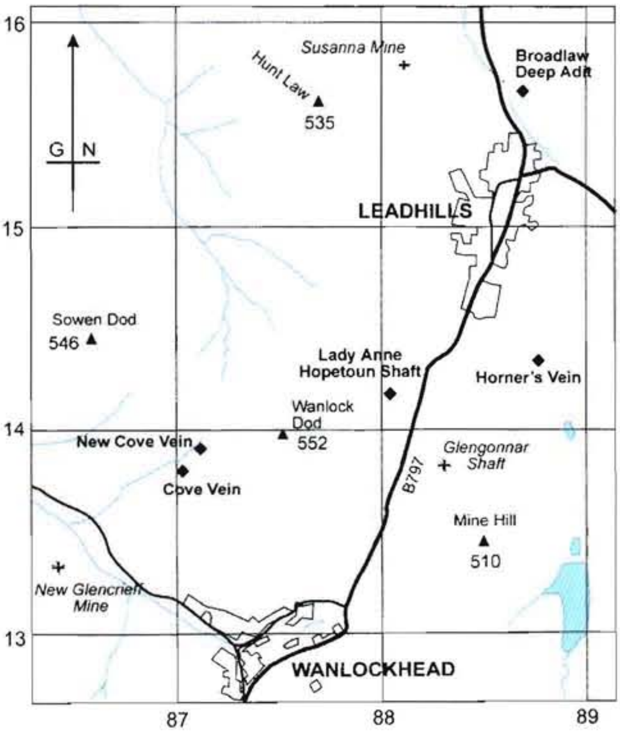

Figure 5. Sketch map showing the scotlandite localities in the Leadhills-Wanlockhead mining district.

LEADHILLS-WANLOCKHEAD DISTRICT

In addition to the classic old-time specimens from the Susanna Mine, we have identified scotlandite from five further locations (see Fig. 5), because of their close proximity, the specimens from Cove vein and New Cove vein are described together.

BROADLAW DEEP ADIT

A large and conspicuous dump just north of Leadhills village (NS 887 156) marks the site of Broadlaw Deep Adit. It was driven as a crosscut onto the Broadlaw vein and also gave access to the northern end of Raik's vein. The dumps consist largely of Ordovician greywackes with quartz veinstone carrying a little laminar white barite, residual sphalerite and galena. Scotlandite occurs as small sprays of the Type 2 habit up to about 0.7 mm in length, associated with residual galena and susannite in blocks of massive hemimorphite with minor pyromorphite and wulfenite (Fig. 6). It was identified by XRD (reference number MANCH: XRD1163).

Figure 6. Radiating white Type 2 scotlandite crystals up to 0.7 mm in length on galena, Broadlaw Deep Adit. Tim Neall collection.

COVE VEIN and NEW COVE VEIN

On the southeastern side of Whytes Cleuch, roughly between NS 870 138 and NS 871 136, there are numerous dumps and dressing floors associated with the workings on Cove vein. Scotlandite was identified as abundant, tightly packed, up-standing Type 2 crystals up to 0.3 mm in length associated with leadhillite plates and susannite rhombs in a cleft in quartz-galena veinstone on a specimen from the most northerly dump by the stream. The XRD reference number is MANCH: XRD1162.

The large and conspicuous tip from New Cove vein (NS 871 139) is situated on the southeastern side of Whytes Cleuch just below the High Pirn mine tips. The dumps comprise Ordovician greywackes with much calcite and hematite-rich quartz veinstone. Chrysocolla-stained veinstone is locally abundant but lead minerals are generally rare. Type 1 and 2 scotlandite crystals up to 0.3 mm in length occur in cavities in quartz with a little residual galena, mattheddleite and anglesite. Identification was by XRD (reference number MANCH:XRD1194).

HORNER'S VEIN

The dumps surrounding a shaft believed to be on Horner's vein (NS 888 142) contain slightly bleached and altered Ordovician greywackes with quartz, laminar white barite, galena and sphalerite veinstone. They have produced numerous specimens of scotlandite. Other rare minerals including lanarkite, susannite, leadhillite, caledonite, chenite and queitite have been identified in cavities in galena and between the galena and cerussite-pyromorphite oxidation rinds (*e.g.* Jackson, 1990; Rust, 1994). Scotlandite occurs as translucent pale brown slightly flattened Type 1 crystals up to about 0.2 mm long (Fig. 7) associated with mattheddleite, leadhillite and rarely caledonite. It was identified by XRD (reference number MANCH:XRD1014).

