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The journal of British Isles topographical mineralogy

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FRONT COVER:

Proustite (1.0mm) with barite and tennantite.
Dolyhir quarry, Old Radnor, Powys, Wales, October 2004.
Collection: Neil Hubbard. Photograph: David Green.

BACK COVER:

Millerite on calcite from Coed Ely Colliery, Tonyrefail, Gwent.
Collected June 1982. Roy Starkey Collection 1722-012.
(crystals 10mm tall)

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Editorial

In 2003, Alan Dyer invited me to take over as Journal Editor. As a long-standing but hitherto inactive member of the Russell Society I accepted, not really knowing how time-consuming the task would be. I suspect that Alan played that point down somewhat! Interesting articles were delivered to me by post and email throughout 2004 and early 2005, and I am very grateful to the authors for their contributions and to the reviewers for their assistance. Ideally this issue should have reached you earlier in 2005, but this was prevented by the demands of my day job - as one of four academic staff providing BSc and MSc Geology courses at the University of Brighton. Work pressure also prevented Rob Bowell from undertaking his role as Journal Manager, so at a late stage Jim Robinson kindly stepped in to undertake the typography and design. Jim and I are delighted to have seen Volume 8 part 2 through to completion and we hope that you are equally pleased with the variety and quality of the papers published in this issue.

Supergene minerals feature strongly and the articles in Volume 8 Part 2 cover a wide geographical range throughout Britain and Ireland. Frank Ince provides a comprehensive account of the mineralogy of Newhurst Quarry, extending the work of Bob King on Leicestershire mineralogy. Of particular interest here are the occurrences of vanadium- and molybdenum-bearing supergene minerals. David Green and co-authors describe supergene galena from six UK localities and discuss the conditions under which late-stage sulphides form. Later in the issue, Trevor Bridges and David Green provide an update on the supergene mineralogy of Hilton mine in Cumbria where they have found the arsenates adamite and mimetite.

Stephen Moreton considers how supergene processes in the overlying rocks have influenced the growth of fluorite in Greenlaws mine, Weardale, and Stephen and David report the discovery in County Limerick of rare phosphates new to the British Isles. Occurrences of carbonate-fluorapatite are documented from several coal mines in South Wales by Stephen Plant and David Evans, who suggest that this mineral has been overlooked due to its resemblance to siderite. Also from Wales, a further occurrence of the lead chloride mineral cotunnite is described by Neil Hubbard and David Green.

Trevor Bridges and David Green report a second British occurrence of the rare fluorine-bearing mineral greaksutite; the first occurrence had been reported in part 1 of this volume. Trevor and David are co-authors of two review papers: one on British occurrences of the uncommon hydrated copper sulphate antlerite, and the other on supergene mineralisation at Silver Gill in the Caldbeck Fells. David Green and his co-authors also contribute a note on the composition of fülöppite from the Caldbecks. Tim Neall and David note the first British occurrence of the rare supergene lead mineral kegelite from Wanlockhead.

Towards the end of this issue, the composition of columbite crystals from Chywoon quarry in the Carnmenellis Granite is documented by David Moulding and Andy Tindle. And last but not least, Alan Dyer and his co-authors describe a remarkable discovery of natural tin-lead alloy in an amygdale in the basaltic lavas of Mull. The find was made in the 1980s and recent advances in non-destructive analytical methods have enabled the 'silvery balls' to be characterised. Two reviews of recent minerals books complete volume 8.

My ambition is to achieve an annual publication of the JRS, as I believe this would best serve the interests of authors and of the members of the Russell Society. However to achieve this, I will need regular submission of articles for publication! I see that this plea has been made in previous editorials - but once again, if you have made new finds, obtained new data, or developed new insights on the mineralogy of your favourite localities, please type your observations and send me your article for publication in the JRS.

Thank you,
Norman Moles

THE MINERALOGY OF NEWHURST QUARRY, SHEPSHED, LEICESTERSHIRE

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The Precambrian and Triassic rocks exposed at Newhurst Quarry, Shepshed, Leicestershire are the hosts for a suite of copper-iron-lead-zinc-vanadium-molybdenum-containing minerals. The Precambrian rocks host a number of quartz- and/or carbonate-rich veins, some sulphide-bearing, and associated with hydrothermal mineralisation. Supergene mineralisation is most prominent in the vicinity of the Precambrian-Triassic unconformity. This paper describes the local geology and the minerals occurring in the quarry, and makes some observations on the hydrothermal and supergene processes responsible for mineral formation.

INTRODUCTION

The Charnwood Quarries, Shepshed, Leicestershire are situated on the N edge of Charnwood Forest (Fig. 1). There are two distinct quarries: Newhurst Quarry (SK 485 179) W of the M1 motorway and Longcliffe Quarry (SK 493 171) E of the motorway. These quarries exploit rocks of the late Precambrian sequence namely the North Charnwood Diorite and its host, the Blackbrook Reservoir Formation of the Blackbrook Group (Carney *et al.*, 2001). The Precambrian rocks are separated from the overlying Triassic sediments by a well-defined unconformity, a feature that is associated with the base-metal mineralisation in Leicestershire (Pearson and Jeffery, 1997). A

number of quartz- and/or carbonate-rich sulphide-bearing veins have been exposed in Newhurst Quarry and these, together with the influence of the Precambrian-Triassic unconformity, have given rise to a suite of minerals containing copper, iron, lead, zinc, vanadium and molybdenum. This unusual mineralogy has resulted in the preservation of the northern half of the faces and floor of Newhurst Quarry as a Site of Special Scientific Interest (SSSI) (English Nature, 1984).

HISTORY OF QUARRYING

Quarrying in Leicestershire began before Roman times (McKinley, 1955); however, large-scale extraction at Newhurst Quarry does not appear to have been in progress until 1892 (Worssam and Old, 1988; Boucher, 1994). In the early years of the 20th century a map produced by Bosworth (1912) notes the "Charnwood Granite Quarries". This map shows that the area now covered by Newhurst Quarry contained two quarries (Shepshed Old Quarry and Big Quarry) together with a third (Stonepit Plantation Quarry). The site of the latter quarry now appears to be buried under the quarry plant and the M1 motorway (Malcolm Rouse, *personal communication*). Newhurst Quarry was the name used by Watts (1947) for the quarry that is W of the M1; that name is still being used. Longcliffe Quarry (Bosworth, 1912; Watts, 1947) is the name used for the quarry E of the M1 motorway. Extraction at Newhurst Quarry finished in 2001 and Longcliffe Quarry is currently (2004) in the process of being back-filled.

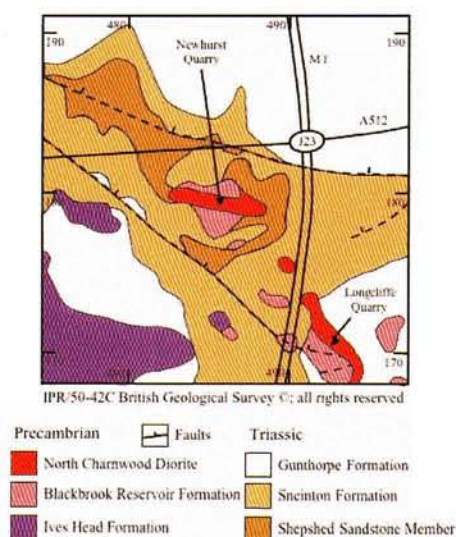


Figure 1. Geological sketch map (solid) of the area around Newhurst Quarry, based on BGS 1:50000 Series England and Wales Sheet 141, by permission of the British Geological Survey.

GEOLOGY

The Charnwood Forest area of Leicestershire contains limited exposures of late Precambrian rocks that are overlain unconformably by Cambrian and Triassic rocks and the entire sequence is partly covered by Pleistocene glacial deposits (Worssam and Old, 1988; Carney *et al.*, 2001; Horton and Gutteridge, 2003). Apart from their significance as some of the oldest rocks in England, the Precambrian rocks of the Charnian Supergroup are particularly important given that Ediacaran fossils occur in some members of the sequence (Boynton and Ford, 1995; Boynton, 1999).

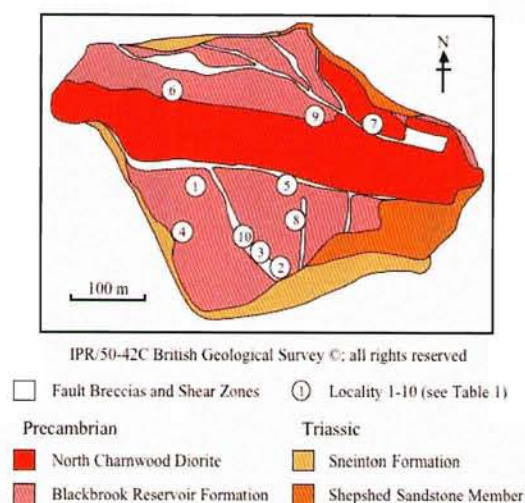


Figure 2. Geological sketch map (Solid) of Newhurst Quarry, based on Carney (1994) by permission of the British Geological Survey.

The rocks of the Charnian Supergroup have a minimum age range of 550-600 Ma (Neoproterozoic III, Vendian) and those exposed in Newhurst Quarry (Fig. 2) are the Blackbrook Reservoir Formation of the Blackbrook Group and the North Charnwood Diorite (Carney, 1994; Carney *et al.*, 2001). The Blackbrook Reservoir Formation comprises a series of about 550 m of mainly grey-green volcanoclastic mudstones, siltstones and sandstones (Carney *et al.*, 2001). The sequence was laid down in an island arc environment on the northern margin of the Gondwana palaeocontinent (Pharaoh and Gibbons, 1994), with the material probably originating from volcanoes in the area around Bardon Hill and Whitwick, 5-6 km to the SW (Carney, 2000; Carney, *et al.*, 2001). Folding, particularly during the Acadian orogeny, has resulted in the rocks of the Charnian Supergroup taking the form of an anticline plunging to the SE, consequently, the rocks of the Blackbrook Reservoir Formation dip steeply (up to 85°) to the NE-ESE in Newhurst Quarry (Carney *et al.*, 2001).

The North Charnwood Diorite was intruded into the rocks of the Blackbrook Reservoir Formation and is usually a mottled greenish-grey rock. The intrusion takes the form of a NW-SE striking sheet up to 60 m thick dipping steeply to the SW in Longcliffe Quarry and turning E-W in the area occupied by Newhurst Quarry where its southern margin dips 20-30° to the S and the northern contact is subvertical (Carney, 1994). A date of 311±92 Ma (rubidium-strontium isotope method) was obtained for the North Charnwood Diorite, however, it has been suggested that this resulted from the resetting of its age during the Variscan orogeny (Worssam and Old, 1988). The rocks of the Charnian Supergroup have been affected by faulting (Watts, 1947; Worssam and Old, 1988; Carney *et al.*, 2001) and in Newhurst Quarry the faulting is represented by a number of fault breccias, shear zones and low angle faults (Carney, 1994). Some of these faults appear to have controlled aspects of the mineralisation.

Features associated with sub-aerial erosion in the Triassic era are common in many of the Leicestershire quarries (Bosworth, 1912; Watts, 1947; Worssam and Old, 1988; Carney *et al.*, 2001). Newhurst Quarry is no exception and the Precambrian-Triassic unconformity is well-exposed (Carney, 1994). The unconformity is covered by a basal breccia that contains Charnian clasts and grades into the buff to red sandstones and siltstones of the Shepshed Sandstone Member of the Sherwood Sandstone Group. This sequence is overlain by red-brown (with greenish bands) siltstones and mudstones of the Sneinton Formation of the Mercia Mudstone Group which are almost horizontally-bedded (Carney, 1994; Carney *et al.*, 2001). Exposed wadis frequently display catenary bedding and it is not uncommon to find exposures of bedding planes in the Mercia Mudstone Group that display ripple effects. Some horizons in the Triassic sequence have provided fine-grained sandstone pseudomorphs after a cubic mineral, presumably halite. Llewellyn (1969) noted the occurrence of "dendritic halite pseudomorphs from the Waterstones Formation of Newhurst Quarry"; a particularly delicate example is depicted in his Figure 2. A specimen held by the Geology Department, University of Leicester comprises fine-grained sandstone pseudomorphs after what appear to be lenticular gypsum crystals up to 5 mm (Roy Clements, *personal communication*). Footprints of *Cheirotherium* (Mark Evans,

Table 1: Description of localities 1-10 and their associated minerals.

Locality	Description	Minerals
1	An E-W oxidised chalcopyrite-pyrite vein at the W end of the quarry	Chalcopyrite (botryoidal), pyrite, aragonite, malachite, calcite
2	A series of almost vertical, WNW-ESE trending, oxidised sphalerite-chalcopyrite-galena veins 5-10 m below the Precambrian-Triassic unconformity on the S side of the quarry	Chalcopyrite, galena, sphalerite, calcite, aurichalcite, azurite, cerussite, hemimorphite, malachite, mottramite, smithsonite, vanadinite, wulfenite, cadmium sulphide
3	A series of oxidised chalcopyrite veins on the S face of the quarry	Chalcopyrite, azurite, malachite
4	Dolomite and calcite in veins on the W face of the quarry	Dolomite, calcite, baryte
5	An almost vertical E-W vein on the S face of the lower levels of the quarry	Calcite, chalcopyrite, malachite
6	A NW-SE vein on the N face of the lowest level of the quarry	Calcite, dolomite
7	The upper N face of the quarry, below the unconformity between the Triassic sequence and the North Charnwood Diorite	Copper, malachite
8	Fractures in the S face of the lower levels of the quarry	Calcite, malachite, mottramite
9	Fractures at the foot of the N face of the quarry	Galena, calcite, mottramite
10	Triassic breccia in a weathered fracture or narrow wadi on the S face of the quarry	Mottramite

personal communication) and/or Coelurosaurichnus (Roy Clements, *personal communication*) have been found in some Triassic horizons in the quarry. These have been tentatively identified as having been produced by a species of Rhynchosaur (Carney, 1994; Carney *et al.*, 2001). Specimens of these trace fossils are housed in the collections of New Walk Museum, Leicester and the Geology Department, University of Leicester.

MINERALS

Petrological studies have identified the minerals that occur in the North Charnwood Diorite: epidote, chlorite, sericite, plagioclase, titanite, quartz, calcite, prehnite, apatite, zircon and probably titaniferous magnetite. Plagioclase was found to be rare, with most of the grains having been altered in part to epidote, sericite, chlorite, carbonate, prehnite, pumpellyite or albite (Worssam and Old, 1988).

A variety of techniques, including wet chemistry, staining methods, optical properties and XRD, have provided data that supports the identification of the individual minerals

described below (a table containing analytical data can be provided on request). The approximate positions of Localities 1-10 are shown on Fig. 2; they are described in Table 1, together with a list of their associated minerals.

ANKERITE, $\text{Ca}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$

Specimens of spheroidal carbonate-rich nodules (up to 50 mm) in Triassic sandstone appear to be cemented by ankerite (Roy Clements, *personal communication*). Other specimens of these nodular concretions are cemented by calcite (King, 1973).

ARAGONITE, CaCO_3

Radiating groups of colourless to white or pale green, partly iron stained, acicular crystals (up to 5 mm) found at Locality 1 (Fig. 2 and Table 1) have been shown to be aragonite (XRD; Craig Williams, *personal communication*). The associated minerals are shown in Table 1.

AURICHALCITE, $(\text{Zn}, \text{Cu})_5(\text{CO}_3)_2(\text{OH})_6$

Pale bluish-green powdery coatings recovered from Locality 2 (Fig. 2 and Table 1) have been

shown to be aurichalcite (XRD; Craig Williams, *personal communication*). The associated minerals are shown in Table 1. Aurichalcite was also found as typical pale bluish-green laths on an iron-stained matrix from the N face of the quarry in 1973 (John Jones, *personal communication*).

AZURITE, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Azurite was recorded as occurring in the oxidised chalcopyrite-containing veins associated with chalcocite, malachite and, rarely, native copper (King and Ford, 1969). King (1973) also noted that azurite was found in the supergene assemblage as thin shell-like foliae interleaved with malachite and as very small (0.3 mm) dark blue crystalline blebs associated with malachite and jarosite. Dark blue hemispherical aggregates (up to 3 mm) of crystals on joints in the diorite were collected from the S face of the quarry in 1979 (John Jones, *personal communication*).

More recently small (up to 5 mm) lustrous dark blue crystals of azurite were found in a number of the oxidised chalcopyrite-containing veins on the S side of the quarry (Locality 3, Fig. 2 and Table 1). The azurite occurs on iron stained host rock adjacent to weathered chalcopyrite and was associated with malachite.

BARYTE, BaSO_4

King (1973) noted that baryte was found on joints in the Charnian rocks below the Precambrian-Triassic unconformity (see also

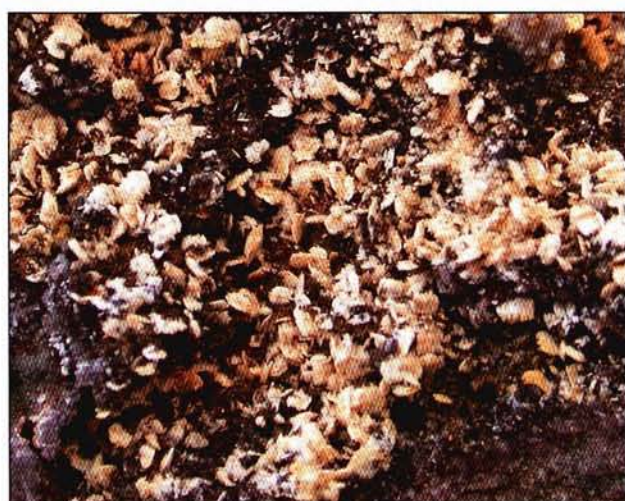


Figure 3. White to pale pink thin tabular crystals of baryte (to 5 mm) on dolomite (Frank Ince specimen and photograph).

King and Ford, 1968). It was also present as the cementing agent in certain sandstone bands (King and Wilson, 1976).

More recently baryte was found in two distinct settings: 1. Small white to pale pink thin tabular crystals (Fig. 3) that form cockscomb groups, associated with dolomite and calcite in veins at the W end of the quarry (Locality 4, Fig. 2 and Table 1); 2. Small hemispherical aggregates of pink crystals associated with hematite and dolomite on the lowest level of the quarry.

BORNITE, Cu_5FeS_4

Four different settings for the occurrence of bornite were reported by King (1973): Type 1 bornite was seen on the old N face of the quarry "covering tens of square metres... as thin strings, up to 3 mm thick, sandwiched between pale yellow dolomite and crushed ferruginous quartz... its colour is estimated to be dark magenta, but it is difficult to assess due to the high lustre". This material was associated with malachite and vésigniéite. Type 2 bornite took the form of anhedral masses embedded in quartz-carbonate veins. This material was reported to be blackish-grey to violet-brown and associated with chalcocite, pyrite, malachite and copper vanadates, e.g., vésigniéite. Type 3 bornite was associated with chalcopyrite in a belt of almost vertical crush breccia (up to 40 mm) exposed on the S face of the quarry in 1965. It occurred as anhedral, highly iridescent masses and veinlets interleaved with chalcopyrite and pale purple quartz. Type 4 bornite occurred as detrital grains in the basal beds of the Triassic sediments. These grains were described as being <9 mm, with a kernel of bornite surrounded by goethite and associated with malachite and dolomite (other grains contained chalcopyrite/goethite).

More recently anhedral masses of bornite (as iridescent purple margins surrounding chalcopyrite) embedded in small calcite veins were described by King (1998) as material of hypogene origin. Similar material can still be found in boulders on the lower levels of the N side of the quarry. Some specimens of malachite-coated nodular bornite on calcite (Fig. 4) were collected from a carbonate-bearing supergene vein on the lower levels of the N face of the quarry in 1976 (John Jones and Franz Werner, *personal communications*).



Figure 4. Malachite on bornite; field of view 170 mm x 110 mm. (John Jones specimen; Frank Ince photograph.)

CALCITE, CaCO_3

Calcite occurs in a number of habits within many of the mineralised veins in the quarry. King (1973) described those associated with the hypogene and supergene copper mineralisation as “never very spectacular” and frequently as poorly developed scalenohedra. The calcite associated with the hypogene mineralisation displayed pink fluorescence under short wave UV, however, the pale purple calcite associated with the supergene copper mineralisation possessed a bright red fluorescence under short wave UV (manganese was shown to be present by qualitative analysis). It was also noted that the coarsely crystalline pale orange ferro-calcite, mentioned as occurring in a NW-striking vein up to 150 mm wide exposed on the lowest level in the quarry in 1968, showed no fluorescence. A less common habit was also described, that of very small globular masses up to 1.2 mm diameter composed of alternating shells of calcite and malachite.

A number of occurrences of calcite were associated with the overlying Triassic sediments. Small (up to 5 mm) scalenohedral crystals of colourless calcite occur in veins of well crystallised dolomite. King (1973) describes these as “always positive rhombohedra [4041]... and often show pronounced rounding of the faces”. It was common to find cavities in the Triassic basal breccia lined with small, colourless scalenohedral crystals with rounded faces. In 1978 more impressive specimens covered with colourless-white scalenohedral crystals were recovered. One of these (Fig. 5) featured a large, colourless, complex-twinned calcite crystal (30 mm x 25 mm x 25 mm) set on smaller (up to 15 mm) colourless-white, scalenohedral calcite crystals (Tom

Cotterell, *personal communication*; specimen in the King Collection, National Museum of Wales, Cardiff).



Figure 5. Colourless to pale yellow, complex-twinned calcite crystal 30 mm x 25 mm x 25 mm set on smaller (up to 15 mm) colourless to white, scalenohedral calcite crystals. (Bob King specimen K6397-1978, NMW 83.41G.M5012; Frank Ince photograph.)

The sandstone components of the Mercia Mudstones contained nodular concretions up to 85 mm that were cemented by calcite, particularly in the SW corner of the quarry. King (1973) reported that these nodules contained over 60% calcite, the remainder being sand identical to the surrounding matrix. Internally they possessed concentric rings of calcite highlighted by slight colour variations and a radiating structure of calcite crystals. More recently some small nodules up to 20 mm in diameter containing calcite and small amounts of galena were recovered from sandstone beds just above the Precambrian-Triassic unconformity on the S face. Other specimens of these nodular concretions appear to be cemented by ankerite (Roy Clements, *personal communication*).

More recently there have been a number of new occurrences of calcite: 1. In 1997 some white to very pale purple, well-formed, scalenohedral crystals up to 45 mm displaying parallel growth (Fig. 6) were found at Locality 5 (Fig. 2 and Table 1). Some of these crystals were doubly terminated and twinned on [0001]. 2. A probable eastwards extension of the vein at Locality 5 yielded some larger (up to 65 mm) iridescent, orange-coated crystals with parallel growth, many twinned on [0001]. Some of these latter crystals were partly coated with small globules of malachite and



Figure 6. White scalenohedral crystals of calcite up to 45 mm. (Frank Ince specimen and photograph.)

associated with small nodules of partly oxidised chalcopyrite. 3. Colourless to pale lilac pseudo-cubic calcite crystals up to 4 mm have been recovered from Locality 6 (Fig. 2 and Table 1). This material has occasionally been mistaken for fluorite.

CERUSSITE, PbCO_3

King (1973) noted that minor cerussite was found associated with galena in a sandstone bed above the basal breccia that was exposed during the cutting of a new access road on the N face of the quarry. The cerussite "surrounded the galena masses, though it remained in and partially cemented the sandstone, forming white pellicles around individual sand grains".

More recently, cerussite was recovered from Locality 2 (Fig. 2 and Table 1) and occurred as small (up to 2 mm) colourless to white or grey tabular crystals some of which show cyclic twinning, or as colourless to white acicular crystals up to 3 mm. The associated minerals are shown in Table 1. Cerussite also occurred with galena, calcite and possible wulfenite in the Shepshed Sandstone Formation close to the Precambrian-Triassic unconformity above the incline on the S side of the quarry.

CHALCOCITE, Cu_2S

Chalcocite was recorded as occurring "in intimate mixture with bornite and chalcopyrite in a quartz-carbonate gangue" (King, 1973). It occurred in thin veins (up to 3mm) with dolomite on the lowest levels of the N face (1957-9). The quantity of coarsely granular, blackish-grey to blackish-blue chalcocite was reported to be rather small. The intensity of the oxidation process had

produced "relics embedded in carious masses of goethite, malachite and vanadates in a quartz-carbonate gangue...kernels of relic material most commonly consist of an intergrowth of bornite and chalcocite" (King, 1973). In an earlier report it was noted that chalcocite occurred in quartz-carbonate veins associated with chalcopyrite, azurite, malachite and, rarely, native copper (King and Ford, 1969). At the E end of the N face of the quarry patches of mid-grey chalcocite coated with malachite can still be seen (Locality 7, Fig. 2). This is part of the area that has been designated as an SSSI (Carney *et al.*, 2001).

A specimen collected in 1967 held by the Geology Department, University of Leicester comprises malachite and dolomite on a carbonate-cemented breccia attached to a red-brown matrix. The accompanying label indicates the presence of chalcocite. Further analysis of the red-brown material has not revealed any chalcocite but indicated the presence of quartz, hematite, chlorite and possibly cornwallite ($\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$) (XRD; Roy Clements, *personal communication*); visually there is little evidence for cornwallite.

In 1999, boulders on the lower levels of the quarry were found to contain a dark grey metallic mineral coated with globules of bright green malachite and associated with calcite. From wet chemistry analyses this was considered to be chalcocite, however XRD analyses indicated that it could be djurleite (David Green, *personal communication*) or anilite (Craig Williams, *personal communication*). King (1973) reported the occurrence of djurleite ($\text{Cu}_{31}\text{S}_{16}$) in Leicestershire, whereas anilite (Cu_7S_4) does not appear to have been recorded. It is known that the conversion of anilite to djurleite and/or digenite occurs readily (Starkey and Hubbard, 1998), and consequently the unambiguous identification of the grey-black copper sulphides at Newhurst Quarry will require further investigation.

CHALCOPYRITE, CuFeS_2

King and Ford (1969) noted that chalcopyrite occurred in quartz-carbonate veins "in the lowest level of the quarry" associated with chalcocite, azurite, malachite and, rarely, native copper. Subsequently the occurrences of chalcopyrite in Leicestershire were reviewed (King, 1998). At Newhurst Quarry two distinct settings were described: (1) chalcopyrite associated with



Figure 7. Yellow nodular chalcopyrite 25 mm x 25 mm with minor malachite. (Bob King specimen K7896, NMW 83.41G.M452; Frank Ince photograph.)

bornite and calcite in hypogene veins; and (2) supergene botryoidal chalcopyrite associated with dolomite in joints and hollows on the Precambrian unconformity. These are now described in more detail.

Chalcopyrite was one of the more important members of the hypogene system associated with bornite and calcite. It occurred in anhedral masses up to 13 mm thick and constituted 76% of the sulphide content of the veins exposed at the W end of the quarry in 1968. King (1998) suggested that these veins represent a high temperature hypogene source. Where the vein-like joints intersected the hypogene veins the latter showed marked oxidation and one such occurrence was described in some detail. In some cases the vein-like joints contained a mixture of chalcopyrite, goethite, calcite, Charnian rock fragments and red clay from the overlying Triassic sequence. A brecciated vein bearing chalcopyrite, together with bornite and sericite, was exposed on the S face of the quarry in 1968.

King (1998) also described chalcopyrite occurring as roughly crystallised botryoidal masses (Fig. 7) reminiscent of "blister copper" that, when fractured, show interleaving with goethite and malachite. This material was associated with dolomite in open joints and as an infilling of low points on the Precambrian topography.

Material collected in 1974-6 contained thin veins up to 8 mm of chalcopyrite associated with pyrite

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(small cubic crystals up to 1 mm), galena and goethite (John Jones, *personal communication*). Veins also exposed in 1976 contained a small amount of chalcopyrite associated with sphalerite, galena and calcite (John Jones and Trevor Bridges, *personal communications*). More recently chalcopyrite, surrounded by a typical iridescent purple margin of bornite, and embedded in small calcite veins, has been found in boulders on the lower levels of the N side of the quarry; this appears to be similar to the hypogene material described by King (1998). In 1996 a small vein in boulders on one of the lower levels of the S side of the quarry contained some quite large (40 mm x 35 mm) masses of crudely crystalline chalcopyrite partly coated with a ferric encrustation and associated with scalenohedral calcite and minor malachite (Fig. 8). Small amounts of chalcopyrite were recovered at Locality 2 (Fig. 2); the associated minerals are listed in Table 1. Roughly crystallised botryoidal chalcopyrite has also been found at locality 1 (Fig. 2 and Table 1); this appears to be similar to the supergene material described by King (1998), although its association with pyrite and aragonite is different.



Figure 8. Crudely crystalline chalcopyrite 40 mm x 35 mm, partly covered with a ferric encrustation, on scalenohedral calcite and minor malachite (Frank Ince specimen and photograph).

CHLORITE GROUP

A chlorite-rich fault gouge was recovered from a series of NW-SE trending veins extending into the North Charnwood Diorite that were exposed on the S face in 1974. These veins also contained quartz, ferroan dolomite, chalcopyrite and bornite (altering to chalcocite and covellite), calcite and galena, (King, 1983). A number of

veins that have been exposed in the quarry from time to time contained dark green masses typical of chlorite together with white quartz and feldspar (John Mason, *personal communication*).

CHRYSOCOLLA, $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$

King (1973) recorded chrysocolla as occurring as small pale green to bluish-green masses associated with cuprite and malachite.

COPPER, Cu

King and Ford (1969) noted that native copper occurred rarely in quartz-carbonate veins "in the lowest level of the quarry" associated with chalcopyrite, chalcocite, azurite and malachite. King (1967, 1973) recorded that in 1937 an impressive occurrence of copper mineralisation was exposed on the upper N face of the quarry, situated immediately below the unconformity between the Triassic sequence and the North Charnwood Diorite (Locality 7, Fig. 2). An area of 12 m x 9 m was covered with thin sheets, dendritic and filigree masses of native copper coated with bright green malachite. The largest component of this occurrence was reported to be a sheet that measured approximately 3 m x 1.5 m. Unfortunately this exceptional specimen appears to have been lost. Small amounts of native copper, associated with copper carbonates, also occurred elsewhere in the quarry, most commonly in the Triassic basal breccia (King, 1973).

More recently (1993) a small amount of native copper, associated with malachite, was tentatively identified in material from an oxidised chalcopyrite-bornite-pyrite-calcite vein in a boulder on the lowest level of the quarry.

COVELLITE, CuS

Two occurrences of covellite were reported by King (1973): 1. As small (1-2 mm) plates embedded in calcite and it was thought that plate-like masses of acicular malachite associated with this material could be pseudomorphs after covellite. 2. As anhedral masses and, in one case, an indigo blue, euhedral hexagonal plate (0.6 mm), in the basal breccia of the Triassic sequence amongst the dolomite-cemented clasts of the North Charnwood Diorite.

It is not unusual to find that specimens of copper-containing sulphide minerals, e.g., chalcopyrite and bornite, have become partly covered with

thin plates of purple covellite (John Jones, *personal communication*). For a discussion of this post-collection phenomenon the reader is referred to Wirth (2002).

CUPRITE, Cu_2O

King (1973) noted that cuprite "is found in the supergene system, associated with malachite and goethite, as dark red masses up to 1.5 mm in diameter". Other specimens showed patches of cuprite up to 5 mm associated with chrysocolla and malachite. In 1976 material was collected from a thin vein of cuprite in a calcite-rich sandstone matrix that contained some cavities containing fine needles of cuprite var. chalcotrichite (Trevor Bridges, *personal communication*; material collected by John Sheppard).

DOLOMITE, $\text{CaMg}(\text{CO}_3)_2$

Dolomite was recorded by King (1973) who indicated that it was restricted to the supergene system and occupied joints and vein-like structures below the Precambrian-Triassic unconformity. Its colour ranged from white to greyish orange and generally the simple rhombohedral crystals were small, up to 1 mm. Some leaching and recrystallisation had resulted in highly drusy veins in the Precambrian rocks that contained well crystallised dolomite with larger individual crystals up to 4 mm, frequently forming parallel and reticulated aggregations.

King (1973) described ferroan dolomite (identified by staining techniques) as pink to brown cleavage masses in a thin hydrothermal vein "associated with a little specular hematite and minor euhedral quartz" on a sample "said to have come from the top level of the S face of Newhurst Quarry". Ferroan dolomite was recovered from a series of NW-SE trending hydrothermal veins extending into the North Charnwood Diorite that were exposed on the S face in 1974. These veins also contained quartz, chalcopyrite and bornite (altering to chalcocite and covellite), calcite, galena and a chlorite-rich fault gouge (King, 1983).

Material similar to that described above is still quite common and specimens of colourless to cream crystals up to 4 mm of dolomite (sometimes iron stained) have been found associated with hematite, baryte, malachite and calcite in both scalenohedral (Locality 1, Table 1)

and pseudo-cubic habits (Locality 6, Table 1). Given the report of ferroan dolomite mentioned above, it might be prudent to re-evaluate any material that has been tentatively identified as dolomite.

EPIDOTE, $\text{Ca}_2\text{Al}_2(\text{Fe}^{3+}, \text{Al})_3\text{Si}_3\text{O}_{12}(\text{OH})$

Veins of epidote in the North Charnwood Diorite are not uncommon. A specimen held in the collection of the Geology Department, University of Leicester, is a typical vein of green epidote 30 mm wide containing reddish-brown (hematite?) flecks with a brownish margin (Roy Clements, *personal communication*). Small green prismatic crystals (to 5 mm) embedded in white quartz have been shown by XRD analysis to be epidote (Craig Williams, *personal communication*; Trevor Bridges specimen).

FELDSPAR GROUP

A number of veins that have been exposed in the quarry contained feldspar together with white quartz and dark green chlorite (John Mason, *personal communication*).

GALENA, PbS

The occurrences of galena in Leicestershire have been reviewed (King, 1983). At Newhurst Quarry two distinct settings were described: 1. A NW-SE striking, quartz-carbonate vein up to 400 mm wide cutting the North Charnwood Diorite that was exposed in 1974-6 on the S face of the quarry contained strings of microcrystalline galena up to 16 mm wide associated with ferroan dolomite, calcite, chalcopryrite, chalcocite, bornite and a "chlorite-rich gouge". 2. Two occurrences were noted in the Triassic sediments: (a) As the cement in a series of sandstone-mudstone-sandstone beds (all 30-45 mm thick) that were exposed on the upper level of the N face of the quarry in 1966. The lower sandstone bed contained fine-grained galena that appeared to be replacing the calcite that was cementing the sandstone. The higher bed contained galena which, when extracted from the matrix, was found to form aggregates of cubo-octahedral crystals. King (1983) suggested that this galena was epigenetic in origin. (b) As the sporadic cement in white sandstone beds in the basal breccia on the S face of the quarry where it was associated with malachite and hematite pseudomorphs after coulsomite (King, 1983); however, see hematite, next column.

In 1976 veins up to 12 mm wide of galena bearing

small cubo-octahedral crystals were found associated with sphalerite and small amounts of chalcopryrite (Trevor Bridges, *personal communication*). More recently (since 1993) galena has occurred at Locality 2 (Fig. 2 and Table 1) as small (up to 5 mm) cubo-octahedral crystals. The associated minerals are shown in Table 1. Galena also occurred infrequently as poorly-formed cubo-octahedral crystals associated with cerussite, calcite and possible wulfenite in the Shepshed Sandstone Formation close to the Precambrian-Triassic unconformity above the incline on the S side of the quarry.

GOETHITE, $\alpha\text{-FeO}(\text{OH})$

King (1973) described detrital grains up to 9 mm in diameter found in the basal beds of the Triassic sediments that contained goethite, associated with malachite and dolomite, surrounding kernels of his Type 4 bornite (see above); other grains contained goethite and chalcopryrite. He also noted that goethite was a common oxidation product that was found in the supergene mineral suite associated with the oxidised sulphide veins in the quarry and frequently occurred in "masses of compact varnish-like material, threaded through with veinlets of malachite" and that small masses of goethite were found to contain a core of radiating tabular crystals of marcasite up to 1.8 mm.

King (1973) also mentioned a specimen from Newhurst Quarry in the Leicester City Museum (Accession Number 38'28: "Pseudomorphs in hematite. Newhurst Quarry, Longcliffe. Mr F.J. Richards") that was found to be goethite pseudomorphs after pyrite. Brown cubes of goethite pseudomorphs after pyrite were also found associated with calcite and sphalerite (Trevor Bridges, *personal communication*).

HEMATITE, $\alpha\text{-Fe}_2\text{O}_3$

King (1973) reported that specular hematite occurred in steeply dipping veins in the form of radiating groups (eisenrosen) of plates up to 4 mm. King (1973) also described specular hematite and minor euhedral quartz in a thin vein of ferroan dolomite on a sample "said to have come from the top level of the S face of Newhurst Quarry".

Recently hematite was found in a number of settings: 1. Specular hematite associated with dolomite in the lowest levels of the quarry; 2.

Reniform hematite associated with baryte and dolomite in the lowest levels of the quarry; 3. Dark reddish-brown coatings of hematite on joint faces in the North Charnwood Diorite.

In 1980 small (up to 0.3 mm), lustrous, dark brown to black, octahedral crystals (Fig. 9) associated with earthy hematite, calcite, dolomite, galena and malachite, were recovered from white sandstone beds in the basal breccia of the Triassic rocks on the S face of the quarry (King, 1983; John Jones and Bob King, *personal*



Figure 9. "Coulsonite", hematite possibly pseudomorphing vanadian-magnetite; field of view 10 mm x 10 mm. (John Jones specimen; Frank Ince photograph.)

communications). Analyses at the Natural History Museum, London indicated that the individual crystals were hematite, however, the presence of 3% vanadium was also noted (Bob King, *personal communication*). The material was subsequently described as hematite pseudomorphs after coulsonite (King, 1983). Further examination at the Natural History Museum proved inconclusive and it remained an unconfirmed report (Ryback and Tandy, 1992). The occurrence was noted in later documents as coulsonite (FeV_2O_4 requires 45.95% vanadium) or as a vanadium-rich magnetite (consistent with 3% vanadium) (English Nature, 1984; Carney, 1997; Carney, 2001). Recent analysis of the material collected in 1980 confirms that it is hematite, however the presence of vanadium was not noted (XRD and EDAX; David Green, *personal communication*). It seems likely that these specimens are hematite pseudomorphs after magnetite (that probably contained some vanadium), although the possibility of hematite

pseudomorphs after coulsonite cannot be ruled out. Even the occurrence of hematite pseudomorphs after magnetite in the Triassic breccia would be intriguing, as euhedral crystals of magnetite do not appear to occur anywhere else in Newhurst Quarry.

HEMIMORPHITE, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$

Small radiating aggregates of colourless to white blades to 1 mm and pale greenish-brown crusts found at Locality 2 (Fig. 2 and Table 1) have been shown to be hemimorphite (XRD; Craig Williams, *personal communication*; also Neil Hubbard specimen). The associated minerals are shown in Table 1.

JAROSITE, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

King (1973) noted that jarosite occurred as reddish brown to dark brown microcrystalline crusts and masses and that it was not uncommon to find azurite and globules of malachite associated with and/or coated by jarosite.

KAOLINITE, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

On the footwall of joints exposed on the S face of the quarry in 1973 a kaolin-like mineral was associated with chalcopyrite, bornite and ferroan dolomite (John Jones, *personal communication*). Recent analysis of this material has confirmed it to be kaolinite (XRD; Craig Williams, *personal communication*).

MALACHITE, $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Malachite is a common mineral in the neighbourhood of any veins that contain chalcopyrite, bornite or chalcocite. King (1973) described 4 main types of occurrence: Type 1 malachite formed films and encrustations of fibrous malachite associated with other copper-containing minerals, e.g., native copper (King, 1967); Type 2 malachite formed fan-like aggregations of bright green acicular crystals up to 3mm that may coalesce to form globules and spheres. Internally some of these globules had a repeating calcite-malachite-calcite-malachite structure. It was not uncommon to find this material coated with jarosite; Type 3 malachite occurred as roughly tabular crystalline masses that had a microscopic, honeycomb-like structure. This type was often found coating a thin vein of bornite on the old N face of the quarry; Type 4 malachite occurred as

pseudomorphs after chalcopyrite and/or bornite. The majority of these types can still be found in the quarry.

There are a number of more recent occurrences of malachite: 1. Bright green globules in a small chalcopyrite-pyrite vein were found at Locality 1 (Fig. 2 and Table 1); 2. Small (up to 2 mm) globules at Locality 2 (Fig. 2 and Table 1); 3. Bright green coatings of globules on material that was thought to be chalcocite (see above) associated with calcite on boulders in the lower levels of the quarry; 4. Green pellets up to 2 mm and fans of acicular crystals up to 1 mm within Triassic sandstones in a wadi on the upper N face (John Mason, *personal communication*).

MARCASITE, FeS_2

Marcasite was recorded by King (1973) as occurring in the quarry as the relics of tabular crystals up to 7 mm in a series of oxidised supergene veins up to 32 mm wide that also contained dolomite. Marcasite was also found as a core of radiating tabular crystals up to 1.8 mm in small masses of goethite.

MOTTRAMITE, $\text{PbCu}(\text{VO}_4)(\text{OH})$

In his description of *vésigniéite*, King (1973) noted that "a greenish-yellow mineral as yet unidentified... closely resembles mottramite in form and chemistry" was found cementing a bed of sandstone just above the Precambrian-Triassic unconformity on the NE face of the quarry.

Over the last 10 years mottramite has been the dominant vanadium-containing mineral to be found in the quarry. It occurs in a number of different settings: 1. Light green to dark green aggregates of very small globules (up to 1 mm) have been shown by XRD analysis to be mottramite (Monica Price, *personal communication*). These occurred with malachite and calcite within fractures exposed in the S face of the lower levels of the quarry in 1991 (Locality 8, Fig. 2); 2. Dark green to greenish-brown crusts of microcrystals of mottramite, some as epimorphs after a cubo-octahedral mineral (presumably galena), associated with oxidised galena and calcite occurred at the foot of the N face of the quarry in 1994 (Locality 9, Fig. 2); 3. Mottramite also occurred at Locality 2 (Fig. 2 and Table 2) as very small (up to 1 mm) light green to dark green and brown crystals, the associated minerals are shown in Table 1; 4. Most recently,

three benches below the galena-chalcopyrite-sphalerite-carbonate veins, yellowish-green to dark olive green crusts have been shown by XRD analysis to be mottramite (David Green, *personal communication*). These were coating a triangular-shaped exposure (6 m wide and 7 m high, dipping $\sim 70^\circ$ to the N) of what appears to be Triassic breccia in a weathered fracture or narrow wadi on the S side of the quarry (Locality 10, Fig. 2).

The mottramite from Newhurst Quarry occurs in habits that are quite distinct from the other notable occurrence of mottramite in Leicestershire at Springhill Quarry, Peldar Tor, Whitwick and situated 4 km to the SW of Newhurst Quarry (Faithfull and Ince, 1992). This latter material was found as large (for mottramite), up to 7 mm, dark brown to black, lustrous crystals and smaller "cog-wheels" with a yellowish-green coating, associated with pyrolusite, baryte and calcite in quartz-chlorite veins.

MUSCOVITE, $(\text{K},\text{Na})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

Muscovite var. *sericite* was recorded by King (1973) as veinlets and on joint surfaces associated with shatter belts and aplite veins. It occurred as very small (up to 0.2 mm) colourless to greenish-white plates with ferroan dolomite, quartz and chlorite. He noted that "the lustre tends to be high, almost metallic, and the mineral has been collected in the mistaken belief that it was gold". A series of brecciated veins were exposed in the S face of the quarry in 1968 that contained sericite with bornite and chalcopyrite (King, 1998).

PALYGORSKITE, $(\text{Mg},\text{Al})_2\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4\text{H}_2\text{O}$

The possible occurrence of palygorskite at the Precambrian-Triassic unconformity was reported by King and Ford (1968). A white coating up to 8 mm thick observed on joints in the diorite in 1973 was thought to be palygorskite (John Jones, *personal communication*).

PYRITE, FeS_2

King (1973) noted that "pyrite must have been common in the hypogene system of Newhurst Quarry ... but only relics now remain". In 1973 some small (up to 1.5 mm) cubic crystals of pyrite (frequently altered to goethite) were found in a goethite - chalcopyrite matrix (John Jones, *personal communication*).

More recently pyrite has been found at Locality 1 (Fig. 2 and Table 1). There had been a significant amount of surface alteration leading to a coating

of reddish-brown earthy "limonite" and the pyrite showed little evidence of crystal faces. The vein section (25 mm x 15 mm) displayed a radiating crystalline structure reminiscent of marcasite (Fig. 10), however, XRD analysis has indicated that it is pyrite (Craig Williams, *personal communication*). Very small (up to 0.5 mm) yellow to golden-yellow cubic crystals of pyrite, associated with calcite, malachite and a small amount of native copper, were found embedded in a partially oxidised chalcopyrite-bornite vein in a boulder on the lowest level of the quarry in 1993.

QUARTZ, SiO_2

White quartz veins are frequently exposed in the North Charnwood Diorite, however, they possess few, if any, cavities suitable for crystal growth. King (1973) described a number of occurrences: 1. Minor euhedral quartz was present in a thin vein associated with specular hematite and ferroan dolomite and on a sample "said to have come from the top level of the S face of Newhurst Quarry"; 2. Another specimen possessed small (up to 4 mm) euhedral quartz crystals associated with muscovite; 3. Pale purple quartz occurred with the type 3 bornite and chalcopyrite in a belt of almost

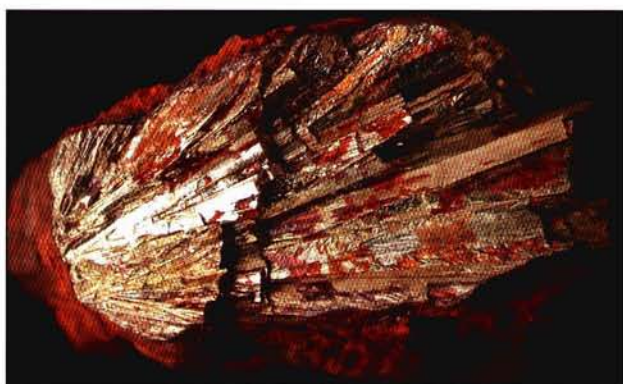


Figure 10. Vein section of radiating crystalline pyrite 25 mm x 15 mm with a red-brown limonite coating (Frank Ince specimen and photograph).

vertical crush breccia up to 40 mm wide exposed on the S face of the quarry in 1965. In some places the quartz is associated with epidote (Trevor Bridges, *personal communication*) and chlorite.