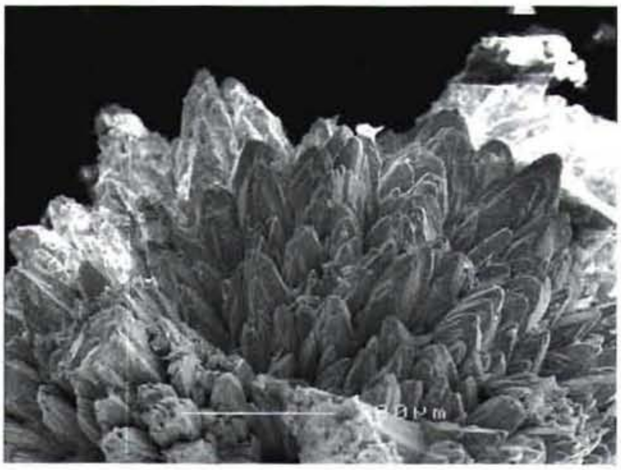

Figure 7. A radiating group of slightly flattened, pointed Type 1 scotlandite crystals up to 0.1 mm in length from Horner's vein. Tim Neall collection.

LADY ANNE HOPETOUN SHAFT

Lady Anne Hopetoun Shaft (NS 8806 1416) is located on the Brow-Hopeful vein system. Most of the dumps around the shaft are composed of heavily altered and brecciated greywackes veined by ankerite or dolomite that carries small amounts of quartz, calcite, chalcopyrite, sphalerite, galena and aragonite. Many of these latter minerals occur in drusy cavities in the carbonates. At one end, the dump contains a small proportion of finer debris that contains considerable amounts of laminar white barite, galena with cerussite, and highly cellular quartz. These minerals are commonly encrusted in either pale grey-green pyromorphite or white plumbian apatite. Scotlandite occurs associated with anglesite, lanarkite, leadhillite and susannite on galena in fractures or cavities in the kernels of pyromorphite encrusted galena-cerussite veinstone. Type 1 and 2 crystals are probably about equally abundant and a little Type 4 also occurs. A group of Type 1 crystals is illustrated in Fig. 8 and a particularly fine specimen displaying frosted Type 2 crystals in Fig. 9. Identification was by XRD (reference number MANCH:XRD1012).

Figure 8. Flattened pointed scotlandite crystals up to 0.05 mm long from Lady Anne Hopetoun Shaft. Tim Neall collection.

Figure 9. A radiating spray of partially frosted Type 2 scotlandite crystals up to 0.4 mm in length from Lady Anne Hopetoun Shaft. Neil Hubbard collection.

CALDBECK FELLS

In addition to the occurrence in Higher Roughton Gill, we have identified scotlandite from three further locations (see Fig. 10).

DRY SMALE GILL TRIAL

In Dry Smale Gill a trial was made on an east-west trending lead vein in andesitic rocks of the Eycott Volcanic Group (Ordovician). Quartz veinstone with a little white laminar barite is present on the dump at NY 2965 3532. The vein appears to have been almost completely devoid of base metal mineralisation and only a trace of yellow pyromorphite is present on most specimens. A few blocks containing traces of oxidised galena with supergene minerals including minute crystals of scotlandite were found. Scotlandite occurs with leadhillite and mattheddleite in cavities and thin fractures in the centre of poorly-mineralised veinstone blocks, sometimes with partly corroded galena. It is the first supergene mineral to have formed on all of the specimens that were examined. Prismatic to blocky Type 2 crystals and Type 4 prisms are the predominant habits. The scotlandite from Dry Smale Gill was identified by XRD (reference number MANCH: XRD765). A specimen is preserved in the Manchester Museum collection under accession number N16035.

RED GILL MINE

At Red Gill mine (NY 2950 3478) several small levels were driven on an east-west trending lead-copper vein in rocks of the Eycott Volcanic Group. The mine was relatively unsuccessful while it was being worked, but has since become internationally famous as a locality for rare supergene lead- and copper-bearing sulphate and carbonate minerals (Cooper and Stanley, 1990). Scotlandite occurs as minute thin prismatic Type 2 crystals (<0.3 mm) in cavities in quartz veinstone with a trace of galena, elongated prismatic mattheddleite and blocky leadhillite (ref. number MANCH: XRD955).

ROUGHTON GILL SOUTH VEIN

Scotlandite was briefly described from the Roughton Gill South vein (NY 3006 3383) by Green (1989). The specimens were collected in 1988 from a northeast-southwest trending stringer of galena (<50 mm wide) which was exposed *in situ* in steep scree in the northwest bank of higher Roughton Gill (also described as Thief Gill in some works). The stringer was mineralised over a strike length of *ca.* 5 m, but it rapidly pinched to an unmineralised fracture in depth. Pyromorphite, cerussite, malachite and chrysocolla were present in crystalline crusts surrounding the vein. The less oxidised interior contained lanarkite, anglesite, leadhillite, susannite, caledonite, mattheddlite and rarely scotlandite. Scotlandite was found in cavities as translucent pale brown pointed Type 1 crystals exceptionally to 0.6 mm long associated with leadhillite, lanarkite (Fig. 11). The only hand specimen that was collected was donated to the Natural History Museum (London). A recent resurvey of the area revealed that flooding had removed about 1.5 m of scree and the locality had been obliterated.