SMITHSONITE, ZnCO_3

Small (up to 1 mm) pale green to brownish-green globules and crusts found at Locality 2 (Fig. 2 and Table 1) have been shown by XRD to be smithsonite (Craig Williams, *personal communication*). The associated minerals are shown in Table 1.

SPHALERITE, ZnS

In 1976 sphalerite was found as small (up to 1 mm) colourless to pale brown crystals associated with veins of galena (up to 12 mm) and small amounts of chalcopyrite (Trevor Bridges, *personal communication*).

Thin veins of small pale greenish-yellow crystalline aggregates found at Locality 2 (Fig. 2 and Table 1) have been shown to be sphalerite (XRD; Craig Williams, *personal communication*). The associated minerals are shown in Table 1.

TOURMALINE var. DRAVITE, $\text{NaMg}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_2$

A blue-grey coating of striated microcrystalline "blue peach", present on slickensided faults/joints in the diorite, has been identified as tourmaline var. dravite (Bob King, *personal communication*).

VANADINITE, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$

Colourless to pale brown transparent hexagonal crystals (Fig. 11) recovered from Locality 2 (Fig. 2 and Table 1) have been shown to be vanadinite (XRD; John Faithful, *personal communication*). The associated minerals are shown in Table 1. This material has a number of similarities with the vanadinite reported from Judkins Quarry, Nuneaton, Warwickshire (Ince *et al.*, 1991). Small quantities of similar material were also found on boulders on the bench below the area on the incline (Locality 3, Fig. 2). More recently some very small (up to 0.2 mm), colourless vanadinite crystals, similar to those described above, were found in the same area on a few boulders covered with a thin crust of dark green mottramite.



Figure 11. Pale yellow hexagonal prisms of vanadinite up to 0.2 mm. (Frank Ince specimen; David Green photograph.)

VÉSIGNIÉITE, $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$

King and Wilson (1976) described the first UK occurrence of vésigniéite from Newhurst Quarry, see also King (1973), as “tiny rosettes (up to 2.4 mm in diameter) of thin tabular yellowish-green crystals” in a “highly oxidised hypogene bornite system... showing a boxwork structure of malachite and goethite, with relic bornite and the original quartz gangue” (Fig. 12). This material was collected from the bottom level of the NE face of the quarry. Other vanadium-containing minerals, in particular mottramite, have been found more recently and it is, perhaps, surprising that vésigniéite does not have a wider distribution in the quarry.

WAD

In their paper on the occurrence of vésigniéite, King and Wilson (1976) noted that “wad carrying



Figure 12. Greenish-orange rosettes of thin tabular crystals of vésigniéite, 2-3 mm. (Bob King specimen K5524-1968, NMW 83.41G.M8140; Frank Ince photograph.)

traces of vanadium” occurred in the Waterstones Formation and in pipe-like bodies below the Precambrian-Triassic unconformity.

WULFENITE, PbMoO_4

Wulfenite has been found recently at Locality 2 (Fig. 2 and Table 1) where it was present in a variety of habits: 1. Small (up to 5 mm), pale yellow to orange, square plates, sometimes very thin and with some internal zoning (Fig. 13); 2. Small (up to 1 mm) pale-brown to brown, tetragonal bipyramidal crystals (XRD; John Faithfull and Mike Rothwell, *personal communications*), in the latter habit the development of [001] faces was quite common and many of these crystals appeared to be hemimorphic (Fig. 14). The associated minerals are shown in Table 1. Wulfenite, as a small yellow-orange tabular crystal, has also been

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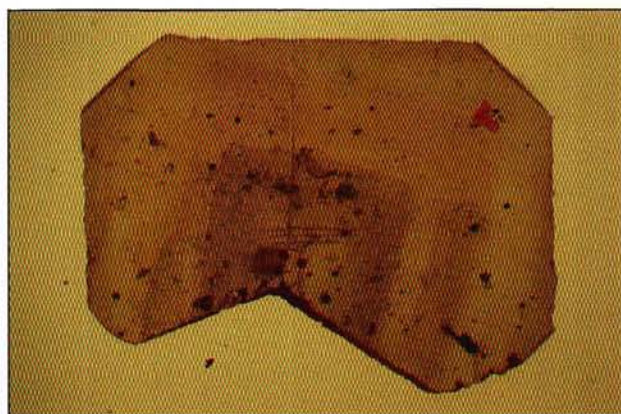


Figure 13. Thin orange tabular crystal of wulfenite, 5 mm x 3 mm; transmitted light. (Neil Hubbard specimen; Frank Ince photograph.)



Figure 14. Orange square tabular crystal of wulfenite, 2 mm. (Frank Ince specimen; David Green photograph.)

tentatively identified associated with galena, cerussite and calcite, in a sandstone bed in the Triassic sediments close to the Precambrian-Triassic unconformity above the incline on the S side of the quarry. These habits appear to be similar to the other occurrences of wulfenite in Leicestershire (King, 1980).

DISCUSSION

In his thesis, King (1973, pp. 525-569) provided “Some thoughts on the genesis of the local mineral deposits” in Leicestershire. As might be expected, only a proportion of these thoughts were related to the mineralisation of Newhurst Quarry. In this discussion the mineralisation will be considered in three parts: hydrothermal mineralisation, supergene mineralisation and paragenetic sequence.

Hydrothermal mineralisation

The hydrothermal mineralisation in Newhurst Quarry takes the form of both quartz and quartz-carbonate veins. The majority of these

Table 2: Paragenetic sequence for the mineralisation at Newhurst Quarry

Paragenetic Event	Major Minerals	Temporal relationship					
Hydrothermal-1	Quartz	x					
	Epidote	x					
	Chlorite	x					
Hydrothermal-2	Tourmaline		x				
Hydrothermal-3a* (King, 1973)	Ferroan-dolomite			x			
	Quartz			x			
	Hematite (specular)			x			
Hydrothermal-3b* (King, 1998)	Quartz			x			
	Calcite			x			
	Chalcopyrite			x			
	Bornite			x			
Hydrothermal-3c* (King, 1998)	Chalcopyrite			x			
	Bornite			x			
	Sericite			x			
Hydrothermal-3d* (King, 1983)	Quartz			x			
	Ferroan-dolomite			x			
	Calcite			x			
	Chalcopyrite			x			
	Pyrite			x			
	Galena			x			
Hydrothermal-3e* (Locality 2)	Calcite			x			
	Chalcopyrite			x			
	Galena			x			
	Sphalerite			x			
Hydrothermal-3f* (King, 1983)	Dolomite			x			
	Hematite (reniform)			x			
	Baryte			x			
Hydrothermal-4a* (King, 1983)	Calcite				x		
	Galena				x		
	Baryte				x		
Hydrothermal-4b* (King, 1973)	Ankerite (nodules)				x		
	Calcite (nodules)				x		
	Galena				x		
Supergene-1 (King, 1998)	Dolomite					x	
	Calcite					x	
	Chalcopyrite (nodular)					x	
Supergene-2	**						x

* Temporal relationships of Hydrothermal 3a-3f and 4a-4b uncertain

** Copper-iron-lead-zinc-vanadium-molybdenum supergene minerals

veins trend approximately NW-SE, are almost vertical, appear to occupy shear zones or small faults in the Precambrian rocks and represent a post-faulting phase of mineralisation. Gangue minerals are quartz, calcite, ferroan dolomite, chlorite and minor epidote. The major metallic minerals are chalcopyrite and bornite together with smaller amounts of galena, sphalerite, pyrite

and hematite. An attempt has been made to rationalise these hydrothermal events and they are listed in Table 2.

The epidote- and chlorite-bearing quartz veins (Hydrothermal 1) were probably a late-stage episode in the emplacement of the diorite or related to a later tectonic event. It was

suggested that the 'blue peach' of microcrystalline tourmaline represents a boron-rich metasomatism (Hydrothermal 2) related to, but not necessarily cogenetic with, the diorite masses and is related to a later tectonic event (King, 1973). These two episodes would appear to be the earliest phases of hydrothermal activity; however, the temporal relationship between them is unclear.

A variety of quartz- and/or carbonate-rich veins bearing copper-iron-lead-zinc sulphides or hematite have been sporadically exposed in the Precambrian rocks over the last 40 years (Hydrothermal 3a-3f, Table 2). King (1998) indicated that chalcopyrite and bornite in quartz-calcite veins exposed at the W end of the quarry (Hydrothermal 3b) formed one of the more important members of the hypogene system and he considered that they provided evidence for mineralisation at 200-300°C and a depth of 1200-4500 m, i.e. mesothermal as defined by King (1973), see Evans (1980).

Unfortunately there do not appear to be any reports of fluid inclusion studies of the primary minerals from Newhurst Quarry and consequently it is difficult to come to any conclusions about the conditions during the crystallisation process. Pearson and Jeffrey (1997) reported the results of their fluid inclusion studies on minerals from the South Leicestershire Diorite (primarily Croft Quarry) and noted that their results were relevant to other occurrences of unconformity-hosted base-metal (Cu-Mn) mineralisation. The mineralisation at Croft Quarry was associated with the Caledonian diorite and resulted from the influence of two distinct mineralising fluids: 1. A relatively high temperature (100°C-320°C) and low salinity (0.2-5.9 wt%, NaCl equivalent) probably of meteoric origin; 2. A relatively low temperature (41°C-165°C) and high salinity (0.4-16.7 wt% NaCl equivalent) probably representing a basinal brine. The mineralisation at Croft Quarry was reported to be post-Triassic in date based on evidence from a vein that penetrated both the diorite and rocks of the Triassic sequence. This relationship has not been seen at Newhurst Quarry as the veins in the Precambrian rocks terminate at the Precambrian-Triassic unconformity. This indicates that the quartz- and/or carbonate-rich veins bearing copper-iron-lead-zinc sulphide or hematite mineralisation exposed at Newhurst Quarry are post-Precambrian but pre-Triassic in age. Whilst some or all of these episodes (Hydrothermal 3a-

3f) could be independent, the paucity of field evidence makes it difficult to establish their temporal relationships and it is possible that they could be different expressions of the same hydrothermal event.

King (1983) suggested that the galena deposition in the Triassic sandstones represents mineralisation at ~100°C and near the surface, i.e. telethermal as defined by King (1973), see Evans (1980). This would appear to be a separate event (Hydrothermal 4a) that occurred during Triassic or post-Triassic periods. It is possible that the calcite cemented nodules in the Triassic sandstones were formed at this time (Hydrothermal 4b) as some are associated with small amounts of galena. In the absence of any direct evidence, the crystallisation conditions and their relationship to Hydrothermal 1-3 (above) or Supergene-1 (below) remains unclear.

Supergene mineralisation

King (1998) described an occurrence of a "supergene pipe" containing Charnian and Triassic debris crosscutting an earlier quartz-calcite-chalcopyrite-bornite-bearing vein (Hydrothermal 3b). He considered that the roughly crystallised botryoidal masses of chalcopyrite (reminiscent of "blister copper") associated with dolomite in the "supergene pipe" provided evidence for the remobilisation of the chalcopyrite in a supergene setting (Supergene 1) at 20-50°C and near the surface, possibly originating in the Triassic period (King, 1973). The deposition of pyrite and botryoidal chalcopyrite in a small vein exposed at the W end of the quarry (Locality 1) and crudely crystallised chalcopyrite associated with calcite (Locality 5) could be related to this event. From a chemical point of view the conditions prevailing during this supergene process are not clear. Presumably the original chalcopyrite (Hydrothermal 3b-3e) was dissolved and re-precipitated in a nodular habit under non-oxidising conditions.

The circulation of oxygenated groundwater has produced an extensive suite of supergene minerals (Supergene 2), both in the quartz-carbonate veins and also in the adjacent Precambrian and Triassic rocks. The supergene mineralisation is more intense in the Precambrian rocks that are closer to the unconformity with the Triassic rocks, although it is evident that the supergene mineralisation had reached the lowest benches of the quarry exposed in 2001, up to 65m

below the unconformity. In addition to the expected copper, iron, lead and zinc minerals, the supergene mineral suite also includes vanadium- and molybdenum-containing minerals. The primary copper-iron-lead-zinc mineralisation occurring in Newhurst Quarry would have provided a convenient source of those elements. The primary sources of the vanadium and molybdenum are less clear and are considered in more detail below. As the vanadium- and molybdenum-containing minerals appeared to be more closely associated with the rocks near the Precambrian-Triassic unconformity, King (1973) suggested that the Triassic rocks were the source of these elements. Alternatively, fluids potentially rich in these elements could have been expelled from overlying rocks, particularly shales (Jones and Plant, 1989), during diagenesis or tectonic activity, with the more porous members of the Triassic rocks acting as conduits. Coleman *et al.* (1989) prefer the latter metallogenic model for the mineralisation in the Pennine Orefields (including the Derbyshire Orefield); however, they did not specifically include the mineralisation in the Charnwood Forest area in their discussions.

King and Wilson (1976) noted that wad carrying traces of vanadium occurred in the Triassic rocks (Waterstones Formation) and in pipe-like bodies below the Precambrian-Triassic unconformity and they considered that the Triassic rocks had provided the vanadium necessary to form the vanadate-containing minerals. King (1983) also reported the occurrence of hematite pseudomorphs after coulsonite, an identification that has not been confirmed in this study. Microprobe analysis of magnetite grains in the North Charnwood Diorite from Longcliffe Quarry demonstrates that they contain appreciable amounts of vanadium (up to 0.8% V_2O_3) and whole rock analyses of the North Charnwood Diorite from Newhurst Quarry indicate up to 290–490 ppm vanadium (Worssam and Old, 1988; Webb and Brown, 1989). It seems more probable that remobilisation of the vanadium from a vanadium-rich magnetite contained within the North Charnwood Diorite provided sufficient vanadium to form the vanadiferous wad and the vanadate-containing minerals.

In analyses of rocks from Newhurst Quarry, molybdenum is conspicuous by its absence (Worssam and Old, 1988; Webb and Brown, 1989) or very low levels (John Carney, *personal communication*). However, the Lubcloud Microgranite, a late Precambrian dyke exposed

on Ives Head 2 km SSW of Newhurst Quarry (Carney *et al.*, 2001), contains significant amounts of molybdenite (Gill Weightman, *personal communication*; specimens held in the Leicestershire County Collection), as does the Ordovician granodiorite at Buddon Wood Quarry, Mountsorrel, 8 km ESE of Newhurst Quarry (King, 1959).

It has been noted that molybdenum in solution (presumably as molybdate ions) can travel many kilometres before being precipitated as wulfenite in areas of oxidising lead deposits (Wilson, 2003). It is interesting to note that wulfenite was also one of the supergene minerals identified on the remains of an oxidised galena ore-body hosted by Triassic rocks in the Tickow Lane Lead Mine, only 2.5 km WNW of Newhurst Quarry (King and Ludlam, 1969). King (1980) suggested that the relatively abundant black wad at this site contained material consistent with jordisite (amorphous MoO_2). Given its chemical instability (King, 2004), jordisite could be a source of the molybdate required for crystallisation of wulfenite. In his review of the occurrences of wulfenite in Leicestershire, King (1980) provides two hypotheses for the source of the molybdenum in the minerals occurring at Tickow Lane Lead Mine: (1) mobilisation from molybdenum-containing hydrothermal veins in the rocks of Charnwood Forest and the re-deposition of the molybdenum as wulfenite, possibly in the late-Triassic period; (2) mobilisation of trace elements from the shales of the Coal Measures adjacent to Charnwood Forest, possibly during the Pleistocene period. There is little field evidence from Newhurst Quarry that allows a choice between these two alternatives.

Paragenetic sequence

A paragenetic sequence is not easy to deduce, however, Table 2 provides an interpretation of the available evidence. The earliest hydrothermal events would appear to be the formation of the epidote- and chlorite-containing quartz veins (Hydrothermal 1) associated with the emplacement of the North Charnwood Diorite followed by the tourmalinisation (Hydrothermal 2) that was probably related to a later tectonic event (King, 1973). A variety of mineralised veins that have been exposed sporadically over the last 40 years provide evidence for hydrothermal activity that has produced the copper-iron-lead-zinc sulphide and hematite mineralisation

(Hydrothermal 3a-3f). It is possible that these events and concomitant alteration of rocks of the Charnian sequence may have been associated with the emplacement of the Ordovician granodiorite at Mountsorrel (although the presence of molybdenum at higher concentrations than those recorded might have been expected) or that they took place during the Acadian (Siluro-Devonian) orogeny. Hydrothermal activity during the Variscan orogeny could also have produced the copper-iron-lead-zinc sulphide mineralisation and might be related to the date of 311 ± 92 Ma that is thought to be a tectonic resetting of the age of the North Charnwood Diorite (Worssam and Old, 1988).

A period of mineralization/alteration took place during Triassic or post-Triassic periods when galena was deposited, possibly replacing calcite (King, 1983), in some of the Triassic sandstone beds (Hydrothermal 4a). The ankerite- and calcite-cemented nodules (Hydrothermal 4b) were also produced. A datable period of alteration occurred during the Triassic period, as shown by an age of 232 ± 7 Ma for the potassium-argon isotopic dating of clay minerals (King, 1983), and this could be related to the influx of fluids derived from the overlying Triassic sediments, as proposed for the mineralisation of the South Charnwood Diorite (Pearson and Jeffery, 1997). The latter event might also have provided the supergene conditions (Supergene 1) that remobilised some of the primary chalcopyrite leading to the formation of the nodular masses found in a number of the dolomite-rich veins that also contain Charnian and Triassic debris (King, 1998).

Subsequent sub-aerial oxidative-leaching (Supergene 2) would have started during exposure in the Triassic period and continued following uplift in the Tertiary and Quaternary periods. The remobilised material was precipitated as the suite of supergene minerals that can be seen in the Precambrian and Triassic rocks exposed at Newhurst Quarry.

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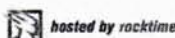
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THE OCCURRENCE AND FORMATION OF GALENA IN SUPERGENE ENVIRONMENTS

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Galena of supergene origin is reported in small quantities from five locations in northern England and one in southern Scotland. It occurs in association with cerussite and other supergene lead minerals, which it commonly encrusts. The presence of supergene galena records a local change to reducing conditions during the oxidation process in orebodies. This phenomenon appears to be locally common at a microscopic level.

INTRODUCTION

The vast majority of the sulphide minerals that occur in hydrothermally generated base metal orebodies are primary. Indeed in most orebodies, galena is tacitly assumed to be primary in origin unless there is strong evidence to the contrary. It has, nonetheless, been reported as part of the supergene assemblage at a few localities worldwide, including the huge base metal deposits at Broken Hill, New South Wales, Australia and Broken Hill, Kitwe, Zambia (Lawrence and Rafter, 1962; Taylor, 1958; Birch, 1999). These reports are based on paragenetic studies which show galena crystallising on or replacing minerals of undoubted supergene origin.

The classic British locality where galena has replaced a supergene mineral is Wheal Hope, Perranzabuloe, Cornwall (Hosking, 1963). In the 19th century superb specimens of galena replacing tapering hexagonal prisms of pyromorphite were found. Examples are now in most of the world's major natural history museums and a fine specimen is illustrated in Embrey and Symes (1987, p.108). Similar pseudomorphs of galena after pyromorphite occur at a number of other localities including Wheal Goat, Brittany, France and the Bad Ems mining district, Germany (Dietrich and Bode, 1984).

Where large quantities of supergene galena occur, as at the localities described above, its formation is interpreted in terms of major fluctuations in the local water table, so causing a

change from oxidising to reducing conditions (e.g. Hosking and Camm, 1981; Taylor, 1958). The reduction of sulphate to sulphide in these circumstances is catalysed by micro-organisms (Trudinger *et al.*, 1985).

We describe a number of localities where galena has replaced or coated supergene minerals. These occurrences are on a much smaller scale than at Wheal Hope or Broken Hill. They are not explained by the well known phenomenon of secondary enrichment, where solutions from the oxidation zone penetrate regions of primary mineralisation and react to form a large zone of secondary sulphide enrichment. The supergene galena described here is well removed from the zone of secondary sulphide enrichment in the orebodies.

LOCALITIES

Supergene galena is described from six localities below. It is characterised as supergene on paragenetic grounds, either by its occurrence on minerals of undoubted supergene origin - such as cerussite, or by its presence as fresh euhedral crystals in cavities in highly oxidised galena. Some of the specimens described were identified by XRD but where tiny amounts were present, the characteristic silvery-grey colour and metallic lustre combined with microchemistry or SEM and energy-dispersive X-ray analysis was considered sufficient.

DRYPRY VEIN, CO. DURHAM

The approximately north-south trending Drypry vein (NZ 0676 4327) near Salters Gate in County Durham was worked for lead ore in the Namurian Second Grit (Dunham, 1990). Quartz is the principal primary vein mineral with very minor baryte. A small ore pile left at the site includes blocks of galena disseminated in quartz containing numerous small cavities. The cavities are commonly lined with small crystals of anglesite, some cerussite and bindheimite. In some cases, crystals which are clearly recognisable as cerussite, on morphological grounds, are coated with silver to grey galena. On one specimen, where a sixling twin of galena-coated cerussite had broken, white cerussite was conspicuous within the crystal. This clearly establishes the oxidation sequence as galena-cerussite-galena. A specimen is preserved in the Manchester Museum collection under accession number N17841 and there are several examples in the TFB collection.

LADY ANNE HOPETOUN SHAFT, LEADHILLS

Supergene galena has been found on dumps associated with the Brow-Hopeful vein system in the Leadhills-Wanlockhead mining district in Scotland's Southern Uplands. The shaft is marked on old mine plans as Lady Anne Hopetoun shaft (NS 8806 1416). It is probably one of the later shafts associated with the major workings on Brow vein. Just north of this shaft, Brow vein is cut by Hopeful vein, the position being marked by a cluster of older and smaller spoil heaps. Around the Lady Anne Hopetoun shaft there is a fairly extensive dump consisting largely of mudstone and ankerite-veined or -cemented mudstone breccia. Small amounts of quartz, laminar white baryte, calcite, pyrite, galena and chalcopryrite are present. Supergene galena has been found as a coating of minute (<0.1 mm) lustrous cubes in a small cavity in baryte, quartz and deeply corroded galena matrix, in which there are also covellite coatings and minute supergene plumbian baryte crystals. The specimen is preserved in the TN collection.

MIDDLEGROVE HUSH, CO. DURHAM

Park Level mine (NY 8258 4308) worked a complex of veins to the east of the level entrance which is situated in the Killhope Lead Mining Museum in Weardale, Co. Durham (Dunham, 1990). Long before Park level was driven, the

veins were worked in a series of hushes, one of the largest of which was Middlegrove hush. In the mid 1990s local estate workers removed a quantity of waste material from the hushes and in so doing exposed a small flat at the intersection of a minor un-named vein and Middlegrove vein (NY 8218 4325). A more detailed note on the minerals present at this locality is being prepared and here it is sufficient to say that the flat mineralisation occurs in the Great Limestone (Namurian) and is dominated by alteration of the limestone to an oxidised ankerite-quartz matrix containing abundant galena and fluorite. Small cavities, often lined with oxidised ankerite or fluorite or both, are common. In one cavity, approximately 40 mm by 10 mm, in a block of galena, numerous oxidised saddle-shaped crystals of ankerite (or siderite) are extensively coated with minute silvery galena cubes. Small fluorite cubes are also sometimes coated with the same crystals, but needles of cerussite to 5 mm in length in the same cavity are free from the coating. The presence of minute well formed galena crystals on cellular oxidised carbonate crystals, the surfaces of which are altered to goethite (Fig. 1) clearly establishes the galena as supergene in origin. The specimen is preserved in the TFB collection.

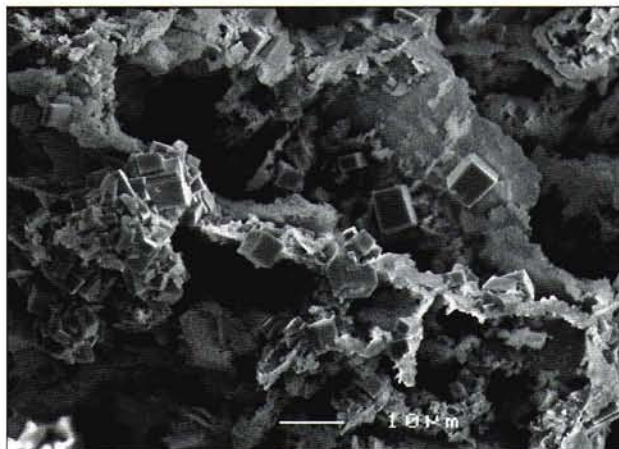


Figure 1. SEM image showing minute cubes of galena to about 7 μm on edge (identified on the basis of their form, lustre and the presence of Pb and S) on cellular iron-rich matrix (probably goethite) produced by the oxidation of iron-rich carbonate minerals. Specimen in the Trevor Bridges collection from Middlegrove Hush.

MILLDAM MINE, DERBYSHIRE

Milldam mine is a modern underground operation which ceased production recently. It is situated near the village of Great Hucklow in Derbyshire (c. SK 177 781). The mine worked the

east-west striking Hucklow Edge vein and associated deposits in the Carboniferous rocks of the South Pennine Orefield. The major primary vein minerals present are fluorite (for which the deposit was worked), baryte and calcite. Galena and sphalerite are also common and a variety of supergene minerals including anglesite, cerussite, wulfenite, smithsonite and a cadmium sulphide have been identified. Cerussite is the commonest supergene lead mineral present in the underground workings at Milldam mine. It occurs as blocky to prismatic crystals, which reach a few millimetres in length. The crystals are usually white and translucent, but occasionally they are dark and coated by galena. Some broken cerussite crystals with galena overgrowths are white and unaltered. In these cases the supergene sequence can be unequivocally established as galena-cerussite-galena. A specimen showing supergene galena lining a small cavity in typical fluorite-rich veinstone and coating cerussite (Fig. 2) is preserved in the Manchester Museum collection under accession number N16405.

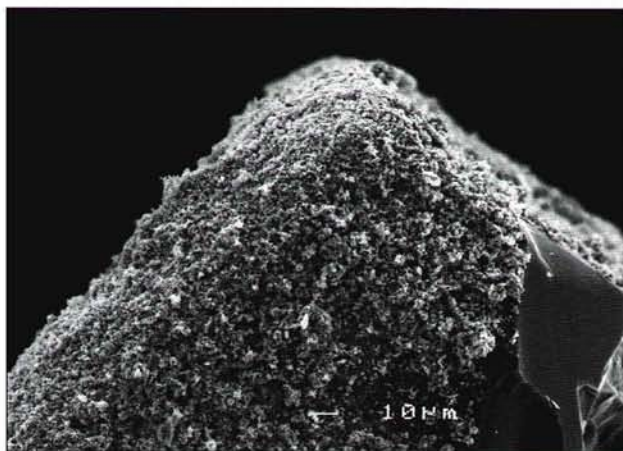


Figure 2. SEM image showing a powdery encrustation of supergene galena on a small fluorite cube. The galena also coats cerussite in the same cavity, which establishes it as supergene. Manchester Museum specimen N16405.

SADDLEBACK OLD MINE, CUMBRIA

Saddleback Old mine is little more than a trial situated remotely in the valley of the river Glenderamackin below Foule Crag (NY 332 287) in the Lake District. It exploited a NE-SW trending lead vein in mudstones and siltstones of the Kirkstale Formation, part of the Ordovician Skiddaw Group. The history and topography of the site has recently been summarised by Tyler (2003). A small dump around the uppermost trial level (marked as "Level on vein run in" by Tyler,

2003, p.137) contains galena as small discrete masses, typically a centimetre or so across, enclosed in vein quartz or baryte. The supergene minerals cerussite and pyromorphite are also present. Cerussite usually occurs as small (<2 mm) white, blocky to prismatic, poorly-formed crystals in rims and crusts surrounding partly oxidised galena. It is also present as somewhat larger crystals in cavities in quartz veinstone. The crystals are sometimes blackened and occasionally coated by a thin layer of a dark sulphide mineral. Dissolution in dilute nitric acid followed by XRD analysis showed this to be galena. Galena occurs both as inclusions within the cerussite and on top of it.

WHITWELL QUARRY, DERBYSHIRE

In the 1980s, a galena-bearing vein was exposed in the Magnesian Limestone (Permian) worked at Whitwell quarry near Whitwell in Derbyshire (c. SK 528 766). The vein, which followed the line of the Park Hall fault, contained a wide variety of lead-bearing supergene minerals. Galena is present as thin coatings and crusts on supergene minerals found in cavities in massive galena. The oxidation sequence from primary galena to cerussite and then supergene galena is very clear in some cases. A particularly fine specimen showing galena as a coating on lanarkite, leadhillite and cerussite is preserved in the Manchester Museum under accession number N15542 and is illustrated in Figs. 3 and 4.



Figure 3. A thin coating of slightly tarnished silvery grey galena coats lanarkite crystals to 7 mm and leadhillite in a cavity in a large block of primary galena collected in 1988 at Whitwell quarry. Manchester Museum specimen N15542

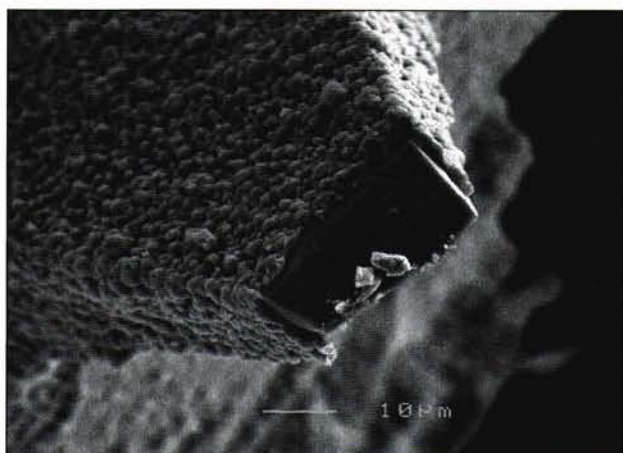


Figure 4. SEM image showing granular galena a few micrometres thick encrusting cerussite. Slight dissolution of the cerussite is visible on the exposed termination. Manchester Museum specimen N15542 collected in 1988 at Whitwell quarry.

DISCUSSION

Where orebodies come into contact with downward percolating oxygenated groundwater, the ore minerals gradually oxidise and secondary sulphates, carbonates, phosphates and a variety of other supergene minerals which are stable in oxidising conditions precipitate. It is clear that this process can take a significant time, even by geological standards, as the common occurrence of sulphide minerals in the oxidation zones of orebodies attests (see for example Mason, 2004). The presence of well developed and defined zones of supergene oxidation and supergene enrichment overlying orebodies containing primary sulphides suggests that a gradual and progressive lowering of the water table typically occurs as a result of surface erosion and exhumation. Sulphides are replaced by supergene minerals as conditions become more oxidising, the end point of the process being the development of stable iron oxide gossans.

Where major replacements of supergene minerals by sulphides occur, as exemplified by the galena-pyromorphite pseudomorphs from Wheal Hope in Cornwall or where supergene galena is abundant as at Broken Hill, Zambia, a major reversion of the normal process of progressive oxidation is required. This is typically explained by a significant rise in the local water table (e.g. Hosking and Camm, 1981; Taylor, 1958), creating conditions which are reducing once again. At the localities we have described, there is no evidence of large scale fluctuations in the water table, so major geological changes cannot be invoked as an explanation.

When examined in detail, the oxidation of orebodies is a heterogeneous process. The sulphide minerals in some areas may be protected from oxidation by impermeable barriers while in other areas free access to oxidising groundwater allows rapid alteration. The way mineral deposits oxidise, although driven by increasing oxidation potentials, is also controlled by kinetic and geological factors. Potentially important influences include the porosity of the vein system, the wallrock and vein geochemistry and the particular sulphide assemblages present.

At the localities described above, the supergene galena was found in minute quantities in small cavities or fractures which were relatively well sealed. The presence of supergene galena signifies a lowering of the oxidation potential in the cavity where it formed and a change in chemical conditions from oxidising to reducing. In normal progressive supergene alteration, the diffusion of oxygenated groundwater along cracks into a cavity increases the oxidation potential, while the oxidation reactions act to reduce it. If the supply of oxygenated groundwater was simply cut off, the oxidation of galena would be expected to stop when chemical conditions reached the Eh boundary between galena and cerussite (Garrels and Christ, 1965). Supergene galena would not be expected to precipitate. For supergene galena to form, more reducing conditions must develop. It seems unlikely that these could be generated internally by chemical reactions within a cavity containing only cerussite and galena, so an external change in fluid chemistry is required. This might be generated by alterations in the pathways of fluid flow through the ore body, climatic changes, or in the near-surface environment by increased vegetative cover since reducing conditions are generated by the decomposition of organic matter (in peat bogs and anoxic soil layers). For a small volume of material, local changes would be sufficient to push the oxidation potential down to a value where supergene galena could form.

The reduction of sulphate to sulphide by purely chemical processes has not been demonstrated in the mildly anoxic conditions encountered in mineral veins at low temperatures. It is almost certainly the case that the reactions within the cavities were catalysed by sulphate reducing micro-organisms, which are widely distributed in low-temperature near-surface environments (Trudinger *et al.*, 1985).

Only minute amounts of supergene galena would be expected to form in association with *unaltered* supergene minerals as the available lead in solution would be rapidly used up. On our specimens the supergene minerals are more or less unaltered and the galena is present in very small amounts; e.g. close inspection of Fig. 4, the SEM photograph of the specimen from Whitwell quarry, shows that the platy cerussite beneath the supergene galena shows traces of dissolution. In more aggressively reducing conditions the supergene minerals would be expected to dissolve. In these cases, the only way that a record of fluctuating oxidation would be maintained is in large scale replacement of the supergene minerals producing pseudomorphs of the sort found at Wheal Hope.

On most of the specimens described the supergene galena forms as a discrete phase on top of minerals such as cerussite – this is well illustrated in Fig. 4. At Saddleback Old mine however, galena occurs as *inclusions* within cerussite crystals which are commonly dark-coloured or black as a result. The galena here may be present simply as a result of mechanical incorporation of small resistant particles. Alternatively it may have crystallised, but if so a different mechanism to that proposed for the coatings noted at the other localities is required. More detailed study of cerussite crystals with galena inclusions is desirable.

CONCLUSION

On occasion, probably as a result of external changes, previously oxidising conditions in a cavity can revert to reducing conditions, giving rise to galena in what is a substantially supergene environment. It is probable that further erosion usually results in a reversion to oxidising conditions with the consequent oxidation of the crystals and coatings. In the cases reported above, the cavities remained sealed, preserving the supergene galena. There seems to be no reason why other sulphides should not form by the same mechanism and they may be more important in controlling the way in which orebodies oxidise than hitherto suspected. Most specimens are small and inconspicuous and many may simply have been overlooked.

ACKNOWLEDGEMENTS

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MUD-FILLED FLUORITE VUGS IN GREENLAWS MINE, WEARDALE, CO. DURHAM

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Fluorite lined vugs in Greenlaws mine, Weardale, Co. Durham, show evidence of gravitational effects during crystallisation. Upward-facing crystals are duller and more opaque than downward-facing ones. Oxidation and alteration has resulted in fracturing of the wall-rock and the filling in of the cavities with detrital clay and sand derived from strata above.

INTRODUCTION

Greenlaws mine is a Victorian lead mine on the hillside south of Daddry Shield, Weardale, Co. Durham, centred around NY 886367. Two veins are described by Dunham (1990). The west vein was weak and output of ore was modest. The principal workings were developed on the east vein and were extensive. Where this vein intersected the Great Limestone a series of flats (horizontal replacement orebodies) occurred in the High Flat horizon towards the top of the limestone. These were vuggy and became noted for fine purple and amber fluorite specimens.

In the 1990s a group of amateur collectors and mine explorers dug out the Hydraulic shaft which gave access to the flat drift, a horizontal level that once connected all the flat workings.

Due to the extremely dilapidated condition of this level only a few peripheral flats have, so

far, been accessed. These have, however, permitted an *in situ* examination of the Greenlaws mineralisation for the first time in nearly a century. Of particular interest are the vugs containing the fluorite sought by collectors.

Four flat workings are presently accessible (Fig. 1). The first three encountered, on proceeding south-west along the flat drift away from the Hydraulic shaft, are unnamed. The fourth is shown on mine plans as "Joseph Brown's Cross Cut". A fifth flat ("G. Ritson's Cross Cut") beyond this was accessible for a short time until a roof collapse blocked it off. Two of the unnamed flats were given the patriotic names "Britannia flat" and "Victoria flat" by the explorers. On heading inwards from the shaft one encounters in succession Britannia flat (east side), unnamed (west side), Victoria flat (east side), Joseph Brown's Cross Cut (west side), G. Ritson's Cross Cut (east side).

The first two flats are of limited extent and contained only a few cavities. These had already been emptied by a previous team of diggers before the present incumbents arrived. The other three are much larger and were untouched when first accessed in November 1999 and the following years. The large number of pristine cavities they contained allowed a detailed examination of the mineralisation and associated phenomena. The description that follows is based on observations made in these three flats.

MINERALISATION

The Greenlaws East vein is exposed in the roof of the flat drift. Cavities are very small (a few centimetres at most) and, in most places, scarce. The bulk of the vein is friable, iron-stained, massive fluorite containing occasional ribs of galena. The wall rock is tough, silicified and iron-stained limestone. Scattered crystals of acicular, white cerussite are occasionally seen.

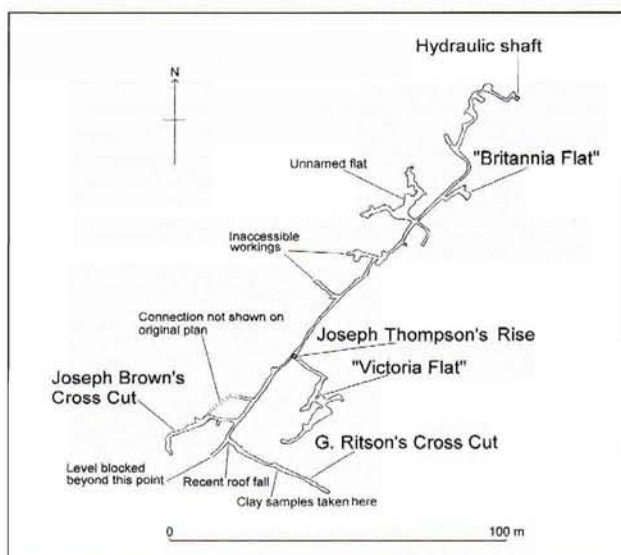


Figure 1. Plan of Greenlaws mine workings referred to in the text, based on 19th century original in Kingsley Dunham manuscripts, Durham Records Office.

Dunham (1990) described the flats as containing fluorite, galena crystals and clay in altered limestone. The limestone also contained ankerite and siderite, converted to limonite near the surface. This is confirmed by modern observations. Cavities abound in the flats. They range from a few centimetres to over a metre across and are of irregular shape, with no obvious preferred orientation. They are commonly lined with fluorite crystals ranging from a few millimetres up to about 12 cm on edge. Occasional associates are galena, as corroded cubes with octahedral modifications, dull black sphalerite crystals up to 3 mm, calcite often as etched crystals of various habits, siderite and/or ankerite largely altered to limonite and, very rarely, drusy quartz and malachite stains. XRD of the limonitic coatings on two fluorite specimens from Joseph Brown's Cross Cut revealed only poorly crystalline goethite.



Figure 2. Amber fluorite cubes with an outer purple zone. These were downward facing in their vug and show good clarity (albeit with some milky areas) and surface lustre. From J. Brown's Cross Cut. Specimen measures 24 x 13 cm.

The crystal habit of the fluorite is nearly always simple cubes (Figs. 2-4). These are usually colour zoned with an amber core and purple outer zone. Penetration twins of {1 1 1}, typical of many Weardale localities, occur but are rare. These generally have better clarity than the simple cubes. As is normal with Weardale fluorite, specimens from Greenlaws are strongly fluorescent.

THE FLUORITE VUGS

It has been consistently observed that the fluorite cubes facing upwards in a vug are dull, opaque and often pitted. Those facing downwards have better clarity, colour and lustre, making them the more desirable as specimens. Those on the sides of cavities are dull on their upward facing surfaces and lustrous on their downward facing surfaces. Upwards facing surfaces are sometimes also coated in limonite pseudomorphous after siderite or ankerite.



Figure 3. Reverse of the specimen in Figure 1. Crystals are dull and opaque. These were upward facing when found.

Another almost ubiquitous feature of the vugs is the presence of a mud, sand or clay infill. Commonly the vugs are entirely filled with brown mud. Enclosed within this there are slabs and crystals of fluorite, detached from the walls. The deposits in the cavities are commonly graded. Material towards the bottom of the cavity is the finest grained and consists of sticky clay. It becomes progressively coarser towards the top. The upper parts are often well stratified with horizontal sandy layers. Sometimes these upper layers contain pieces of country rock embedded in the sandy infill, and the rock in the roof is in various stages of fracturing and flaking off.

It is usual for the majority of fluorite specimens recovered from these vugs to be already detached from the sides, although they are often still located close to their original positions, being held there embedded in mud. Those few cavities that are not totally filled with mud tend to be small, only a few centimetres across. One exception is a vug about 30 cm high and up to 1 metre in its longest dimension at the back of G. Ritson's Cross Cut. This was only about half full of fine clay. Apart from one detached slab, the 5 cm fluorite crystals that lined it were well attached to the roof and walls. Unusually, they were also partly coated with a crystalline crust of white calcite.

The muddy deposits in the vugs have no appeal to collectors but are such a consistent feature of the cavities that they merit some detailed investigation, as described below.

EXPERIMENTAL

Sieve analyses were carried out by washing a known weight of clay on a 53 µm sieve, or 150 µm sieve, until all fine material had passed through. Any residue was dried at 105°C and weighed. Microscopic examination of the coarser fractions

aided in the identification of their components. The < 53 µm fraction was analysed by XRF and XRD.

Moisture contents of clays were determined by weight loss at 105°C. Elemental compositions, expressed as oxides, were determined by using the mixed oxide program on a Philips PW2400 Wavelength Dispersive XRF Spectrometer. The sample, dried at 105°C, was fused with lithium tetraborate and presented to the spectrometer as a glassy bead.

The particle size of the <53 µm fraction was measured using a Malvern Mastersizer Analyser fitted with a 300RF lens. A few grams of sample were dispersed in water and laser light passed through the suspension. The scattered light was focused onto a detector array, with each element optimized for a particular size. The output from the array was transferred to a computer, which calculates the particle size distribution from this information. The calculation assumes a refractive index of 1.33 for the dispersion. Different R.I.s result in variations of a micron or two for the APS (average particle size).

Neither of the samples showed any effervescence in acid and so they were assumed not to contain carbonate.

ANALYSES OF THE MUD

Two samples of the mud were taken from one vug, approximately 30-40 cm high, in G. Ritson's Cross Cut before it was rendered inaccessible by a roof fall. One was from near the bottom of the cavity, and consisted of fine clay. This was called sample A. The other, sample B, was from near the top and was noticeably sandier. These were analysed with the following results.

Sample	A	B
%moisture	25.1	18.8
>150 µm	0%	9.3%
53-150 µm	0%	36.9%
<53 µm	100 %	53.8%
D50	3.9 µm	n.d.
D90	12.5 µm	n.d.

Table 1. Data for clay samples "as found".

n.d. - not determined

D50 = 50% of particles below this size

D90 = 90% of particles below this size

All particles >600 µm (<1% of the whole) are either wall-rock or fluorite. Microscopic examination of the >53 µm fraction of B found mostly quartz sand with minor mica, wall-rock

fragments and fluorite. The maximum particle size of the quartz sand/mica is ca. 400-600 µm but most is very much smaller than this. X-ray diffraction of the <53 µm fraction of both samples detected mostly quartz with lesser muscovite. Illite is probably also present but many of its peaks overlap with muscovite. Five peaks could be matched with kaolinite, numerous minor peaks were not assigned.

Oxide	Sample A	Sample B
Al ₂ O ₃	25.46	17.56
CaO	0.59	0.58
Fe ₂ O ₃	7.46	7.69
K ₂ O	3.78	2.59
MgO	1.33	0.96
Na ₂ O	0.55	0.51
SiO ₂	53.90	64.13
TiO ₂	0.92	1.07
Total	93.99	95.09
Balance (100-total)	6.01	4.91

Table 2. XRF analyses of <53 µm fractions, dried at 105°C. The balance is assumed to represent hydration water and hydroxyl groups.

DISCUSSION

The primary mineralogy of Greenlaws mine (fluorite and galena with minor siderite, ankerite, sphalerite, quartz and calcite) is typical of the district. There is abundant evidence to show that the deposit has been subjected to supergene alteration. The galena crystals are all dull and corroded, cerussite is widespread albeit small in overall quantity, and limonitic staining is everywhere.

The observation that in vugs in the flats, upward facing fluorite crystals are dull and opaque, whereas those facing downwards are lustrous with some clarity and brighter colour (Figs. 2 and 3) is significant. The settling of particulate matter onto upward facing surfaces seems the most likely explanation. If so then the mineralising solutions in the cavities must have been almost static to allow sinking of fine particles in suspension to occur. The tendency for downward facing fluorite crystals to be of better quality is commonplace in Weardale. It has been reported at Rogerley mine (Fisher and Greenbank, 2003) and is also seen at Heights and Hollywell (Robert Lawson, *personal communication*). It is also

a feature of Rampgill mine, Nenthead where the upward facing crystals are frequently coated with siderite, but not the downward facing ones (Bridges and Wilkinson, 2003).

As with Rampgill, the upward facing crystals at Greenlaws are commonly coated with siderite (or possibly ankerite) now altered to limonite. At Rampgill this has been attributed to the sudden deposition of numerous tiny crystallites of siderite as a result of a disturbance (Bridges and Wilkinson, 2003). The same effect appears to have occurred also at Greenlaws. Close examination shows that in most, if not all cases, there has been a slight overlap in deposition of the two minerals. The fluorite has continued to grow for a short time after deposition of the iron carbonate mineral (Fig. 4). Consequently the surfaces of the fluorite crystals are roughened and pitted where the oxidised iron carbonate has subsequently fallen or dissolved off. Doubtless this accounts for some of the dulling of the surfaces, but even where iron carbonate is absent the upward facing crystals still tend to be cloudier and duller. Microscopic examination of polished sections to look for included matter would be a worthwhile exercise.

Mud-filled cavities are common in fluorite deposits in Weardale. Clay fills the cavities at Rogerley mine (Fisher and Greenbank, 2003), and is abundantly present at Heights, Hollywell, West Pasture and Billings Hill (Robert Lawson, *personal communication*). One feature that these localities all have in common is that they are above the water table. Beaumont, Cambokeels, Frazers Hush and Whiteheaps were not noted for muddy cavities and are all below the water table (Robert Lawson, *personal communication*).