SHORT GRAIN LOW LEVEL

There are several trials in the Ordovician rocks of the Eycott Volcanic Group in Short Grain, one of the two tributaries that join to form Hay Gill in the Caldbeck Fells. The lowest trial at NY 3130 3583, which is described as Short Grain Low Level here, was used until recently as a water supply. Cooper and Stanley (1990) were the first to describe the minerals from this locality. They refer to site as the "barite trial in north bank". Scotlandite is not uncommon in blocks of veinstone on the dump. It occurs with anglesite, leadhillite, mattheddleite and susannite, on or closely associated with corroded galena, in quartz and barite. Crystals range up to about 2 mm in length but are usually between 0.3 and 0.5 mm. They are often white and opaque, and pseudomorphous replacement by anglesite and cerussite is quite common. Type 1 crystals were identified by XRD at the Natural History Museum (London) and Type 2 material by the same technique at Manchester Museum

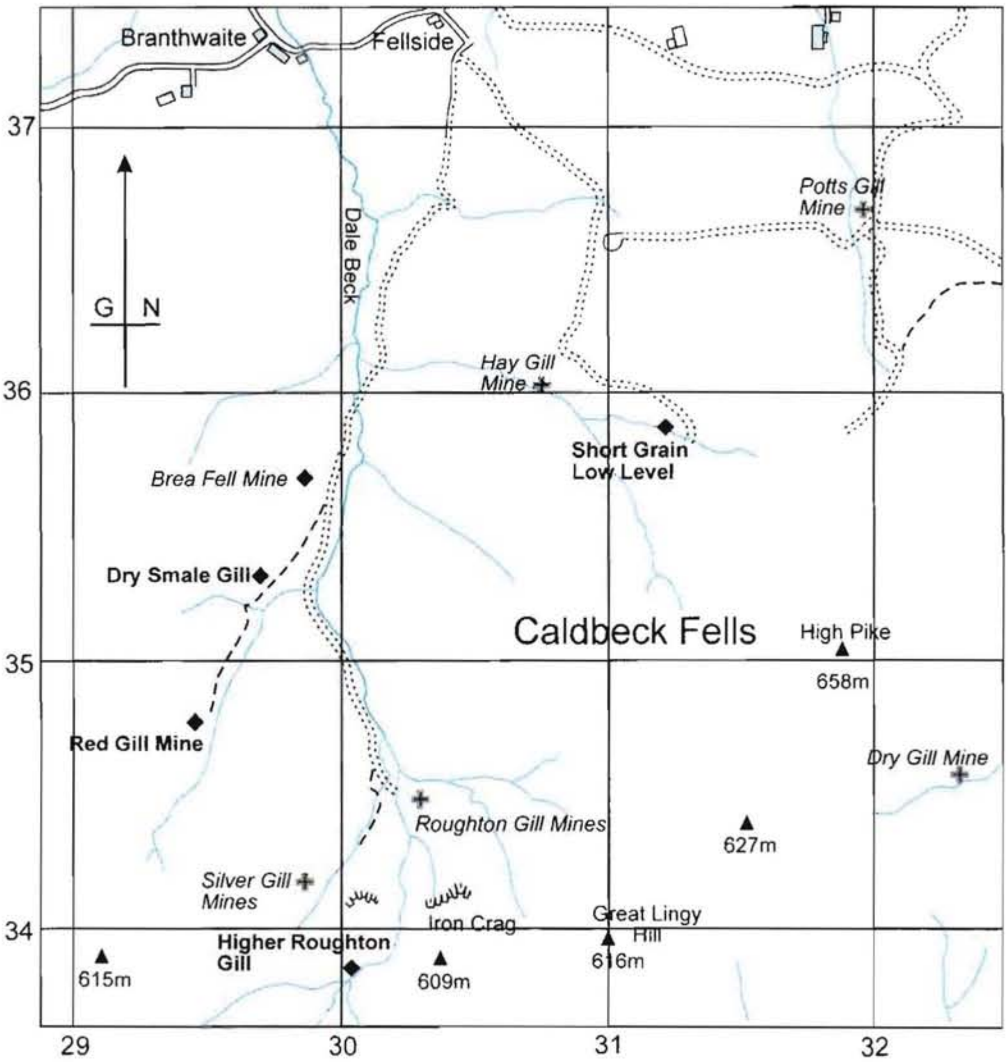

Figure 10. Sketch map showing the scotlandite localities in the Caldbeck Fells.