Figure 4. Cubes up to 22 mm showing continued growth of fluorite after deposition of siderite/ankerite. From "Victoria Flat". As this specimen was not found in situ its original orientation is unknown.

The lack of fluorite and the profusion of rounded quartz sand grains, suggest a detrital rather than hydrothermal origin for the mud. The well-developed stratification is also consistent with deposition from muddy, percolating water. The sandy shales and flaggy sandstones, above the Great Limestone and just a few metres above the flats are an obvious source, as are partings within the limestone itself (for example, there is a ca. 12 cm shale parting in the limestone about two metres above G. Ritson's Cross Cut).

A scenario can be envisaged in which supergene processes affecting the flats above the water table oxidise and alter wall-rock minerals, probably ankerite and siderite, which are common in flats in the district, and are reported by Dunham (1990) as being present at Greenlaws. As siderite (S.G. 3.9) or ankerite (S.G. 3.1) alter to goethite (S.G. 4.3) there is a reduction in volume. The resulting shrinkage would open cracks allowing percolating water to seep down carrying with it suspended matter. At first the cracks will be small so only the finest silt and clay could gain access to the vugs. Hence the tendency for the finest sediment to be in the lowest layers. As the oxidation and attendant volume changes progressed the cracks would become wider, slabs and crystals would detach from the sides and roofs of cavities and land in the accumulating mud below. As the cracks widened so progressively larger particles would be able to pass through them and enter the cavities. Consequently the later layers will be coarser and sandier, which is what is observed. This is also reflected in the analyses. Sample A has a higher alumina and lower silica content than the much sandier sample B. A greater proportion of fine clay minerals in A, and quartz sand in B seems likely.

It may be significant that the one large vug in G. Ritson's Cross Cut that was only partly filled with clay was also relatively intact with most of the fluorite still on the walls and roof. Presumably the fracturing process had not yet advanced enough to detach the fluorite and allow coarser sand to enter.

These observations have implications for the collector of fine fluorite specimens. When above the water table, cavities may be expected to be muddy to varying degrees. Some may still be relatively mud-free, whilst others will be completely filled. Close attention should therefore be paid to any areas where fluorite is observed in mud. It may be a vug. Furthermore,

preference should be given to downward facing crystals, as these are most likely to be of good quality. Finally, in Greenlaws mine, wooden sticks are used to dig the mud out of the cavities to avoid damage to crystals.

ACKNOWLEDGEMENTS

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GEARKSUTITE, A SECOND BRITISH OCCURRENCE, FROM THE BALL EYE OPENCAST, CROMFORD, DERBYSHIRE.

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The rare calcium aluminium fluoride gearsutite occurs as white masses on anglesite at the Ball Eye Opencast, Derbyshire. It appears to have formed by the late-stage low temperature supergene alteration of the surrounding mineral assemblage which comprises fluorite and galena in a flat-type deposit hosted by dolomitised limestone and contemporary basic lava of Lower Carboniferous age.

This is the second report of gearsutite as a component of the supergene mineral assemblage in Pennine lead veins. It appears to have formed in relatively acidic conditions (pH ~ 4) with fluoride being supplied by the dissolution of primary fluorite.

INTRODUCTION

Gearsutite, $\text{CaAlF}_4(\text{OH})\cdot\text{H}_2\text{O}$, is an uncommon mineral, which is usually found as white nodular or earthy masses, formed by the hydrothermal alteration of fluorine-bearing minerals (Bailey, 1980). It was first described by Hagemann (in Dana, 1868) from the cryolite deposit at Ivigtut, Greenland and was named from the Greek "Ge" for earth because it is usually earthy and "arksutite", from the locality near Arksut fjord. Gearsutite has subsequently been reported from a wide variety of geological environments including fumarole deposits,

miarolitic cavities in granite, evaporite deposits, cryolite-bearing pegmatites and hydrothermal mineral veins (see Green, 2003 for a summary of world-wide occurrences). Visible crystals are known only from the Cleveland Mine, Tasmania, Australia, where gearsutite occurs as elongated prisms up to about a millimetre in length in a suite of supergene minerals (Birch and Pring, 1990). It has recently been reported from the Old Gang Mines, Swaledale (Green, 2003) in a post-mining supergene environment with gypsum and ktenasite. This report is of a second occurrence in the UK of gearsutite in what is clearly a natural supergene situation.

EXPERIMENTAL

During recent analytical work aimed at characterising supergene mineral assemblages from different localities in the British Isles, a white powdery phase collected by one of us (TFB) in 1977 at Ball Eye Opencast was examined. The mineral was initially thought to be a clay. However, energy dispersive X-ray analysis showed that it contained calcium, aluminium and fluorine, which is an unusual combination of elements, so it was set aside for further study.

The commissioning of a new Bruker D8 advance XRD system at the University of Manchester gave the opportunity to examine the mineral using a modern diffractometer, which is capable of identifying small quantities of material. A tiny fragment of the mineral was ground to a powder and mounted on a monocrystalline silicon wafer (monocrystalline silicon as a substrate has the advantage that the scattering of Xrays is reduced and thus the signal to noise ratio much improved). An angular scan between $2\theta = 5^\circ$ and $2\theta = 50^\circ$ gave sufficient scattered intensity for standard pattern matching analysis, which showed the mineral to be gearsutite (X-ray reference MANCH:XRD865).

LOCALITY

Ball Eye Opencast, which was worked for fluorite, is located on the north side of the Via Gellia near Cromford, Derbyshire (SK 287 573). It is immediately above and to the north of the Ball Eye limestone quarry (SK 287 572). In the late 1970s, a small galena-bearing flat deposit was exposed during quarrying operations. Small cavities in the galena containing a number of crystalline supergene minerals, including wulfenite, anglesite, native sulphur and cerussite, were found (Bridges, 1983). The gearsutite occurred as roughly spheroidal aggregates on anglesite in one of these cavities (TFB collection, specimen reference number SK.1C38).

The history and geology of the locality is described in some detail by Bridges (1983). In summary, the main quarry worked Carboniferous limestones of late Brigantian age. These limestones are capped by the Matlock Upper Lava and above this is approximately 8 m of dolomitised limestone. To the north of the quarry, this dolomite has been extensively replaced by fluorite, with some baryte and calcite and it is this deposit that was worked by the Ball Eye Opencast. A flat of galena, which was up to 11 cm thick, was situated directly on top of the

lava flow. There was abundant limonitic clay above and below the galena. Cavities at the edges of the galena contained mainly small crystals (usually <5 mm) of cerussite, although one cavity contained crystals up to 35 mm long with the clear morphology of anglesite but entirely replaced with cerussite. Within the flat deposit there were cavities completely enclosed by galena which contained numerous small crystals of anglesite and the other minerals noted above, including the gearsutite.

DISCUSSION

At Ball Eye Opencast, gearsutite is a late-stage supergene mineral which formed on anglesite. Unlike the first reported British occurrence at the Old Gang Mines, where the mineral occurs on the walls of an abandoned mine level, the occurrence at Ball Eye appears to be entirely natural.

It is worthwhile speculating on the mode of formation of gearsutite and the closely related aluminofluoride mineral prosopite, $\text{CaAl}_2(\text{F},\text{OH})_8$, which has been reported recently at Coldstones Quarry, Pateley Bridge, North Yorkshire in a similar supergene environment (Young *et al.*, 1997). The elements calcium and fluorine are available at all these localities in the form of fluorite and calcite (which occurs both in the veins and the limestone host rock). The most likely source of aluminium is the clays, which were abundant at the Ball Eye Opencast and present in micritic limestones at the Old Gang mines. Acid leaching is well known to remove aluminium from clay minerals. The presence of mobile aluminium in the supergene environment at Coldstones Quarry is indicated by the occurrence of doyleite, $\text{Al}(\text{OH})_3$. While fluorite is theoretically capable of generating a sufficiently high fluoride ion activity (a_{F^-}) and calcium ion activity ($a_{\text{Ca}^{2+}}$), mobilising enough aluminium to form the aluminofluoride ion in the gearsutite structure would seem possible only at low pH (see below).

At the Old Gang locality, the gearsutite formed on a gypsum crust (which shielded it from direct contact with the carbonate wall rock) and the $\log(a_{\text{Ca}^{2+}})$ in equilibrium with gypsum would be a little under -2 mol.dm⁻³. There is significant variation in the literature on the thermodynamic data for fluorite, but using an average figure for $\log K_{\text{sp}}$ of -9, $\log(a_{\text{F}^-})$ in the presence of gypsum could theoretically reach -3.5 mol.dm⁻³, which is also relatively high. At the Ball Eye and Coldstones localities, in the absence of gypsum, the $\log(a_{\text{Ca}^{2+}})$ would be expected to be a little lower and the $\log(a_{\text{F}^-})$ a little higher

than these figures. Mobilising aluminium as $\text{Al}^{3+}_{(\text{aq})}$ ideally requires quite a low pH, preferably about 4 (Garrels and Christ, 1965, p.354; Williams, 1990, p.91), but at this pH the activity of the hydroxyl ion (which is also required by both minerals) would be very low at $\log(a_{\text{OH}^-})$ of -10 mol.dm⁻³. At Coldstones Quarry, prosopite was associated with smithsonite and many of the cavities in the galena at the Ball Eye Opencast contained good crystals of cerussite in addition to anglesite. The fact that these carbonate minerals occur commonly in the supergene assemblages at these localities requires a pH of a little greater than 5 in typical conditions. At this pH, $\log(a_{\text{Al}^{3+}})$ would be of the order of -10 mol.dm⁻³, which is very low indeed. However, the gearsutite cavity in the galena from Ball Eye opencast did not contain any cerussite, and the smithsonite associated with the prosopite was described as being iron-stained, which could have protected it from a slightly lower pH. Indeed the iron staining might indicate an influx of acidic solutions produced by the oxidation of pyrite. Taking everything into account, it seems likely that the actual pH at which the aluminofluorides formed was probably between 4 and 5. Small differences in ionic concentrations of the relevant ions probably controlled which of the minerals formed.

While the conditions for their formation would seem to be fairly restricted and specific, it is quite possible that these and other secondary aluminofluoride minerals may be more common than hitherto suspected, since they can easily be mistaken for clays or white carbonates. It would be worthwhile looking for them in any assemblage of supergene minerals derived from an orebody containing abundant primary fluorite. They are easily distinguished from carbonates, such as aragonite, hydrozincite and brianyoungite, by the application of dilute hydrochloric acid.

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PHOSPHATE MINERALS INCLUDING KONINCKITE AND PLANERITE FROM GROUSE LODGE QUARRY, SHANAGOLDEN, CO. LIMERICK

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At Grouse Lodge Quarry, near Shanagolden, Co. Limerick, Republic of Ireland, phosphate minerals occur in fractures in fine-grained sedimentary rocks of the Clare Shales Formation. They include the rare iron and aluminium phosphates koninckite and planerite, which have not been reported previously from the British Isles. Turquoise, gibbsite and kaolinite are also present and wavellite is common locally as radiating crystalline masses.

INTRODUCTION

Grouse Lodge Quarry is located on a hillside to the west of the Shanagolden to Ardagh road about 5 km south of Shanagolden, Co. Limerick (Irish grid reference R 252 424). The rock being quarried is a steeply-dipping black shale, typical of the Upper Carboniferous (Namurian) Clare Shales Formation, which is widespread around the Shannon Estuary (Hodson and Lewarne, 1961; Wignall and Best, 2000). The quarry supplies shale to a cement works near Limerick.

Following a report of wavellite and turquoise (Richard Unitt, Cork University, *personal communication*), the site was visited in October 1999. Wavellite was found to be locally abundant, while turquoise was found sparingly. Subsequent visits revealed progressively less of these minerals as quarrying advanced. Minor amounts of other minerals, mostly kaolinite, were found sporadically and we have recently identified koninckite and planerite. On a final visit, in March 2004, no phosphate mineralisation was observed, the productive areas having been completely quarried away.

MINERALS

The species described below were identified by XRD, supplemented by energy-dispersive X-ray analysis (SEM EDAX). They include koninckite and planerite; these two are reported for the first time from the British Isles.

GIBBSITE, $\text{Al}(\text{OH})_3$

One specimen of friable, cream-coloured, granular material, containing small (<1 cm)

cavities with mammillated linings, was identified by XRD as gibbsite. Gibbsite also occurs as cream coloured grains in intimate association with planerite (X-ray reference number MANCH:XRD860) in the same specimen.

KAOLINITE, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Kaolinite occurs as typically soft, snow-white masses and coatings on joints in the shale. Analysis by XRD indicates that much of the kaolinite from the quarry is intimately mixed with quartz (X-ray reference number MANCH:XRD855).

KONINCKITE, $\text{FePO}_4 \cdot 3\text{H}_2\text{O}$

Koninckite is a rare and poorly characterised mineral, first described from Richelle, Belgium (Cesaro, 1884; van Tassel, 1968; Deliens, 1977). It was named for Laurent Guillaumen de Koninck (1809-1887) a Belgian geologist. It has subsequently been reported from Turkestan (Beus, 1950), the Suwa Mine, Nagano, Japan (Sakurai *et al.*, 1991), Hardtkopf near Sundern-Linnepe, Sauerland, Germany (Blass and Graf, 1995), Oberbuchach, Carinthia, Austria (Puttner, 1997), and the Pollone Mine, Tuscany, Italy (Senesi, 2000). At the type locality it occurs in phosphate-rich solution breccias underlying Namurian (Carboniferous) deposits where it is associated with delvauxite, and richellite (Legrande, 1957). Specimens from Turkestan are an alteration product of triphylite and are manganese-rich.

At Grouse Lodge Quarry, koninckite was identified as a mass of hard, colloform, iron-

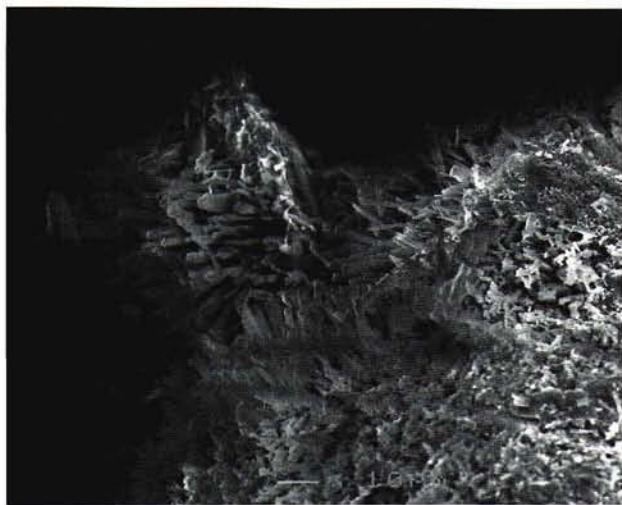


Figure 1. SEM photo showing tiny, lath like koninckite crystals up to about 10 μm long, but less than 1 μm thick.

stained, white material several centimetres across (X-ray reference number MANCH:XRD858). Qualitative analysis by SEM EDAX showed that iron and phosphorus were the only elements present with an atomic number greater than 10. SEM images resolved the surface of the koninckite into radiating masses of tiny lath-like crystals up to about 10 μm long but less than 1 μm thick (Fig. 1).

PLANERITE, $\square\text{Al}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH})_8 \cdot 4\text{H}_2\text{O}$

Planerite has a complex history and has been regarded as a calcian variety of turquoise, but was revalidated as a species by Foord and Taggart (1998). It is a member of the turquoise group, these being phosphates of a general formula: $\text{A}_{0-1}\text{B}_6(\text{PO}_4)_{4-x}(\text{PO}_3\text{OH})_x(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, where $x = 0-2$. Planerite is the species with a dominant A-site vacancy. It was named for D. I. Planer, director of the copper mine at Gumeshevsk, Ural Mountains, Russia, which is the type locality.

At Grouse Lodge Quarry, planerite occurs as a component of a single specimen of a buff coloured, granular and very friable material. It is intimately in association with gibbsite and kaolinite. Spot analyses of translucent grains containing planerite showed that aluminium, silicon and phosphorus were the only elements present with an atomic number greater than 10. XRD identified the grains as a mixture of planerite, kaolinite and gibbsite (X-ray reference number MANCH:XRD860).

TURQUOISE, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$

Turquoise occurs sparingly as blue-green coatings on joints in light grey shale and as fracture-fillings in hard, brown nodular masses.



Figure 2. Hemispherical aggregates of green to blue-green wavellite up to about 5 mm across.

WAVELLITE, $\text{Al}_3(\text{PO}_4)_2(\text{OH},\text{F})_3 \cdot 5\text{H}_2\text{O}$

Wavellite occurs as mammillated crystalline crusts up to 6 mm thick on joints in soft, black shale. Individual rosettes and botryoidal aggregates reach about 8 mm across. The colour varies from light green to an attractive, translucent blue green (Figure 2). Wavellite also occurs as minutely mammillated green coatings on harder grey shale and as iron-stained white to grey coatings about up to 2 mm thick in cavities in quartz veins. Identification was by XRD (X-ray reference number MANCH:XRD861).

DISCUSSION

The Clare Shales are phosphate-rich (Hodson and Lewarne, 1961; O'Connor and Pyne, 1986) and host at least two other wavellite occurrences. These are Doolin, Co. Clare (specimen in the Russell collection, Natural History Museum) and Ballybunnion, Co. Kerry (Moreton *et al.*, 1995). Grouse Lodge Quarry is 4 km south of another wavellite occurrence, at Ballycormick (Ryback and Moreton, 1991). The absence of exposure at this location makes it difficult to place in a geological context, although limestone boulders are present. It appears to be close to the junction of a limestone and the shales. The presence of gibbsite and kaolinite at Grouse Lodge indicates a ready supply of aluminium so the formation of wavellite by percolating ground waters would be facilitated in more phosphatic horizons.

A source of copper is less obvious, but turquoise is also known from Ballycormick (Ryback and Moreton, 1991) and from Ballybunnion (Moreton *et al.*, 1995) and the latter is in the Clare Shales Formation. This suggests that some horizons within the shales have an elevated copper concentration.

Koninckite and planerite are very rare worldwide and have not been reported previously from the British Isles. However both minerals are relatively inconspicuous and they may simply have been overlooked in the past.

Despite their considerable extent, there are few working quarries in the Clare Shales and inland exposures are limited. The widely distributed nature of known phosphate occurrences in the shales suggests that more await discovery and any fresh exposure of these rocks is worthy of careful examination.

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A REVIEW OF THE OCCURRENCE OF ANTLERITE IN THE BRITISH ISLES

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The uncommon copper sulphate mineral antlerite has been reported from eight localities in the British Isles. The first British report of antlerite is based on a specimen collected by A.W.G. Kingsbury in 1936, from Old Gunnislake mine in Cornwall, and is almost certainly genuine. Geochemical data are used to suggest that a second specimen collected by Kingsbury from Potts Gill mine in Cumbria in the early 1950s is likely to be fraudulent. Antlerite nonetheless occurs at Potts Gill, as a genuine specimen was collected at about the same time by W.F. Davidson. This underlines the complexity of the Kingsbury fraud and the difficulty of mapping its extent. Localities for antlerite in the British Isles include several in Cornwall; Alderley Edge, Cheshire; Parys Mountain, Anglesey; Potts Gill mine, Cumbria and East Avoca mine, Co. Wicklow. The occurrence at East Avoca mine appears to be the first Irish location for the mineral.

INTRODUCTION

Antlerite, $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$, is an uncommon supergene mineral that typically occurs as green crusts in the oxidation zone of copper rich ore deposits in desert regions. Antlerite was the principal supergene ore in the great Chuquicamata copper deposit at Antofagasta in Chile and has also been described from a number of mines in the western USA including the Antler mine, Mojave County, Arizona which is the type locality (Palache, 1939). At both Chuquicamata and the Antler mine excellent crystals of antlerite were found.

Antlerite has been reported from only eight localities in the British Isles. Two of these were reports on specimens collected by Arthur Kingsbury, but it is now established that some of his reports are spurious (Ryback *et al.*, 2001). Recent work on the synthesis and determination of thermodynamic data of antlerite (Pollard *et al.*, 1992) has thrown light on the expected mode of its occurrence in a temperate climate such as that of the British Isles. We can now report three further occurrences of antlerite (one from an unreported specimen in the collections of the

Natural History Museum) and this combined with the work of Pollard *et al.* (1992) and the doubt about the Kingsbury specimens has prompted this review.

Pollard *et al.* (1992) investigated the synthesis of antlerite over the range 10 to 45°C and noted that antlerite itself only formed at temperatures above about 30°C, while the equivalent dihydrate $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ formed below 30°C. However, removal of the dihydrate from its mother liquor resulted in it dehydrating to antlerite quite quickly. This means that, in a temperate climate where oxidation zone temperatures are generally less than 30°C, such as that of the British Isles, antlerite would be expected to occur as earthy or, at best, microcrystalline deposits, not as good euhedral crystals which should be restricted to relatively high temperature environments.

RECORDS, SPECIMENS AND LOCALITIES

The first record of antlerite in the British Isles is that of Kingsbury (1954) who reported it from the Old Gunnislake mine, Calstock, Cornwall.

This specimen, now in the Natural History Museum (NHM) (BM 1957,486 originally Kingsbury's No.1735), was collected from the dumps by Kingsbury in June 1936. The antlerite occurs in a few patches as a fine-grained and earthy emerald green crust that has a faintly botryoidal appearance, upon iron-stained quartz associated with decomposed chalcopyrite. Kingsbury's catalogues state that the specimen was examined further in 1949. Optical examinations were performed at Oxford University and Heinrich Neumann took X-ray powder photographs at Leeds University. The identity was confirmed when the X-ray photographs matched those of antlerite from Chuquicamata, Chile. The matrix of the specimen is similar to material known to be from Gunnislake and there is no obvious reason to doubt its validity. The fact that the specimen was collected in 1936 and analysed in 1949 also suggests a legitimate occurrence, as it appears that most of Kingsbury's fraudulent claims were made later on in his career (Alan D. Hart, *personal communication*).

The NHM collection also contains a specimen (BM 1986,23) confirmed as antlerite from Perran St-George, Perranzabuloe, Cornwall, which was acquired from M.G.H. Merry in 1986. This specimen is a light green, very fine powdery coating similar to that from Old Gunnislake mine. Howell (1992) reported antlerite as green coatings on gypsum and limonite from the 100 fathom level of the Wheal Hazard section, Crowns Lode, Botallack, St. Just and coating jarosite on specimens from Botallack cliff. In the Wheal Hazard locality, Howell noted minute (<0.1 mm) crystals.

At the nearby Geevor mine, antlerite was found with gypsum, atacamite, brochantite, chalcantite, metazeunerite, scorodite and sodium-zippelite in a small area of partially altered and collapsed wallrock traversed by primary sulphide veins on the 17 level, Levant North Lode (No. 2 Branch) (Elton and Hooper, 1993). Here the antlerite took the form of an amorphous-looking green crust. We can now report a further occurrence of antlerite from the Geevor mine spoil heaps. This was collected by the late F. Bell in the early 1990s and on this specimen the antlerite forms an earthy green encrustation on covellite on a matrix of quartz and feldspar. Both minerals were identified by the authors using XRD (reference numbers MANCH:XRD894 and 914 respectively).

Golley and Williams (1995) reported antlerite

from Tresavean mine, Gwennap, also in Cornwall, but did not state how it was identified.

At Alderley Edge, Cheshire, Braithwaite (1994) reported antlerite as a green crust associated with posnjakite and langite from a baryte gossan near the surface at the north-west end of Engine Vein.

Antlerite has recently been identified at Mynydd Parys (Parys Mountain), Anglesey, Gwynedd, Wales by XRD at the University of Wales, Bangor (Jenkins *et al.*, 2000). At Mynydd Parys, antlerite is the commonest post-mining copper mineral to form on the chalcopyrite exposed in the underground workings. Here it takes the form of blocky crystals of the order of 5 μ m across, overgrowing brochantite.

Within the collections of the NHM there is a specimen of antlerite from Potts Gill mine, Caldbeck Fells, Cumbria, donated by W.F. Davidson in 1957. The specimen, which approximates to an 8 cm cube, is encrusted mainly on one face by an earthy pale green coating of antlerite on a matrix of quartz and baryte. The antlerite was identified using XRD in the NHM (No. 7514). On another side of the specimen is a thin botryoidal dark green crust of cornwallite, which is similar to recently collected material from the dumps.

Hartley (1984) reported antlerite from Potts Gill mine on the basis of a specimen collected by Kingsbury. This specimen, now at the NHM (BM 1958,138 originally Kingsbury's K50/92) was the only other specimen of antlerite that Kingsbury claimed to have found during his career. Labels with the specimen indicate that he collected it in September 1950 from "Caldbeck, Cumberland". However, in his X-ray log book, specimen K50/92 is recorded as being from "Potts Gill", which potentially correlates to an entry in his field notebook on the 6th September 1950, namely "Potts Gill...one or two unidentified copper minerals on a small dump from the highest level on the west side of the beck (old mine)". The specimen is a highly irregular, porous matrix of hackly dark green malachite on limonite. The antlerite occurs as earthy, emerald green masses within cavities and embayments in the porous matrix. It is often poorly consolidated within a single cavity and some earthy bundles have completely fallen off the specimen. Those that are left are loose and only kept in place by the irregular geometry of the matrix. This specimen

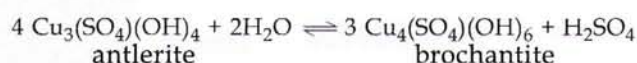
is a typical of Potts Gill specimen material. Furthermore, the association of antlerite in close proximity to malachite requires a very high level of free carbon dioxide to be present as the minerals formed, certainly in excess of a $p(\text{CO}_2)$ of 30 kNm^{-2} ($>30\% \text{ v/v}$). At lower levels of free carbon dioxide the brochantite (and related minerals) stability field intrudes between antlerite and malachite. The widespread occurrence of minerals such as leadhillite and the generally low levels of primary carbonate minerals in the Caldbeck Fells shows that the $p(\text{CO}_2)$ was usually very low during the oxidation phase. It has to be concluded that this specimen is almost certainly fraudulent.

Young (1987) reported antlerite from Sandbeds mine, Caldbeck Fells, Cumbria on the basis of a specimen in the R.J. King collection at the National Museum of Wales, but subsequent analysis showed it to be malachite (Cooper and Stanley, 1990).

Antlerite occurs at East Avoca mine in Co. Wicklow, Ireland as soft amorphous-looking crusts and patches. It appears to be post mining in origin as it is found in the walls and floors of the mine levels. The Avoca mines worked massive or fine grained pyritic ores containing chalcopyrite, galena and sphalerite and the environment is highly acidic (Ryback and Moreton, 1993). This appears to be the first report of antlerite in Ireland. It was identified using XRD at Manchester University (reference number MANCH: XRD1000).

DISCUSSION

The geochemical work by Pollard *et al.* (1992) and also Balarew and Markov (1986) serves to show why antlerite is a rare mineral in the British Isles. Firstly, in natural systems the dihydrate precursor of antlerite requires a pH of about 3 to crystallise from solution and then only does so in a very narrow pH range of about 0.5 units. These are quite specific low pH conditions. Secondly, if antlerite is immersed in water, it is unstable with respect to brochantite and reacts with the water to form this latter mineral. The chemical reaction can be expressed simply as:



The sulphuric acid released by this reaction will lower the pH until either all the antlerite has reacted, or the brochantite/antlerite stability

fence is reached, at which point the two minerals can co-exist at equilibrium. However, on a spoil heap, percolating rainwater reaching an antlerite specimen may wash away the sulphuric acid until all the antlerite has altered to brochantite. This process probably explains why several earthy green copper sulphate specimens collected by one of us (TFB) from surface localities in Central Wales and the Caldbeck Fells all proved to be brochantite. The most likely place to find antlerite is as an earthy post-mining deposit on the walls of copper rich mine workings or deep in spoil heaps where the antlerite is protected from surface water and particularly if the oxidation takes place in thin cracks in a specimen. Note that any specimen suspected of being antlerite should not be washed in water.

While it is impossible to be absolutely certain, it seems highly likely that Kingsbury's Gunnislake specimen, the first record in the British Isles, is genuine, but regrettably the Potts Gill specimen is almost certainly fraudulent.

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A REVIEW OF THE SUPERGENE MINERALISATION AT SILVER GILL, CALDBECK FELS, CUMBRIA

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Low temperature lead- zinc- and copper-rich veins at the southwest end of a NE-SW trending mineralised fracture system have been exploited over a long period at Silver Gill in the Caldbeck Fells, Cumbria. The primary mineralisation is relatively simple, comprising galena, sphalerite and chalcopyrite in quartz veinstone with minor baryte and carbonates. Two distinct supergene assemblages have been identified. There is a relatively simple suite of supergene minerals comprising common and stable phases found at the natural vein outcrops and a more complex assemblage including several rare minerals associated with post-mining mineral formation. Rare species identified for the first time in this study include bechererite, lanarkite, ramsbeckite, schulenbergite and susannite and the first Cumbrian fraipontite. In addition to these, Silver Gill is the type locality for the basic copper sulphate mineral redgillite, which has recently been accepted as a new species by the International Mineralogical Association.

INTRODUCTION

The mineral veins of the Caldbeck Fells in Cumbria contain one of the richest and most diverse assemblages of supergene minerals in the British Isles (Cooper and Stanley, 1990, 1997). Unusual species continue to be discovered and there have been several reports of minerals new to Britain in the past decade.

The Roughton Gill mines, which include all of the workings in Silver Gill, are among the most important in the Caldbeck Fells. They are notified as a GCR site for their remarkable mineralogy and are part of the Skiddaw Massif Site of Special Scientific Interest (SSSI). An archaeological survey carried out in 2000 at the request of Lake District National Park Authority (LDNPA) summarised their documentary history and described the topography of the site in detail (Jecock *et al.*, 2001). It revealed a complex palimpsest of remains most of which appear to date from the sixteenth and seventeenth centuries.

The first reference to mining at Silver Gill dates from 1319, but Smith *et al.* (2001) make a convincing argument that the major workings are Elizabethan in origin and that they played a significant part in the operation of the Company of Mines Royal. The mines were described as exhausted as early as 1700, and while this is not entirely true the focus of mining was undoubtedly shifting toward Roughton Gill by that time. Some mining occurred in the late 17th and early 18th century at a mine known as the Golden Hugh or Vugh and exploratory trials continued in Silver Gill until the third quarter of the 19th century. These later operations appear to have been comparatively minor works which met with little success.

The name Silver Gill taken at face value suggests that some of the orebodies were rich in silver. Indeed legend has it that a family once lived in a hut and coined silver money from the produce of the vein, till they were discovered and had to flee (Cooper and Stanley, 1990). There is no modern evidence of major primary silver

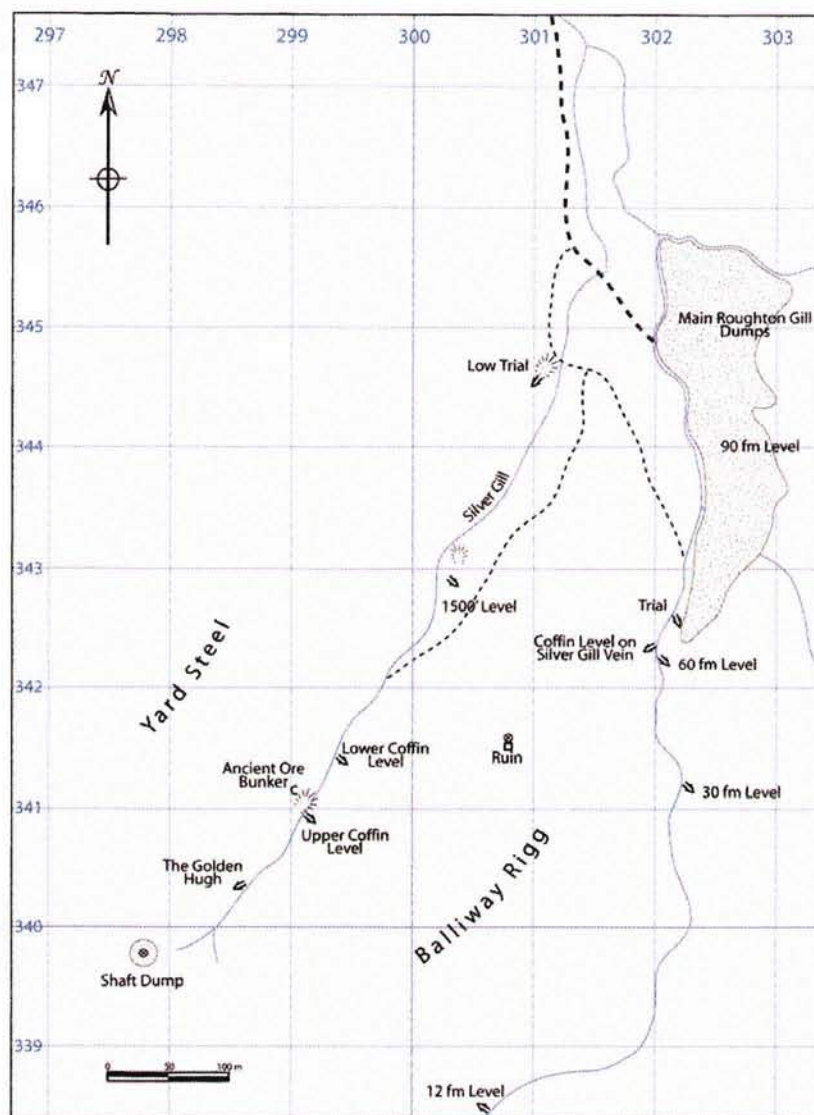


Figure 1. A sketch map based on a GPS survey of Silver Gill showing the position of the major features described in the text.

mineralisation in the area and the galena from the mines does not appear to have been especially silver-rich (Postlethwaite, 191, p. 59 quotes a figure of 25 ounces per ton). More recent research conducted by a group at Leeds University gave a value of 754 ppm Ag in Pb (John Hodgkins, *personal communication*). The silver appears to have been concentrated along slightly altered cleavages in the galena. There is a suggestion that some deposits mined in the Middle Ages in northern England were rich in silver and that they were entirely removed by mining (Dunham *et al.*, 2001).

At present the collecting of geological specimens from Silver Gill is forbidden because of the archaeological importance of the site. However, as part of a wider project reviewing the supergene mineral assemblages in the Caldbeck Fells, we decided to investigate the mineralogy on the basis of material already in collections. A

major impetus for this investigation is the description of a new mineral species, redgillite, from Silver Gill (Pluth *et al.*, in prep). This is the first new mineral to be described from the Caldbeck Fells. The majority of the specimens we have used during this investigation were collected between the mid 1970s and the early 1990s and are well located. Older specimens from the area tend to be only vaguely located (e.g. "Cumberland") and even the more precise term "Roughton Gill" is used rather loosely.

METHOD

Initially we made a detailed visual inspection of the specimens using a stereomicroscope. Where this revealed material that merited further study, small fragments were detached and analysed by SEM EDAX. Those 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, 40kV, 20mA) and the diffraction pattern recorded. Pattern matching software was used in combination with the chemical data to match the XRD pattern to known standards.

MINE WORKINGS IN SILVER GILL

A survey of the Silver Gill workings using a hand held GPS was carried out to locate features of mineralogical 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).

Silver Gill is a steep ravine which runs for about 750 m from the moorland plateau east of Great Sca Fell to Dale Beck (NY 2978 3397 to NY 3018 3469). Most of the workings in the gill are driven from the stream as crosscuts onto the Silver Gill Vein, a NE-SW trending mineralised fracture which crosses the valley in its upper reaches. There are at least five workings. The lowest of these at NY 3011 3446 is driven from the north side of the stream near the main Roughton Gill workings and appears to have been a small trial or perhaps an opencut for some other purpose. It may be the Silver Gill 90 fathom level described by Shaw (1975). There is no obvious mineralisation present.

A larger dump at NY 3004 3430 lies at about 445 m above sea level and almost certainly corresponds to the "lowest level at 1500 feet" at "[NY] 299341" described by Hartley (1984). It is identified as the 50 fm level by Dean (1852) and was considered to be an early nineteenth century trial by Smith *et al.* (2001). The dump contains some quartz-rich vein material with chalcopyrite and malachite, but is mostly made up of country rock as might be expected in a relatively long crosscut.

Two coffin levels were driven south toward the Silver Gill Vein in the upper reaches of the gill (grid references NY 2994 3414 and NY 2991 3409). The lower level gives access to a flooded stope on the Silver Gill vein and is illustrated by Cooper and Stanley (1990, p.31). A compelling argument that this is the 'New Stolne', begun around 1573 by the Company of Mines Royal is provided by Smith *et al.* (2001). It may also be the "Middle level" of Kingsbury (1957) as it is the middle of three levels marked on a Kingsbury MSS map of

the Caldbeck Fells in the Natural History Museum. The upper coffin level, the position of which was guessed by Cooper and Stanley (1990), was discovered by members of the Mines of Lake District Exploration Society (MOLES) and can be distinguished by a large bank of fresh spoil containing abundant boulders of vein quartz with goethite, malachite and chalcopyrite. It is thought to be an Elizabethan working, the 'Emanuel Stolne', begun around 1571 by the Company of Mines Royal (Smith *et al.*, 2001)

An ancient ore bunker (described as a bouse teem by Smith *et al.*, 2001) was uncovered on the north bank of the stream near the upper coffin level in about 1988 by amateur archaeologists (Jecock *et al.*, 2001, p.6; Cooper and Stanley, 1990 p.58). The grid reference for this structure is NY 2990 3412 (GPS): it was estimated as NY 2995 3415 by Cooper and Stanley (1990). The ore bunker contained a small quantity of rich highly oxidised ore, much of it finely ground and cemented by post-mining supergene minerals. Sphalerite, galena, chalcopyrite and pyrite were common in this material which was probably a cache of good quality copper ore abandoned by the miners in the Elizabethan Period. Very little of this material remains now remains on site.

The Silver Gill Vein crosses Silver Gill beck in its upper reaches (NY 2987 3404). It is conspicuous as a quartz rib on the north side of the valley. Due to its northwesterly dip and the steep contour of the northern flank of the ravine, it appears to change course and follows the stream on its northern side where it was tried by a small level. This was equated by Cooper and Stanley (1990) with the ancient working known as 'the Golden Hugh' (NY 2987 3405) and by Smith *et al.* (2001) with the 'Fortune Stolne' driven in 1575. The latter authors considered that the 'Golden Hugh' described all of the upper workings in Silver Gill, however we retain the term to describe the working at NY 2987 3405 to maintain consistency with Cooper and Stanley (1990); Pluth *et al.* (2004) and with labelled material in mineral collections. The level was open in the early 1980s and gave access to several small stopes, but the entrance has since been buried in scree.

There is a low circular dump about 20 m in diameter surrounding a shaft or bell pit at the very top of Silver Gill, just where the stream crosses onto the moorland plateau (NY 2978 3398). This appears to be the most southwesterly working on the Silver Gill Vein.

GEOLOGY and MINERALISATION

The mineral veins at Roughton Gill occupy NE-SW trending fractures within relatively competent rocks belonging to two major groups: the Eycott Volcanics and the Carrock Fell Complex. Both of these are Lower Palaeozoic in age. Fine grained sediments of the Skiddaw Group are encountered at the extreme southwestern end of the veins in higher Roughton Gill and Silver Gill, but the mines were not productive in these less competent rocks.

The Silver Gill Vein is mapped by the British Geological Survey (1997) as a NE-SW trending mineralised fault structure between NY 308 357 and NY 297 339. There is an excellent *in situ* exposure of the vein where it crosses Roughton Gill (NY 3424 3020). Here it is exposed in a fracture zone about 3 m wide containing quartz veins up to 0.5 m in width with minor chalcopyrite and malachite. The vein runs across the flank of Balliway Rigg, past a ruin at NY 3008 3416, crossing Silver Gill beck at NY 2987 3404.

In all of the workings in Silver Gill, the south wall of the vein is in an intrusive apatite-rich ferrodiorite belonging to the Carrock Fell Complex. The northern wall of the vein is initially in volcanoclastic rocks of the Eycott Volcanic Group where it crosses into the valley (NY 3008 3416). These are replaced by microgranite belonging to the Carrock Fell Igneous Complex southwest of the ruin on Balliway Rigg. Near the top of the gill a fault brings the north wall into the siltstones of the Bitter Beck Formation (Tremadocian), which are part of the Skiddaw Group and which can be seen on the upper shaft dump.

Subsidiary veins, which are not marked by the British Geological Survey (1997), but which are nonetheless conspicuous, cross Silver Gill in its upper reaches and run approximately NW-SE. One vein up to about a metre wide runs up the flank of Yard Steel opposite the upper coffin level.

The primary assemblage at Silver Gill is relatively simple. The major primary sulphides present are chalcopyrite, galena and sphalerite, ores of lead, copper and zinc which were historically important in the Caldbeck Fells. Pyrite is uncommon as is the black copper sulphide digenite, which has been identified replacing galena (Chris Stanley, *personal communication*). Quartz is the dominant gangue mineral with minor baryte and the carbonates

calcite and dolomite. The mineralisation is thought to be early Carboniferous in age (Cooper and Stanley, 1990).

The wallrock surrounding the vein has a bleached appearance and is commonly soft and friable. The vein at surface has undergone intense supergene oxidation leaving quartz and iron oxides with minor malachite, cerussite and pyromorphite. Sulphide minerals are present on the mine dumps and are visible *in situ* in some of the upper workings.

SUPERGENE MINERALS

Recent investigations of mineral specimens in the collections of two of the authors (NT and TFB) and the Mike Leppington collection have revealed a remarkable suite of supergene minerals from the workings in Silver Gill. Minerals which have been identified beyond reasonable doubt have headings typed IN CAPITALS; where there is some doubt attached to an identification or specimen, or a mineral should not be regarded as part of the natural assemblage (if it formed post-collecting for example), it is listed in *ITALICS* (Nickel, 1995 gives the accepted up-to-date definition of a natural mineral).

There are two key references which contain significant original research on the supergene mineralisation at Silver Gill: Hartley (1984) lists material identified by himself and Arthur Kingsbury in the 1950s, while Cooper and Stanley (1990), in addition to their summary of previous work, describe new discoveries from the upper workings. Unfortunately some of the minerals (especially the rarer ones), supposedly collected by Arthur Kingsbury which are listed in both of these works have subsequently been shown to be fraudulent (Ryback *et al.*, 1998, 2001). The validity of any records based solely on Kingsbury specimens has to be checked very carefully. Fortunately Kingsbury did relatively little work at Silver Gill. Hartley (1984) notes that "the only fruitful collecting locality was the dump outside the lowest level at 1500 feet" and records only covelline, psilomelane, malachite, cerussite, rosasite, smithsonite, pyromorphite, linarite, chrysocolla and hemimorphite from this locality.

ANGLESITE PbSO_4

Anglesite occurs at the Golden Hugh as small transparent tablets with a rhombic outline which are occasionally altered to leadhillite (Cooper and

Stanley, 1990). Blocky crystals to 7 mm were collected from the vein exposure outside the level (Fig. 2). Minute colourless euhedral blocky to prismatic anglesite crystals were not uncommon on quartz with partly oxidised galena on the old ore pile at NY 2990 3412.



Figure 2. A blocky anglesite crystal 7 mm long surrounded by numerous smaller crystals on iron stained quartz matrix collected from an outcrop near the Golden Hugh by David Middleton. Photo David Green.

AURICHALCITE $(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$

Aurichalcite was noted from Silver Gill without description by Hartley (1984). Radiating sheaves of pale green crystals occur with rosasite at the low dump at NY 3004 3430. Aurichalcite also occurs on specimens from the ore pile at NY 2990 3412 as radiating aggregates of a pale turquoise colour up to about 0.6 mm across associated with brochantite and langite (X-ray reference number MANCH:XRD947). It is relatively common as hand specimens displaying sheaves of pale green feathery crystals up to about 1 mm in length on hemimorphite in partly oxidised sphalerite-rich veinstone in the upper workings at Silver Gill. In all of the specimens we have examined aurichalcite is later in the paragenesis than hemimorphite.

BARYTE BaSO_4

Thin transparent baryte blades have been identified by SEM EDAX associated with malachite on goethite encrusted quartz on specimens collected from the upper workings in Silver Gill. Their occurrence as well formed crystals on highly oxidised vein material suggests that they are supergene in origin.

BECHERERITE $\text{Zn}_7\text{Cu}(\text{OH})_{13}[\text{SiO}(\text{OH})_3\text{SO}_4]$

Bechererite occurs as pale green inverted cone-shaped crystals up to 0.1 mm long terminated by a conspicuous pedion face on a specimen collected in the upper part of Silver Gill. Analysis by SEM EDAX shows the presence of copper, zinc, sulphur and silicon in the same ratio as bechererite from Wales. This, together with the characteristic inverted cone-shaped crystal habit (Fig. 3) is sufficient to identify bechererite.

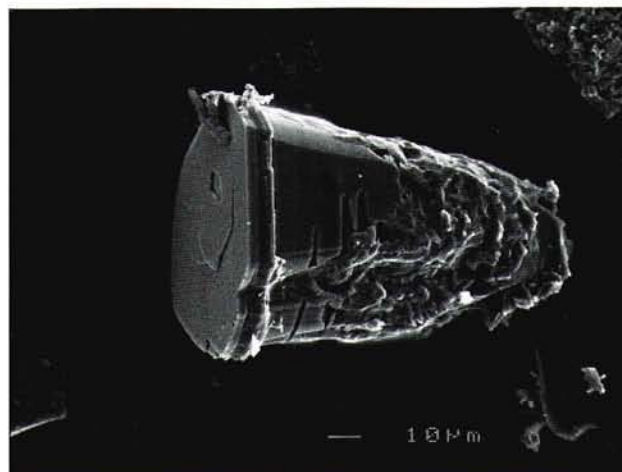


Figure 3. SEM image of a single off matrix bechererite crystal about 0.1 mm long showing the characteristic coned shaped crystal habit. The flat terminating pedion face shows some evidence of screw dislocation, which with the absence of a centre of symmetry may account for the unusual crystal habit.

BEUDANTITE $\text{PbFe}_3[(\text{As,S})\text{O}_4]_2(\text{OH,H}_2\text{O})_6$

Beudantite was identified as a thin yellow crust coating mimetite crystals on iron stained quartz collected from near the upper of the two coffin levels in Silver Gill (X-ray reference MANCH:XRD960). It occasionally forms small drusy brown crusts with individual pointed crystals up to 0.1 mm long (MANCH:XRD951).