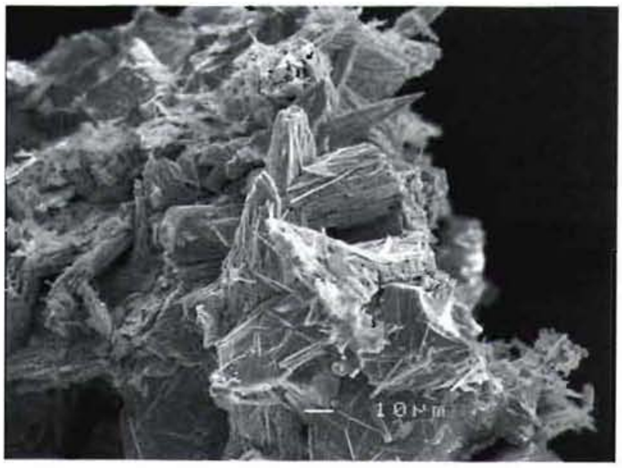

Figure 11. Typical pointed Type 1 scotlandite crystals up to 0.05 mm long from Higher Roughton Gill. David McCallum collection.

(XRD reference number MANCH:XRD570). Two specimens are preserved in the Manchester Museum collection under accession numbers N16029 and N16030.

DERBYSHIRE

WHITWELL QUARRY

In the mid 1980s, a galena-bearing vein was exposed in the dolomitic limestones of the Cadeby Formation (Permian) at Whitwell quarry near Whitwell in Derbyshire. The vein followed the line of the Park Hall Fault and as the quarry expanded, a brecciated area where it cut a small anticline was exposed (at about SK 528 766). A variety of lead-bearing supergene minerals including scotlandite were found in this area.

Scotlandite occurs as honey brown, white or colourless translucent Type 1 crystals up to 1.2 mm in length (Figs. 12 and 13), and as colourless to white Type 2 crystals up to 2.5 mm in length (Figs 14 and 15). Both habits were identified by XRD at the University of Leeds. At Whitwell quarry, scotlandite is associated with bladed lanarkite crystals up to 5 mm in length and euhedral blocky leadhillite. One specimen shows Type 2 crystals in etch pits in corroded, but fairly bright galena. The two different crystal habits have not been found in the same cavity.

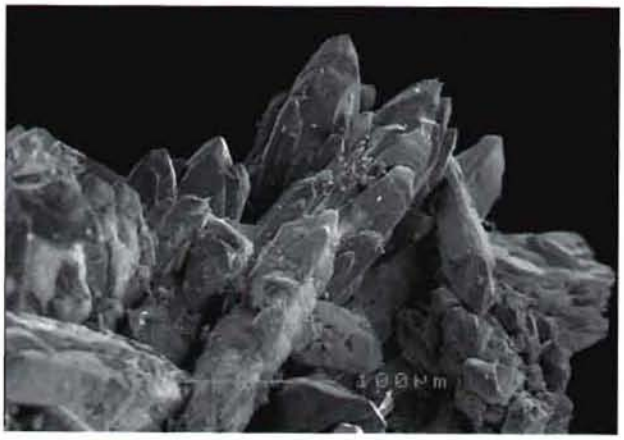

Figure 12. Blocky pointed Type 1 scotlandite crystals up to 0.1 mm long from Whitwell quarry. Peter Briscoe specimen.

Figure 13. Pale brown pointed Type 1 scotlandite crystals up to 1 mm long in corroded galena from Whitwell quarry. Peter Briscoe collection.

DISCUSSION

The oxidation of sulphides to sulphates, while seeming to be a simple chemical process, is in fact rather complicated. It involves the addition of four oxygen atoms to each atom of sulphur and does not proceed in a single step. Several transient, easily oxidised, intermediate anions are involved and of these thiosulphate ($S_2O_3^{2-}$) and sulphite (SO_3^{2-}) anions are likely to be the most stable. Williams (1990) gives a detailed account of sulphide oxidation processes.

The fact that an appropriate oxidation potential for scotlandite to form typically arises in close proximity to oxidising galena is evidenced by the number of localities at which it has been identified. A suitable oxidation potential on its own is not enough to stabilise scotlandite. Where there is a relatively high concentration of sulphuric acid, a common condition in oxidising orebodies, scotlandite is likely to be unstable with respect to anglesite. At a near neutral pH and above, the carbonate ion activity would be expected to render

Figure 14. Prismatic Type 2 scotlandite crystals to 0.4 mm long from Whitwell quarry. Peter Briscoe collection.

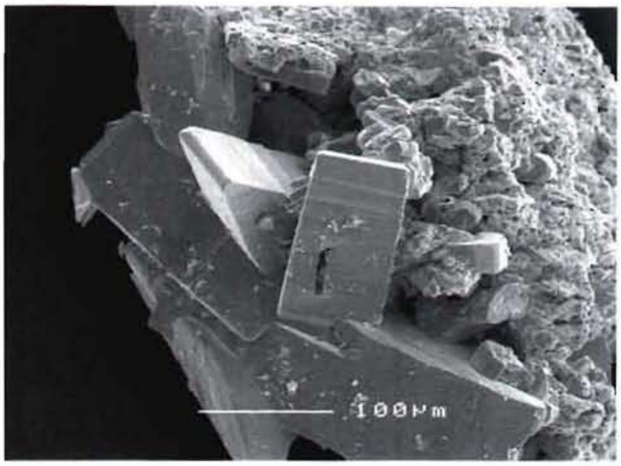

Figure 15. SEM image of Type 2 scotlandite crystals about 0.1 mm long from Whitwell quarry. Peter Briscoe collection.

Figure 16. Scotlandite crystals with later leadhillite from Whitwell quarry, showing the close association and paragenesis. Peter Briscoe collection.

scotlandite unstable with respect to a lead carbonate mineral such as leadhillite, hydrocerussite or possibly cerussite. The persistent association of scotlandite with leadhillite and lanarkite, which are both stable at low carbonate ion activities (Abdul-Sawad *et al.*, 1982) corroborates this observation.

In all of the specimens we have examined, the activity of carbonate in solution has been buffered by the presence of cerussite and hydrocerussite rinds and crusts on the outer edges of galena veins (in some cases carbonate minerals are completely absent). In the carbonate-rich limestone environment at Whitwell quarry, scotlandite only occurs in the centre of galena blocks, well removed from the wallrock. If scotlandite is stable in similar chemical conditions to lanarkite as one might expect given their common close association, the first mineral that would be expected to form as the carbonate activity increases would be leadhillite. Since leadhillite crystallises on scotlandite in several specimens from Whitwell quarry (Fig. 16) and is closely associated with leadhillite in many specimens from the Caldbeck Fells and Leadhills, this prediction is borne out.

Scotlandite is rarely associated with the blue and green supergene copper minerals and, when it is, it is usually heavily altered. This is likely to be because Cu^{2+} ions oxidise sulphite ions in solution. Scotlandite is often found on galena, as at Whitwell quarry, and there is almost always a little residual galena present in the cavities in which it forms. This probably serves two functions, one is to maintain the mildly reducing conditions required to stabilise sulphite ions and the other to precipitate Cu^{2+} ions as highly insoluble sulphides (covellite or the black copper sulphides) before they can oxidise the sulphite.

An interesting feature is the association at Dry Smale Gill of scotlandite with limonite. The presence of a ferric oxide-hydroxide here limits the sulphide ion concentration, suggesting that under nearly neutral conditions scotlandite does not require very strongly reducing conditions to form.

Although scotlandite is a rare mineral it is likely to be identified at further localities as analytical techniques improve. It typically occurs as a transient supergene species in association with partly oxidised galena in low carbonate environments. The crystals are normally small and inconspicuous and are very easily overlooked.

ACKNOWLEDGEMENTS

We would like to thank the Department of Earth Sciences at the University of Manchester for continued access to analytical equipment, Peter Briscoe for providing specimens from Whitwell quarry for study and Neil Hubbard for the loan of the Lady Anne Hopetoun specimen for photography.

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A ZEOLITE BEARING SKARN AT BARNAHALLIA, CONNEMARA, CO. GALWAY, IRELAND

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A small exposure at Barnahallia in western Connemara contains the zeolite group minerals chabazite-Ca, heulandite-Ca and stilbite-Ca, with albite and epidote in cavities in an amphibolite skarn. The skarn also contains scheelite as subhedral crystals. The cavity assemblage is interpreted as a product of relatively low-grade metamorphism post-dating the formation of the skarn which is located within impure calcareous rocks of the Lakes Marble Formation close to the margin of the Omey Granite.

INTRODUCTION

The Connemara region of Co. Galway in western Ireland hosts widespread W-Mo mineralisation in skarn deposits produced by the intrusion of late Caledonian granitoids into Dalradian Supergroup metasediments. The skarns are sulphide-poor and commonly contain W-Mo-Cu mineralisation and there is occasional disseminated or vein-style Mo-Cu ± W mineralisation in the associated granites. Numerous localities are cited by Reynolds *et al.* (1990), but although they attracted some attention from prospecting companies, all proved too small and low-grade to be of economic interest.