BINDHEIMITE $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$

A yellow powdery crust in cavities in quartz veinstone containing partly oxidised galena, cerussite and pyromorphite was identified by SEM EDAX as bindheimite.

BROCHANTITE $\text{Cu}_4(\text{SO}_4)_4(\text{OH})_6$

Brochantite was identified by XRD as minute rounded scales and fibrous sprays, apparently altering from langite, on the old ore pile at NY 2990 3412 (Cooper and Stanley, 1990). It occurs as a dark emerald green drusy crust overgrowing cuprite in association with linarite and cerussite and as rich crusts composed of minute rounded

scaly crystals with langite. Partial to complete replacements of langite or wroewolfeite by brochantite are relatively common.

CALEDONITE $\text{Pb}_5\text{Cu}_2(\text{CO}_3)(\text{SO}_4)_3(\text{OH})_6$

Caledonite was reported from the Golden Hugh as radiating bunches of acicular crystals on decomposing sulphides by Cooper and Stanley (1990). It occurs with leadhillite at the same locality as blocky crystals of a sky-blue colour up to 0.4 mm in length. Caledonite has been identified by XRD as pale-blue rounded aggregates of subhedral crystals up to 0.5 mm across from the old ore pile at NY 2990 3412. It occurs with leadhillite as radiating groups of acicular crystals up to 0.5 mm in length at the same locality.

CERUSSITE PbCO_3

Cerussite is probably the most abundant lead-bearing supergene mineral at Silver Gill and it can be found in most of the *in situ* vein exposures. It was recorded by Greg and Lettsom (1858) from the Golden Hugh as small attractive striated prisms with acicular malachite. Well crystallised specimens showing this association were collected in the 1980s from a vein exposure outside the level (Fig. 4). Cerussite occurs as elongated white jackstraw crystals and colourless to blocky pseudo-hexagonal prisms on iron-stained vein quartz on the old ore pile at NY 2990 3412.

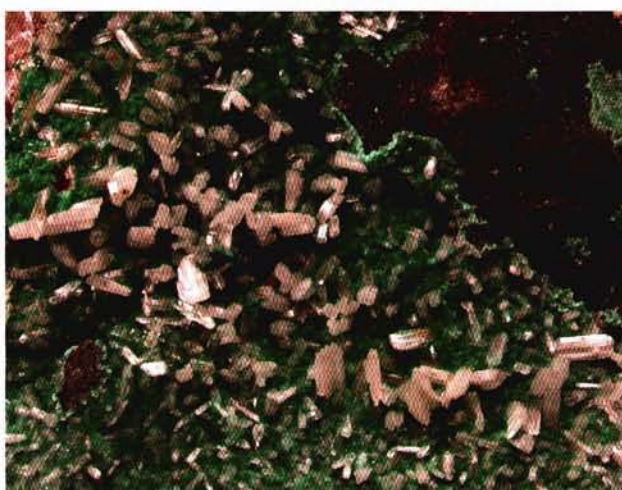


Figure 4. White striated cerussite crystals on bright green malachite, a combination first reported from Silver Gill by Greg and Lettsom (1858). This specimen was collected in the late 1970s by David Middleton. Photo David Green.

CHRYSOCOLLA $(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$

Chrysocolla is widespread and common in the Caldbeck Fells. It was noted without description

from Silver Gill by Hartley (1984). A few specimens which looked like chrysocolla, examined by SEM EDAX in this study, proved to contain elements in addition to copper, silicon and aluminium, however we have confirmed definite chrysocolla on other specimens. It occurs as blue to blue-green spherules.

CINNABAR HgS

Cinnabar is rare as pale orange to red powdery coatings in cavities in oxidised veinstone. These are typical of supergene cinnabar which is formed by the oxidation of mercurian sphalerite. Identification was by SEM EDAX.

CONNELLITE $\text{Cu}_{19}\text{Cl}_4(\text{SO}_4)(\text{OH})_{32} \cdot 3\text{H}_2\text{O}$

A mineral which is likely to be connellite was found on specimens collected from the old ore pile at NY 2990 3412. It was examined by SEM EDAX which revealed the presence of copper, chlorine and sulphur (Mike Rothwell, *personal communication*). This together with its appearance as deep-blue radiating sprays and felted masses strongly suggests connellite. It occurs with cuprite, brochantite and redgillite.

COPPER Cu

Copper occurs rarely as minute metallic masses in cuprite on specimens collected from the old ore pile at NY 2990 3412.

COVELLITE CuS

Covellite was reported from the lowest level in Silver Gill by Hartley (1984). It commonly forms thin 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 specimens collected from the old ore pile at NY 2990 3412. These appear to be post-collecting in origin and cannot be regarded as part of the natural mineral suite.

CUPRITE Cu_2O

Cuprite was described by Cooper and Stanley (1990) as thin strings in masses of altered sulphides from the old ore pile at NY 2990 3412. It also occurs at this locality as arborescent masses, presumably overgrowing copper, and as minute euhedral octahedra up to 0.05 mm across in limonitic matrix. A small amount of cuprite was encountered during the recent excavation of the upper coffin level by MOLES members.

FRAIPONTITE $(\text{Zn,Cu,Al})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4$

Fraipontite occurs in specimens collected from the old ore pile at NY 2990 3412 as soft eggshell-blue crusts up to about 0.1 mm thick, with a dull silky lustre. It is associated with brochantite, cerussite and linarite in quartz veinstone containing galena, chalcopryrite, covellite and sphalerite. Identification was by XRD (X-ray reference number MANCH: XRD896) supported by SEM EDAX. This is the first confirmed report of fraipontite from Cumbria.

GOETHITE $\text{FeO}(\text{OH})$

Goethite is abundant as the major component of pale to dark brown friable limonitic crusts and as hard black encrustations sometimes several centimetres thick on vein quartz. It was identified by XRD.

HEMIMORPHITE $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$

Hemimorphite is the most abundant zinc-bearing supergene mineral at Silver Gill. It was reported by Hartley (1984) and Cooper and Stanley (1990). At the old ore pile at NY 2990 3412 hemimorphite was abundantly present as white to pale blue crusts up to about a millimetre thick in cavities in partly oxidised veinstone. It is relatively common in all of the upper workings in Silver Gill as radiating fans of colourless euhedral bladed crystals up to about 0.8 mm long. Hemimorphite is commonly found with aurichalcite (Fig. 5).

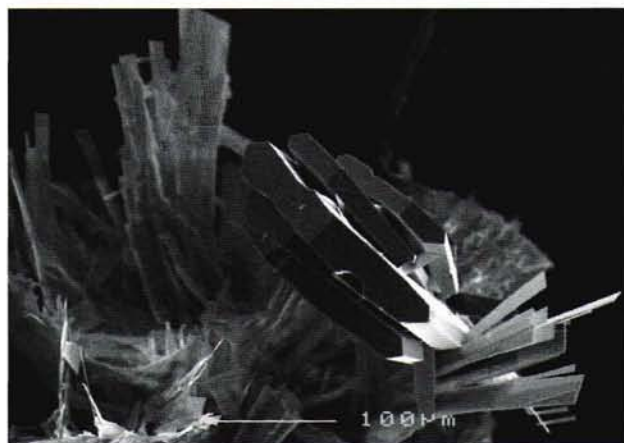


Figure 5. SEM image of tabular hemimorphite overgrown by thin laths of aurichalcite, a relatively common combination of supergene minerals from the upper workings of Silver Gill.

HYDROCERUSSITE $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$

Hydrocerussite was identified on a single specimen as white to pale green pearly crusts on partly oxidised sulphides in association with

caledonite (X-ray reference number MANCH: XRD941). It was collected from the old ore pile at NY 2990 3412.

JAROSITE $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

A number of yellow encrustations which were tentatively identified as beudantite or limonite were found to be jarosite when examined by SEM EDAX. Jarosite occurs as minutely crystalline yellow crusts.

LANARKITE $\text{Pb}_2\text{O}(\text{SO}_4)$

Lanarkite was identified on a single specimen as minute white acicular bladed crystals (<0.2 mm) in a quartz cavity containing remnant galena (X-ray reference number MANCH: XRD940). The specimen is from the upper workings in Silver Gill, but the precise locality is unknown.

LANGITE $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$

Langite was relatively common on the old ore pile at NY 2990 3412 as euhedral dark blue blocky to prismatic pseudohexagonal crystals up to 1.5 mm across (Fig. 6). It occurs at the Golden Hugh as small blocky pseudohexagonal crystals, elongated prismatic crystals with a hexagonal cross section, and flattened tablets. Many specimens of langite from Silver Gill are partly pseudomorphed by green brochantite. Crystals commonly occur with white crusts of hemimorphite and are associated with cerussite, linarite, malachite, brochantite and redgillite.



Figure 6. A typical blocky pseudohexagonal langite crystal on white hemimorphite. This is a composite image assembled from a stack of digital photos by Julie Ballard.

LEADHILLITE $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$

The presence of leadhillite at the Golden Hugh was briefly noted by Cooper and Stanley (1990). It

occurs as characteristic white thick tabular pseudo-hexagonal crystals up to 1 mm across associated with anglesite and caledonite. Leadhillite also occurs on specimens collected from the old ore pile at NY 2990 3412 as white to pale green, tabular to elongated prismatic crystals up to about 0.8 mm long. It is commonly associated with caledonite.

LINARITE $\text{PbCu}(\text{SO}_4)(\text{OH})_2$

Linarite occurs in a wide variety of habits at Silver Gill and is readily recognised by its characteristic deep azure-blue colour. Linarite was described by Cooper and Stanley (1990) from the lowest level in the gill and also from the Golden Hugh, where it appears to have crystallised on the level walls. Linarite is commonly found on limonitic quartz or partly decomposed galena with cerussite. At the ore pile at NY 2990 3412, it occurs as wispy lath-like crystals, radiating acicular aggregates, individual blocky to prismatic and thick tabular crystals. It is commonly associated with brochantite, langite, hemimorphite and cerussite.

MALACHITE $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Malachite occurs at most of the dumps and vein outcrops in Silver Gill, it is one of the commonest supergene minerals present. It typically forms thin green crusts on gossanous veinstone, which can occasionally be resolved into minute acicular crystals. Specimens of malachite with white prismatic cerussite were found at a small vein exposure near the Golden Hugh (David Middleton, *personal communication*) and abundant spherulitic masses and fracture fillings are present in the veinstone recently excavated from the upper coffin level.

MIMETITE $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$

Mimetite of near end-member composition was identified by XRD and SEM EDAX as white elongated prismatic crystals up to 3 mm long associated with yellow crusts of beudantite on a specimen collected from near the upper of the two coffin levels. Yellow to orange-yellow crusts composed of lenticular, elongated prismatic and acicular crystals occur on the old ore pile at NY 2990 3412. Analysis by XRD shows these are phosphatian mimetite. Yellow crusts of phosphatian mimetite, some pseudomorphing cerussite, have also been identified on joint planes in vein quartz collected in the upper part of Silver Gill.

POSNJAKITE $\text{Cu}_4(\text{SO}_4)(\text{OH})_6\cdot\text{H}_2\text{O}$

Posnjakite was identified as minute blocky turquoise-blue crystals on a specimen collected from the ore pile at NY 2990 3412 and submitted to the Natural History Museum, London by Brian Young (Cooper and Stanley, 1990). The species has subsequently been identified as a component of a blue-green crust on a specimen of shale wallrock derived from the shaft dump at NY 2978 3398. It occurs as typical rounded subhedral crystals with ramsbeckite, schulenbergitte and minor dark blue linarite (X-ray reference MANCH:XRD911).

PYROMORPHITE $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$

Pyromorphite is present in situ in the vein outcrops in Silver Gill and also occurs on joints in the surrounding country rock. It occurs as crusts of curved oily-green crystals (Fig. 7) up to several millimetres long at the old shaft dump at the very top of the gill (NY 2978 3398) and is also common as yellow barrel shaped crystals. These were identified by XRD and SEM EDAX which indicated a near end-member composition.



Figure 7. Curved oily green pyromorphite crystals collected from the top shaft dump at Silver Gill in 1987. Photo David Green.

RAMSBECKITE $(\text{Cu,Zn})_{15}(\text{SO}_4)_4(\text{OH})_{22}\cdot 6\text{H}_2\text{O}$

Ramsbeckite was identified on a single specimen as a component of a blue-green crust on a clast of rock derived from the shaft dump at NY 2978 3398 at the top of Silver Gill. It occurs as poorly formed equant emerald-green crystals up to 0.3 mm across sometimes grown together into crusts (X-ray reference MANCH:XRD910). The characteristic blocky pseudo-orthorhombic crystal habit could be distinguished on a few crystals. A specimen showing pseudo-orthorhombic crystals to 0.3 mm associated with linarite and

schulenbergite was identified in material collected from the ore bunker at NY 2990 3412 (Fig. 8). Both specimens are in the TFB collection.

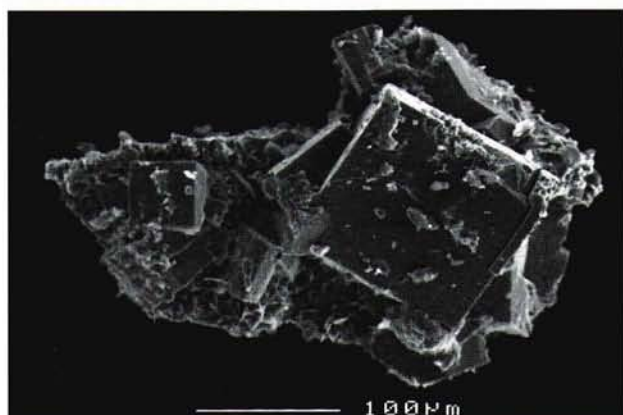


Figure 8. An SEM image showing typical blocky pseudo-orthorhombic ramsbeckite crystals up to 0.15 mm across, collected from the ore bunker in Silver Gill by Trevor Bridges.

REDGILLITE $\text{Cu}_6(\text{OH})_{10}(\text{SO}_4)\cdot\text{H}_2\text{O}$

The presence of an undescribed copper sulphate hydrate species was noted at the Golden Hugh and the old ore pile on the west bank of Silver Gill by Cooper and Stanley (1990). The crystal structure and chemical formula of the species has recently been determined on specimens collected by Peter Braithwaite at Silver Gill. The mineral has been accepted as a new species and name redgillite approved by the IMA Commission on New Minerals and Mineral Names (Pluth *et al.*, in prep). The name is used here with the permission of the authors.

Redgillite occurs as pale green crusts composed of radiating groups of acicular crystals, rarely more than 0.1 mm in length and only a few micrometres thick (Fig. 9). The mineral is



Figure 9. An SEM image showing lath-like crystals of redgillite on partly oxidised chalcopyrite. Collected in the early 1980s by David Middleton.

typically found in thin fractures in partly oxidised sulphides where it is sometimes associated with langite and more rarely with malachite, cuprite, copper, connellite and brochantite.

ROSASITE $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$

Rosasite was described from the "Middle level" in Silver Gill by Kingsbury and Hartley (1957). This may correspond to the coffin level at NY 2994 3414, which is the middle of three levels marked by Kingsbury on a MSS map of Silver Gill in the Natural History Museum. If so we have been unable to confirm its presence as no dump material remains. However, small turquoise-blue spherulitic masses of rosasite up to about 0.3 mm lining cavities in iron-stained quartz veinstone were quite common at one time at the lower level in Silver Gill at NY 3004 3430. They are recorded at this location by Hartley (1984) and have been independently identified on a several specimens. Rosasite occurs with aurichalcite, hemimorphite and malachite.

SCHULENBERGITE $(\text{Zn,Cu})_7(\text{SO}_4\text{CO}_3)_2(\text{OH})_{10}$

Schulenbergite is the major component of a blue-green crust on a specimen of rock found at the shaft dump at NY 2978 3398. It occurs as crudely hexagonal foliated aggregates of a pale turquoise colour which reach 0.3 mm across (X-ray reference MANCH:XRD912). Associated species include ramsbeckite, posnjakite and linarite.

SMITHSONITE ZnCO_3

Smithsonite was listed by Hartley (1984) from the level at 1500 ft in Silver Gill, and Young (1987) described a specimen in the collection of the Natural History Museum, London from the site. Both of these reports appear to be based on a specimen in the Arthur Kingsbury collection. Given the appearance of the specimen which is atypical of other material from Silver Gill (Chris Stanley, *personal communication*), Kingsbury's poor reputation (Ryback *et al.*, 1998, 2001) and the lack of corroborating evidence, the specimen must be considered questionable. However, undoubted smithsonite has recently been identified on a specimen in the Mike Leppington collection.

SULPHUR S

Sulphur occurs as transparent pale yellow globular crystals to 0.25 mm on galena on specimens collected from the ore pile at NY 2990 3412.

SUSANNITE $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$

Pale green tabular to elongated rhombic crystals associated with leadhillite found on the ore pile at NY 2990 3412 have recently been identified by a combination of XRD and optical methods as susannite (X-ray reference MANCH:XRD942).

WROEWOLFEITE $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$

Wroewolfeite was identified by XRD as deep blue equant to elongated prismatic crystals up to 0.3 mm long with a rectilinear cross-section associated with hemimorphite and langite on iron stained quartz veinstone from the ore pile at NY 2990 3412. Some of the crystals are partially altered to brochantite.

WULFENITE PbMoO_4

Wulfenite was described by Cooper and Stanley (1990) as thin yellow to yellow-orange plates, exceptionally up to 1 mm across, on cerussite or on iron-stained quartz from the ore pile at NY 2990 3412. It has also been found at this locality associated with phosphatian mimetite. Wulfenite has been found at the Golden Hugh as yellow tabular crystals (<0.8 mm) and at the old shaft dump at the top of Silver Gill in small (<0.5 mm) platy crystals.

DISCUSSION

Two distinct supergene mineral assemblages are present at Silver Gill. There is a relatively simple assemblage which is exemplified by material collected from the natural outcrops and which is dominated by cerussite, goethite and malachite with lesser anglesite, aurichalcite, pyromorphite-mimetite and hemimorphite. All of 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 mineral assemblages recently described from locations in low carbonate sedimentary rocks in central Wales (Mason, 2004).

A second and more complex assemblage, exemplified by the material from the ore bunker, includes most of the minerals described above (some of which are undoubtedly pre-mining) with other species which are of undoubted post-mining origin. This assemblage can be moderately complex with numerous chemically similar phases crystallised in close proximity. The minerals in the complex assemblage can often be unequivocally identified as post-mining in origin

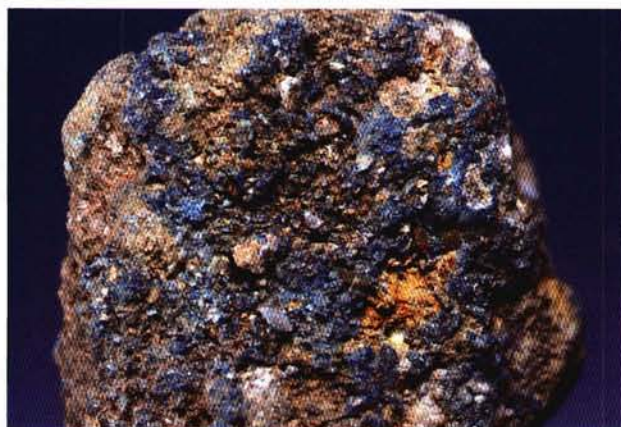


Figure 10. Linarite cemented clasts typical of the material which was present at the old ore bunker. Specimen donated to the Manchester Museum in 1999, accession number N15087. Photo David Green.

as they occur on fracture surfaces and as intergranular cements (Fig. 10). They include the basic copper sulphates langite, wroewolfeite and posnjakite as well as ramsbeckite, schulenbergite, brochantite and linarite. The post-mining assemblage records the chemical alteration which takes place in mine dumps over a relatively short time period. Some of these phases may be important as buffers for heavy metals leaching into the environment.

Langite and wroewolfeite occur commonly in the material from the ore bunker but appear generally absent in the natural outcrops. Alteration of langite and wroewolfeite to brochantite is evident in many specimens and can be seen at a number of different stages varying from a slight green cloudiness in blue langite crystals to complete pseudomorphous replacement (Fig. 11). Over long periods of time it seems that both minerals are unstable with

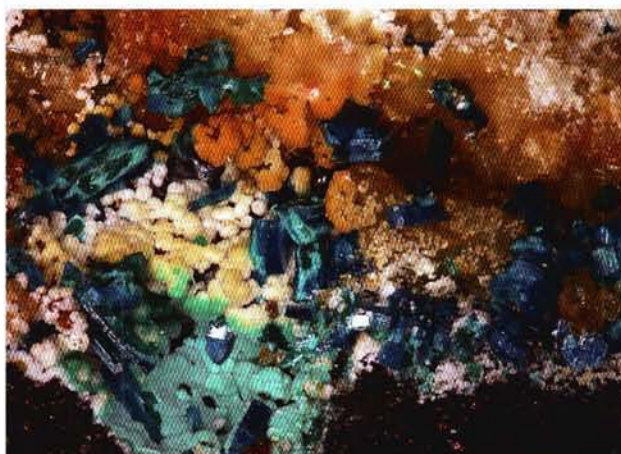


Figure 11. Langite crystals to 0.5 mm showing partial pseudomorphous replacement by green brochantite. Photo David Green.

respect to brochantite, to which they are chemically identical except for two molecules of water of crystallisation.

Ramsbeckite and schulenbergite are components of the post-mining assemblage as indicated by their presence on the broken surfaces of rock clasts. Acidic copper- and zinc-rich fluids percolating through the dump have leached carbonates from thin veins in the rock and precipitated ramsbeckite and schulenbergite in the fractures. Other minerals found in this assemblage include posnjakite which occurs as typical rounded subhedral crystals and minor dark blue linarite. This association is very similar to those described from the other localities in the Caldbeck Fells and the Central Wales Orefield (Green *et al.*, 2001). Ramsbeckite and schulenbergite typically appear to develop in the chemical conditions generated by post-mining oxidation processes in copper and zinc-rich mine spoil. The close association of ramsbeckite, schulenbergite and posnjakite is characteristic and has been reported at most of the localities where the minerals occur (e.g. Rust, 1992; Bevins, 1994; Mason and Green, 1995; Green *et al.*, 1996; Mason and Rust, 1997; Green *et al.*, 2001). The formation of the three minerals clearly requires very similar chemical conditions. The conditions prevalent in thin fractures and the partial leaching of carbonate minerals by acid copper- and zinc-rich solutions seem particularly favourable.

Chloride-rich supergene minerals, with the exception of the highly insoluble lead minerals pyromorphite, mimetite and mattheddleite, are unusual in the Caldbeck Fells. The only other reports are of phosgenite from the Driggith-Sandbeds vein (Kingsbury, 1957) and of atacamite (see Cooper and Stanley, 1990) but neither of these is likely to be trustworthy (Ryback *et al.*, 1998, 2001). The connellite specimens found at Silver Gill are almost certainly the result of post-mining oxidation, where a relatively low chloride ion activity would be expected. Connellite is stable at much lower chloride ion activities than the other secondary copper chlorides (Pollard *et al.*, 1990).

Bechererite is an exceptionally rare mineral that forms as a result of the post-mining oxidation of copper and zinc sulphides. In Britain, which has almost all of the known world occurrences, bechererite has been identified at five mines in the Central Wales Orefield and at Driggith Mine in the Caldbeck Fells (Rust *et al.*, 2003). The crystal habit at Silver Gill, which is the second reported occurrence in the Caldbeck Fells,

is as minute green inverted pyramidal and cone-shaped crystals terminated by bright pedion faces. These are characteristic of the species.