One of the minerals found in the skarns is scheelite and it was while searching for this that John and Robert Lawson of Castle Douglas, and one of the authors (SM), found a small area containing well-crystallised zeolite-group minerals in cavities in amphibolite skarn. Since zeolites are uncommon in skarn assemblages, the occurrence was thought worthy of note.

The zeolite-bearing skarn is located near the northern tip of Barnahallia Lough, Claddaghduff, Connemara. It was described briefly by Reynolds *et al.* (1990) who reported tremolite-diopside-wollastonite-grossular-idocrase skarns, with epidote, calcite, quartz and scheelite mineralisation formed during later brecciation and alteration. Traces of pyrite, chalcopyrite and molybdenite were also recorded, but not found during this study.

The specimens described below were collected from a small area, a few metres across, at the water's edge, the precise grid reference being determined by GPS as L 59245 55757. The best material was found in loose boulders just above the shoreline, there being very little material visible at outcrop.

According to Reynolds *et al.* (1990) the skarn mineralisation is developed in impure calcareous rocks of the Lakes Marble Formation close to the margin of the Omey Granite. A 1:500 scale geological map in the Geological Survey of Ireland (Open File 495-8, item 13, 1977-8) shows the granite margin about 30 m to the northwest of the collecting site with many 'veins' and lenses of granite and aplite in the surrounding rocks. As the richest specimens found in this study often had granite on them it seems likely that the best development of the skarn is at a contact with one of these 'veins', but this is not currently visible *in situ*.

MINERALS

Of the minerals listed by Reynolds *et al.* (1990), tremolite, diopside, wollastonite, idocrase and the sulphides were not found, but epidote, albite and three zeolite group minerals, chabazite, heulandite and stilbite, were identified. The last four of these are restricted to small irregular cavities in amphibolite skarn.

The minerals described below were identified using standard X-ray diffractometry (XRD) techniques. Certain zeolite and amphibole group minerals require chemical analyses in addition to XRD data to identify them to species level. Qualitative analyses by energy dispersive spectroscopy (EDS); semi-quantitative analyses of bulk samples by XRF; and quantitative analyses by wavelength dispersive spectrometry (WDS) were carried out to establish chemical compositions. Analyses by WDS were made at 20kV, 20nA with a 15 micron beam diameter using a Cameca SX100 electron microprobe. Count times of 10 seconds were used to minimize volatilization or decomposition effects during data collection.

ACTINOLITE, $\square Ca_2(Mg,Fe)_5(OH)_2Si_8O_{22}$

Dark green, acicular masses and radiating tufts or patches of fibrous actinolite are very common. In some cases actinolite makes up almost the whole of the skarn, and the rock it produces can be described as an amphibolite. Individual fibre lengths up to ca. 12 mm have been recorded.

Actinolite is a member of the amphibole group, complex silicates that cannot be characterised by XRD alone (*e.g.* Leake *et al.*, 2004). Semi-quantitative XRF analysis of a composite powder sample gave 12.4 % CaO, 4.6 % Al_2O_3, 16.3 % Fe_2O_3, 10.8 % MgO, 2.1 % Mn_3O_4 and 53.5 % SiO_2. These data suggest that the mineral is an aluminium and iron rich actinolite: Mg is just in excess of Fe (calculated as molar ratios) and there is insufficient aluminium present to place the species within the tschermakite or related composition fields.

ALBITE, $NaAlSi_3O_8$

Small, blocky white crystals up to about 1 mm across in a cavity in amphibolite skarn were identified by a combination of XRD and EDS as albite.

CHABAZITE-Ca, $(Ca,K_2,Na_2)_2[Al_2Si_4O_{12}]_2.12H_2O$

Off white, slightly corroded rhombs up to 3 mm on edge present on two specimens were identified by XRD as chabazite. Qualitative examination by EDS showed significant K and Ca, with Ca>K so the species is chabazite-Ca. Insufficient material was available for full analysis without seriously damaging the specimens as the chabazite is present as a single isolated rhomb in both cases.

EPIDOTE, $Ca_2(Al,Fe)_3(SiO_4)_3OH$

Epidote was identified by XRD as occasionally abundant, dark green, euhedral crystals up to 10 mm in length in small cavities in massive crystalline epidote and epidote-actinolite-quartz rock. Granite is also present on some specimens and epidote-rich material can be seen grading into granite. Some of the cavities have angular sides, perhaps representing epimorphs after another phase (possibly calcite) that has been dissolved. A semi-quantitative XRF analysis of a composite sample gave 14.3 % Fe_2O_3, 21.9 % Al_2O_3, 21.9 % CaO, 0.5 % MgO, 40.5 % SiO_2 and 0.7 % Mn_3O_4.

GROSSULAR, $Ca_3Al_2(SiO_4)_3$

Euhedral dark brown grossular garnet crystals up to a few millimetres across occasionally accompany epidote in small cavities. Qualitative analyses by EDS together with the XRD data indicate a composition between grossular and andradite, but nearer to the grossular end-member.

HEULANDITE, $(Ca,Na)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}.12H_2O$

The definition of the minerals of the heulandite series is complex. They share a unique tectosilicate framework structure with the clinoptilolite series. Heulandite is defined as the part of the series having a framework silicon to aluminium ratio of less than four (high aluminium content and high charge on the framework), while in clinoptilolite the ratio is greater than or equal to four (low aluminium content and low charge on the framework) (Coombs *et al.*, 1998). Heulandite requires both quantitative chemical and XRD data for identification.

At Barnahallia, heulandite is relatively common as druses of millimetre-size, creamy crystals in vuggy amphibolite skarn. The chemical formula based on ten microprobe analyses and calculated on the basis of 72 structural oxygen atoms can be written $(Ba_{0.02}Sr_{0.32}Ca_{2.87}K_{0.59}Na_{0.10}Mg_{0.75})[Al_{8.30}Si_{27.66}O_{72}].nH_2O$ (using data collected by Andrew Tindle, *personal communication*). The silicon to aluminium ratio is 3.33, which is well within the heulandite composition field, and since calcium is the dominant cation, the species is heulandite-Ca. There are significant contents of strontium, potassium and magnesium, but none of these elements is present at a level that is particularly unusual for the heulandite series (Passaglia and Sheppard, 2001).

SCHEELITE, $CaWO_4$

Anhedral and subhedral, white to cream crystals of scheelite, occasionally up to a centimetre in size, occur in epidote-rich skarn, and are sometimes found in cavities where they accompany euhedral epidote. Qualitative chemical analyses by EDS show the scheelite is tungstate end-member, containing no detectable molybdenum.

STILBITE-Ca, $NaCa_4[Al_8Si_{28}O_{72}].28\text{-}32H_2O$

Isolated, light brown rosettes of stilbite-Ca up to 5 mm across are present on two specimens of heulandite-bearing amphibolite. They were identified by XRD (which differentiates stilbite from the closely similar stellerite) and the species was confirmed as stilbite-Ca by qualitative EDS. Insufficient material was available for a full analysis by WDS without seriously damaging the specimens.

DISCUSSION

Most of the scheelite-bearing skarns described by Reynolds *et al.* (1990) are simple calc-silicate assemblages, principally comprising grossular, idocrase and wollastonite. The metamorphic grade at one such locality, Fountain Hill, was investigated by Ahmed-Said and Leake (1996) who concluded that the metamorphic conditions were relatively high grade, with temperatures and pressures estimated at 640°C and 3.3 kb.

The Barnahallia locality differs from typical skarns in the area in the presence of numerous small cavities, in the relative abundance of epidote, and in the presence of zeolite group minerals. The mineral assemblage in the cavities at Barnahallia including three zeolite group minerals, albite and epidote is characteristic of low grade metamorphism. Indeed the term zeolite facies was coined to describe the lowest grade of metamorphic alteration while the transition to the next higher grade has been considered to be marked by the first appearance of an epidote-chlorite-quartz-albite assemblage (*e.g.* Frost, 1980). It seems likely that the cavity assemblage is a retrograde metamorphic assemblage produced in a relatively fluid rich environment either during the slow cooling of the skarn or possibly at some later stage. This would account for the presence of zeolites as the last minerals to form, as well as albite and epidote, which are earlier in the sequence. The cavities may at one time have been filled with calcite, as corroded remnants of this mineral sometimes remain.

Late-stage, zeolite-bearing assemblages have been reported at a few other skarns including similar wollastonite-garnet skarns at Demir Tepe, Bursa province, Turkey (Demange *et al.*, 1998) and in skarns in the Central Metasedimentary Belt of the Grenville Province in north America (Van Velthuizen *et al.*, 2006). These assemblages appear to be relatively rare on a worldwide basis and further studies, particularly of the compositions of minerals of the zeolite group present in them, seem worthwhile.

ACKNOWLEDGEMENTS

Dr Andrew Tindle of the Open University is thanked for analysing the heulandite. Stephen Moreton is grateful to Robert and John Lawson for assistance in collecting at the site, and for finding the stilbite. Thanks are also due to the landowner for permission to collect.

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NOTES FOR CONTRIBUTORS

TYPESCRIPTS

Papers should be typed, preferably on A4 paper, on one side only, with double spacing and wide margins. All pages should be numbered. Two complete copies should be submitted to the Editor. Each paper will normally be reviewed by two referees. Submission of a paper to the Journal is taken to imply that it has not been considered for publication elsewhere. Material accepted for publication can not be published elsewhere in the same form without the consent of the Editor.

The submitted material should normally contain original observations or experimental results relating to mineral occurrences in the British Isles, although other suitable topics may be considered. Full articles should include an abstract of up to 250 words summarising the significant points of the paper; notes (up to 1500 words) do not require an abstract. Review articles are also published occasionally.

FORMAT AND PRESENTATION

Papers should be submitted in the style and format of the Journal, and divided into appropriate sections and subsections. A recent issue of the Journal should be consulted for examples. Titles of papers should be adequately informative.

Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, analyses, etc.). It may not be necessary to reproduce such data in full in the text, but they should be supplied to the Editor if required by the referees in the course of their assessment. For mineral occurrences of particular note (e.g. new occurrences in the British Isles or at a particular locality) authors are strongly encouraged to record the specimen number and the institution or collection where the specimen is lodged. National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST40 71).

FIGURES

All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Fig. 1, etc. Figures must have descriptive captions, and a list of these is to be provided on a separate sheet of the typescript.

Line drawings, crystal diagrams, maps, etc., should be of a quality suitable for direct reproduction, with appropriate line thicknesses and letter sizes. The Editor will arrange artwork for authors who do not have access to such facilities. Photographs and drawings (e.g., locality maps) may be submitted initially as draft quality prints or low-resolution electronic files (Jpeg format is preferred), however high quality prints or high-resolution electronic files will be required for publication. Optical photographs of coloured specimens should be supplied as colour images. The scale must be indicated, either on the photograph or by specifying, e.g., frame width or crystal size in the caption.

TABLES

Tables should be numbered consecutively with Roman numbers, and referred to in the text as Table I, etc. Each table should have a descriptive title, separated from the table by a horizontal line. Another horizontal line should mark the end of tabulated data; any footnotes should be placed below this.

TERMINOLOGY

Authors should adhere to the nomenclature and terminology of the International Mineralogical Association. The most recent Fleischer's Glossary of Mineral Species (at present the 9th edition, by Mandarino and Back 2004) can be used as a guide to mineral nomenclature, but where this conflicts with Hey's Mineral Index (1993) or Mineralogical Magazine and Mineralogical Abstracts usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (Acta Crystallographica, **22**, 45 (1967)).

ABBREVIATIONS

Except for common non-scientific abbreviations and those for standard units of measurement, abbreviations should be spelt out in full at their first mention in the article, e.g. platinum group mineral (PGM). If used, 'nd.' in tables must be defined (to 'not determined' or 'not detected').

The following abbreviations may be used without explanation:

XRD = X-ray diffraction
XRF = X-ray fluorescence analysis
EPMA = electron probe microanalysis (electron microscopy analysis)
EDX = energy dispersive analysis (same as EDA, EDAX, EDS)
SEM = scanning electron microscope or microscopy
TEM = transmission electron microscope or microscopy
IR = infrared
UV = ultraviolet
NGR = National Grid Reference

REFERENCES

References should be indicated in the text thus: (Brown, 1967) or 'as stated by Brown (1967)'; (Green and Brown, 1985) for two authors; (Green *et al.*, 1986) for three or more authors. If two or more references would give rise to identical citations in the text, they may be distinguished by appending 'a', 'b', etc. to the publication year.

A list of references in alphabetical order should form the last section of each paper. Some examples of the style used are given below; note that journal names are given in full. Papers in press may be included provided they have been accepted for publication and the journal name is given. Personal communications and unpublished work (except M.Sc. and Ph.D. theses), should not be included here but can be cited in the text, thus: (A. Brown, *personal communication* or *personal communication*, 1992), (B.C. Green, *unpublished work*). Likewise, references to Newsletters and similar publications will normally be cited in the text but not included in the reference list.

Bannister, F.A., Hey, M.H. and Claringbull, G.F. (1950), Connellite, buttgenbachite and tallingite. *Mineralogical Magazine*, **29**, 280-286.

Dewey, H. (1923). *Copper Ores of Cornwall and Devon*. Memoirs of the Geological Survey: Special Reports on the Mineral Resources of Great Britain, vol. **27**.

Heddle, M.F. (1901). *The Mineralogy of Scotland* (ed. by J.G. Goodchild), vol. **1**, p. **25**. David Douglas, Edinburgh.

Jackson, N.J. (1977). The Geology and Mineralization of the St Just District. Unpublished Ph.D. thesis, University of London.

King, R.J. (1973). Mineralization. In: Sylvester-Bradley, P.C., and Ford, T.D. (eds), *The Geology of the East Midlands*, pp. 112-137. Leicester University Press.