The only species found during this study which has not previously been reported from the Caldbeck Fells is fraipontite. Fraipontite is an uncommon zinc- and copper-bearing mineral belonging to the kaolinite-serpentine group. Its formula is written in different ways by different groups of mineralogists (compare for example Anthony *et al.*, 1995, who make no explicit record of the presence of copper with Gaines *et al.*, 1997 who do). Fraipontite was first described in 1927, probably from the Vieille Montagne mines, Moresnet, Belgium and has subsequently been reported from the supergene oxidation zones of a number of zinc- and copper-bearing orebodies worldwide (e.g. Anthony *et al.*, 1995). In the British Isles, it has been recorded from the Copperthwaite Vein, Swaledale, North Yorkshire (Ryback and Tandy, 1992); Virgin Moss Vein, Wensleydale, North Yorkshire (Young *et al.*, 1992) and as euhedral pseudo-hexagonal crystals from Machen Quarry, Mid Glamorgan (Goulding and Price, 1995). Fraipontite is uncommon at Silver Gill. It would be very easy to miss, as it forms a rather amorphous-looking blue crust which could easily be confused with chrysocolla. Our specimen contains significant copper which is at variance with some of the idealised formulae. However, two of the analyses quoted by Anthony *et al.* (1995) show significant amounts of copper, indeed the molar percentage of copper present is greater than zinc in a specimen from the Mohawk Mine, California, USA.

The difference between the supergene mineral assemblages present on the recent (MOLES) dump from the upper coffin level and the material which was left by early miners in the nearby ore bunker is striking. The recent material represents mine waste and would not be expected to contain rich ore, indeed very little ore bearing material was encountered even *in situ* in the level. Visual inspection of the MOLES dump shows that there is a considerable amount of gossanous quartz with conspicuous malachite, but very little lead mineralisation.

The mineralisation present in the ore bunker was very rich and it is unfortunate more was not collected when it was dug out. The samples that have been preserved (primarily in the Norman Thomson and Mike Leppington collections) show

galena, sphalerite and chalcopyrite in quartz matrix with minor baryte and carbonates. The presence of abundant linarite as a recent intergranular cement shows that the ore was very rich in lead and copper. It may be that the bunker simply contained rich material from the upper coffin level (Emanuel Stolne) as suggested by Smith *et al.* (2001). Another possibility is that it might have been derived from a level on the NW-SE lead vein which runs up the flank of Yard Steel opposite the coffin level. Manuscript sources suggest that a level was driven into Yard Steel in the early eighteenth century (Leconfield MSS, D/lec/219). The location of the level is unknown, it may refer to the Golden Hugh, but another possibility is that it is buried in scree somewhere near the upper coffin level in the opposite bank of the gill below the NW-SE lead vein. A more detailed mineralogical comparison of material from the ore bunker and from the recent MOLES dig could be interesting for both mineralogical and archaeological reasons.

The identification here of many previously unreported supergene minerals in the small amount of material we have had access to from Silver Gill demonstrates the value of careful examination and collection of specimens, even in areas such as the Caldbeck Fells which have been extensively researched. A detailed field survey involving some collecting would almost certainly have revealed further noteworthy material. It is unfortunate that there has not been more collaboration between the various groups with an interest in the site, especially as a great deal of material has been moved recently by mine historians.

CONCLUSIONS

A wide variety of lead- zinc- and copper-bearing supergene minerals occur in two distinct assemblages at Silver Gill. Of the forty or so species described in our study, fourteen are reported from the locality for the first time. Unlike most of the other major localities in the Caldbeck Fells, Silver Gill is relatively unaffected by the Kingsbury fraud. Many of the rare species described here were found in scree dug out of an old ore bunker by mine historians in 1988. There has recently been further extensive archaeological work at Silver Gill, but no collecting has been allowed. There is a need to plan mineralogical work alongside archaeological excavations so that the potentially valuable, fragile or vulnerable mineralogical material that is uncovered is not treated as waste.

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CARBONATE-FLUORAPATITE FROM THE WESTPHALIAN COAL MEASURES OF SOUTH WALES, U.K.

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Carbonate-fluorapatite has been identified in the coal measures of the South Wales coalfield. Abundant euhedral crystals have been found in situ within ironstone nodules at one site. The mineral appears to be widespread throughout the central part of the coalfield but is often overlooked because of its similarity to siderite. It appears to be a late-stage mineral and can be found crystallised on siderite and millerite.

INTRODUCTION

Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is the idealised compositional and structural prototype for sedimentary apatite with extensive substitution and vacancies throughout the crystal lattice (McClellan, 1980; Nathan, 1984). The apatite structure can accommodate a wide range of cations and anions, however, the major compositional difference results from the incorporation of variable amounts of structural carbonate ions.

Francolite was first recorded from Wheal Franco, Horrabridge, Devon by Brooke in 1843 (Rust, 1984). Sandell *et al.* (1939) used the mineral name francolite to identify sedimentary apatites that contain at least 1% fluorine and typically between 1–6% carbonate. However, francolite is not formally recognised as a mineral name and carbonate-fluorapatite (CFA) is preferred.

Deans *et al.* (1938) recorded carbonate-fluorapatite from oolitic ironstones found in the roof of coal seams within Westphalian sediments from the Yorkshire coalfield. CFA was found crystallised within the ooliths and also as hexagonal crystals up to 1 mm within septarian cracks. CFA-bearing siderite nodules have also been recorded from Penistone in Yorkshire (Pearson, 1977) and more recently by Neall (2004) as euhedral crystals from coal measures in the Gateshead area, Northumberland and Chapeltown, near Sheffield, south Yorkshire.

In South Wales, apatite, in the form of hydroxylapatite, has been recorded by Baqri *et al.*

(1979) occurring within carbonaceous dirt bands within the lower Hornlo seam in the Brynamman anthracite district of the South Wales coalfield. The authors suggested that low-grade regional metamorphism de-carbonated the original CFA.

Here we report the discovery of well-crystallised carbonate-fluorapatite within the Westphalian coal measures of South Wales.

LOCALITIES

ABERPERGWM COLLIERY TIPS, GLYNEATH (SN 862 063)

CFA occurs here as crystals up to 1mm associated with siderite and quartz. CFA forms crystalline hexagonal plates consisting of low pyramids on either side of the basal plane, divided into six triangular sectors. Minute re-entrant angles occur at the corners of the plates. Identification of CFA has been confirmed by XRD (BM NH: XRD 11969).

ABERCYNON COLLIERY, CILFYNYDD TIPS, ABERCYNON (ST 088 938)

CFA has been visually identified as sub-millimetre hexagonal plates associated with siderite, quartz and siegenite.

CAMBRIAN COLLIERY, CLYDACH VALE, RHONDDA (ST 961 924)

At this locality, CFA occurs as interlocking hexagonal plates to 2 mm coated and included with hydrocarbons (Fig. 1). Associated minerals include siderite, quartz and millerite.

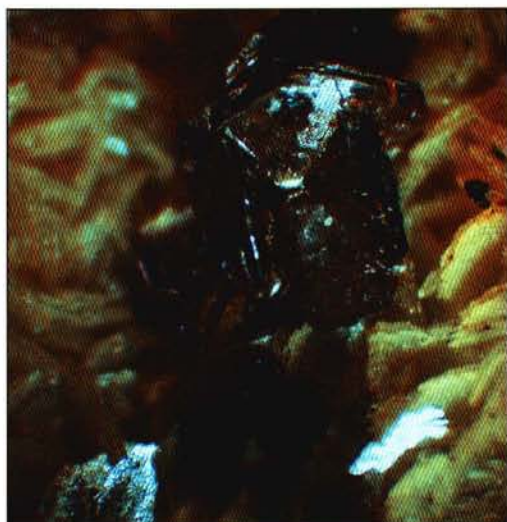


Figure 1. Interlocking plates of carbonate-fluorapatite with a coating of hydrocarbon, perched on siderite, from Cambrian colliery. The field of view is approximately 5 mm.

GELLI COLLIERY, GELLI, RHONDDA (SS 982 945)

Two specimens of CFA have been found here. One specimen consisted of large (to 5mm) interlocking hexagonal plates. The visual identification was confirmed by infra-red spectroscopy (Fig. 2: discussed below).

PARC COLLIERY, CWM PARC, RHONDDA (SS 938 963)

A specimen from this locality of <0.5 mm hexagonal opaque white crystals perched on millerite are probably CFA but this visual identification has not been confirmed by analysis.

PARK SLIP WEST OPENCAST COAL MINE (SS 864 839)

Very rich specimens of CFA were collected in situ from this locality in 2004. The opencast exposes a sequence within the middle coal measures (Westphalian B) from the Bute coal seam up to the Two Feet Nine seam. Ironstone nodules emplaced within seatearth and sandwiched between the upper and lower Four Feet coal seam yielded abundant CFA. The septaria were often completely lined with euhedral hexagonal plates of CFA up to 2mm. The crystals are generally colourless but can occasionally be an opaque white or brown due to inclusions. They can sometimes be found encrusting siderite, or more rarely, millerite. Spoil from other parts of the quarry has also yielded CFA but the exact location within the sequence is unknown.

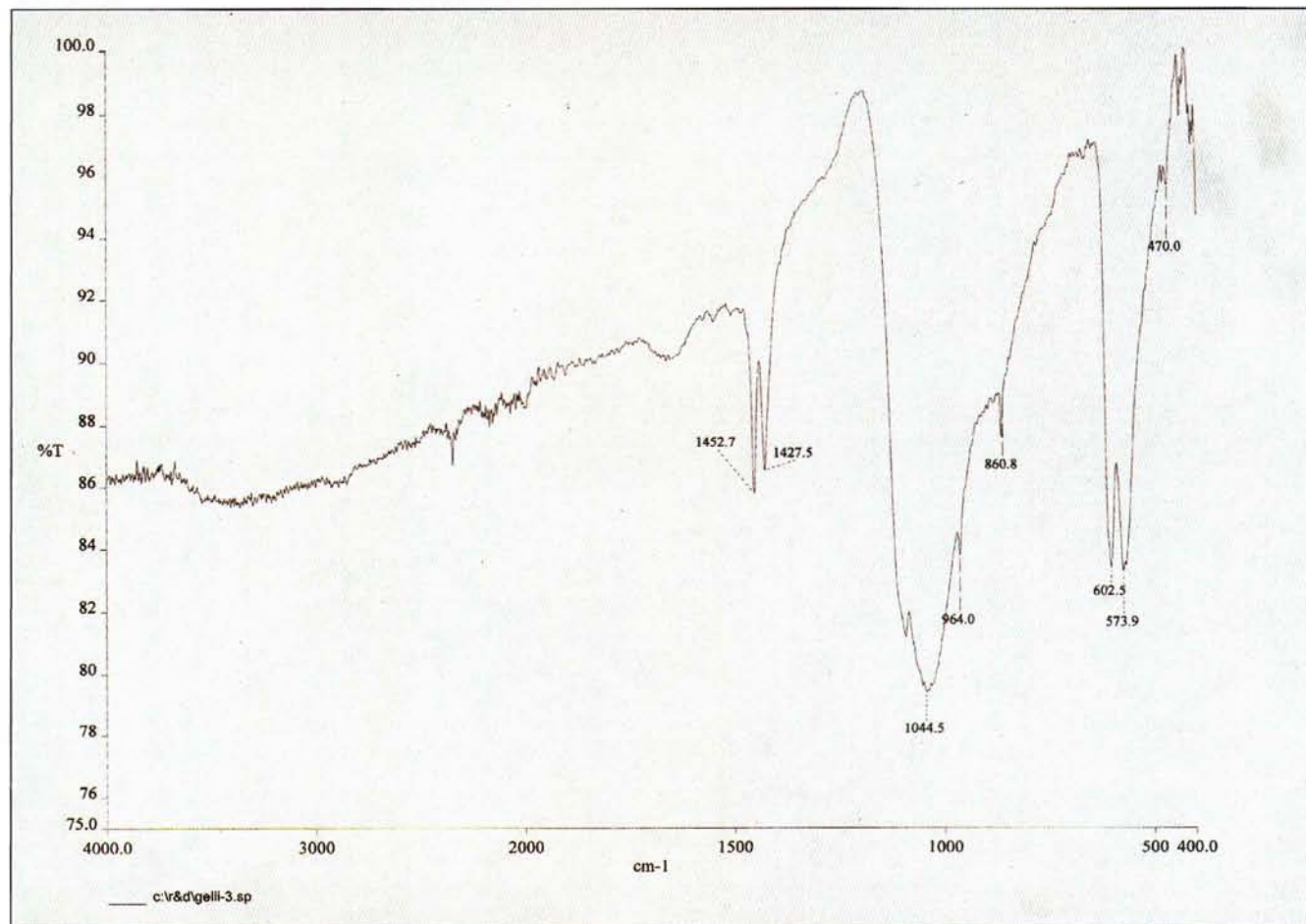


Figure 2. Infra-red spectrum of carbonate-fluorapatite from Gelli colliery.

IONIC GROUP	MODE	WAVENUMBER cm ⁻¹
phosphate	V ₁ , symmetrical stretch	964
phosphate	V ₂ , bend	470
phosphate	V ₃ , asymmetric stretch	1000-1100
phosphate	V ₄ , bend	602
phosphate	V ₄ , bend	574
carbonate	V ₂ , out-of-plane stretch	861
carbonate	V ₃ , asymmetric stretch	1453
carbonate	V ₃ , asymmetric stretch	1427

Table 1. Assignment of absorption bands in the CFA infra-red spectrum.

ANALYSIS

Infra-red analyses of CFA from the South Wales coalfield (e.g. Gelli colliery: Fig. 2) confirm that it has carbonate ions substituted within the apatite lattice. The presence of some hydroxyl groups was confirmed by a faint broad band around 3500 cm⁻¹. Any carbonate contamination is minimal as confirmed by the absence of any strong absorbance in the 710-730 cm⁻¹ region corresponding to the v₄ in-plane bending mode of the carbonate ion. The main bands have been assigned as shown in Table 1.

The infra-red spectrum of the carbonate ion in apatite has been explained by the presence of carbonate ions in two different environments (Bonel, 1972). Carbonate can substitute either for the anions hydroxyl or fluoride, or the phosphate ions within the apatite structure. The carbonate v₃ mode at 1453 and 1427 cm⁻¹ and the v₂ mode at 860 cm⁻¹ correspond to a carbonate substituting for phosphate (Regnier *et al.*, 1994). The slight shift of the carbonate v₂ peak position towards a lower wavenumber may be related to an increase in the fluoride ion concentration.

FORMATION

The coal-bearing strata within the South Wales coalfield are chiefly of Westphalian age (315-290 Ma) and represent sediments which accumulated in a foreland basin on the northern margins of the Variscan deformation. This sedimentary pile comprises alternating layers of mudstone, siltstone, coal and seatearth deposited in a predominantly estuarine-freshwater condition in a rapidly subsiding basin. Associated with the coal-bearing strata are seams of iron-rich concretions, many of which possess an internal septarian structure. These have been mineralised by the circulation of hydrothermal fluids derived from the South Wales basin which was subjected to upward thrusting from the

Variscan tectonic wedge to the south. Fluids at temperatures in the region of 150°C and 500 bar fluid pressure (Alderton *et al.*, 1996) are considered to be responsible for the leaching of metals, silica, sulphur and phosphate from the surrounding sediment and the deposition of various minerals within the septaria. Sulphides, carbonates, quartz and clay minerals developed contemporaneously with this regional low-grade metamorphism. It appears that carbonate-fluorapatite was one of the last minerals to crystallise out.

The formation of apatite depends primarily on the availability of dissolved phosphate, probably derived from a biogenic source, with fluorine and or chlorine derived from pore fluids involved in the transport of the diagenetic minerals. In addition, pH and the presence of calcium, magnesium and dissolved organic matter affect the kinetics of CFA formation. Further analytical data on carbonate/phosphate ratios and the change in apatite composition towards that of fluorapatite may give clues as to the temperature of formation.

It appears that CFA is widely distributed within the South Wales coalfield and has been largely overlooked because of its resemblance to siderite. Work is underway to examine other localities.

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THE COMPOSITION OF FÜLÖPPITE FROM WET SWINE GILL, CALDBECK FELS, CUMBRIA

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Fülöppite, Pb₃Sb₈S₁₅, is a rare mineral which was originally described from Baia Mare in Romania. It is one of a group of monoclinic lead-antimony sulphosalts with the general formula Pb_{3+2n}Sb₈S_{15+2n} (Gaines *et al.*, 1997). Fülöppite was first reported in Britain from Wet Swine Gill, Caldbeck Fells, Cumbria (Fortey *et al.*, 1984). It was described as dark grey metallic patches of fibrous crystals accompanying stibnite. More recently, rare dark red resinous to submetallic subhedral to euhedral crystals associated with

stibnite were identified as being close to fülöppite by XRD (Neall and Green, 2001). The composition of these crystals has been determined by wavelength dispersive X-ray spectroscopy and is the subject of this note.

The quartz-antimony vein exposed at Wet Swine Gill, Caldbeck Fells, Cumbria, was first described by Fortey *et al.* (1984). The primary ore minerals comprise an early Sb-As-Fe assemblage (mainly stibnite and berthierite, with lesser

Element	WSG1	WSG2	WSG3	WSG4	WSG5	WSG6	Baia Mare	Ideal
S	22.35	22.26	22.24	22.29	22.21	22.48	24.10	23.16
Sb	47.24	46.26	46.97	46.94	46.84	47.19	47.50	46.91
Pb	29.94	30.94	30.99	30.85	30.81	30.55	28.29	29.93
Total	99.53	99.46	100.19	100.08	99.86	100.21	100.08	100

Table 1. Fülöppite analyses. The first six columns give data on specimens from Wet Swine Gill and the last two from the type locality, Baia Mare in Romania (Anthony *et al.*, 1990) and the ideal formula. The standards used in the fülöppite analysis were Pb - crocoite, S - pyrite, Sb - stibnite. Conditions were 20kV and 20nA with a 10µm beam diameter.

arsenopyrite, sphalerite, jamesonite and traces of antimony) and a later Sb-Pb assemblage (zinkenite with lesser fülöppite and semseyite). Supergene minerals present at the site include the rare species claudetite and parasymphesite (Leppington and Green, 1998; Neall and Green, 2001).

As part of an investigation of the mineralisation at Wet Swine Gill, which we began in the late 1990s using specimens obtained before the current collecting restrictions were imposed, a small amount of material collected from the antimony vein (NY 3144 3215) was examined. Unusual material was sampled for qualitative chemical analysis by SEM EDAX. Tiny fragments were placed on an aluminium SEM stub and the major elements with an atomic number >10 were identified. If the initial SEM EDAX investigation produced interesting results, further material was sampled for analysis by XRD. This material was 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, 40kV, 20mA) and its diffraction pattern recorded from 5° to 50° in 2.

Rare millimetre-sized, equant, submetallic, subhedral crystals, with a deep cherry-red colour on thin edges, produced an XRD pattern close to fülöppite. These were tentatively identified as fülöppite (Neall and Green, 2001), but they did not match the original description of the mineral from Wet Swine Gill, so they were set aside for further study. We have recently prepared several samples for quantitative chemical examination using an electron microprobe. Mechanically detaching a large grain of fülöppite, for quantitative chemical analysis proved difficult, so a specimen of fülöppite-bearing quartz was etched in hydrofluoric acid to produce a sulphide-rich residue from which appropriate grains were hand picked. These were embedded in resin and polished to produce a flat surface for analysis by wavelength dispersive X-ray spectroscopy.

The results of six analyses of two grains of fülöppite are summarised in Table 1. Comparison of the analyses with both the idealised formula and type material shows excellent agreement. The XRD and compositional data taken together clearly identify the crystals as fülöppite. A small capsule containing a few grains of fülöppite is preserved in the Manchester Museum collection under accession number N18019, and a number of other specimens of fülöppite in matrix will be added to the collection in due course.

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COLUMBITE FROM CHYWOON QUARRY IN THE CARNMENELLIS GRANITE, CORNWALL

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Minerals of the columbite-tantalite group are rare in Britain, though workable deposits occur in various parts of the world (e.g. Fetherston, 2004). They are usually found in Li-rich granite pegmatites and are often associated with other rare Ta-bearing species such as ferrotapiolite, microlite or wodginite. The first British record for columbite-tantalite was from the Meldon aplite, Okehampton, Devonshire (von Knorring, 1951) where it occurs as dark brown well-formed crystals to 0.3 mm. Backscattered imaging later showed the columbite-tantalite to be strongly zoned (von Knorring and Condcliffe, 1984). Columbite has subsequently been reported from the Chiapaval pegmatite, South Harris, Outer Hebrides (von Knorring and Dearnley, 1959 and 1960) where crystals up to nearly 4 cm were found though most were much smaller. Hodgkinson and Clark (1977) found small platy crystals up to 5 mm with the largest fragments up to 2 cm in pegmatite veins in Gunheath Pit near St. Austell, Cornwall; these crystals were rich in Ti, W and Sc. Jackson (1982) listed columbite-tantalite as one of the accessory minerals associated with gem quality elbaite in a Li-pegmatite in Glenbuchat, Aberdeenshire, but did not describe them. In addition to these occurrences Beddoe-Stephens and Fortey (1981) noted columbite grains to 180 μm associated with W mineralisation at Carrock Fell mine in the English Lake District, and Webb *et al.* (1992) report columbite-tantalite (crystals <20 μm across) from a zinnwaldite granite and greisen associated with a W-bearing vein at Glen Gairn, Aberdeenshire. Not too far away, in the Lui drainage basin near Braemar, Aberdeenshire, panned concentrates with high Nb contents were first identified in 1971. X-ray diffraction studies followed in 1974 and columbite was identified. The source of the mineralisation is not known although it is undoubtedly related to the

Cairngorm granite complex (Beer and Bennett, 1988). This was confirmed by Barritt (1983) who identified microscopic ferrocolumbite crystals in the main Cairngorm pluton. More recently Scott *et al.* (1998) found grains of columbite and a little tantalite to 60 μm in heavy mineral concentrates from waste material at Goonvean and Rostowrack clay pits in central Cornwall.

Ferrocolumbite has now been found in specimens collected in 1995 from material that came from a pegmatite-linedmiarolitic cavity in the Carnmenellis granite at the SE end of the main level at Chywoon quarry, Longdowns, Penryn (NGR SW 748 348). The cavity had recently been blasted and much of the material was found lying about nearby, fortunately most of it undamaged. Part of the pegmatite was still in situ but only a small amount of this could be removed due to safety considerations. The cavity contained well formed crystals of alkali feldspar up to 9 cm long which occur as contact twins in both Carlsbad and Baveno habits, quartz, a brown mica and albite together with a little pale blue apatite and, on one specimen only, a very small amount of bertrandite. The ferrocolumbite crystals are well formed, almost square and tabular on [010]. The largest undamaged crystals are 1.5 mm across and 0.2 mm thick. Only the three pinacoid forms [100], [010] and [001] are present. The crystals are black, often striated and have a moderate lustre. They are all found on edge, partially embedded on the [010] faces of the alkali feldspar. One pair of contact twins on [201], the so-called 'butterfly twins', was found. The square tabular crystals are usually in groups of two or three and make attractive specimens. It seems likely that these are among the best examples of this mineral found in the British Isles to date.

Back-scattered imaging of the columbite-tantalite from Chywoon (Fig. 1) using the

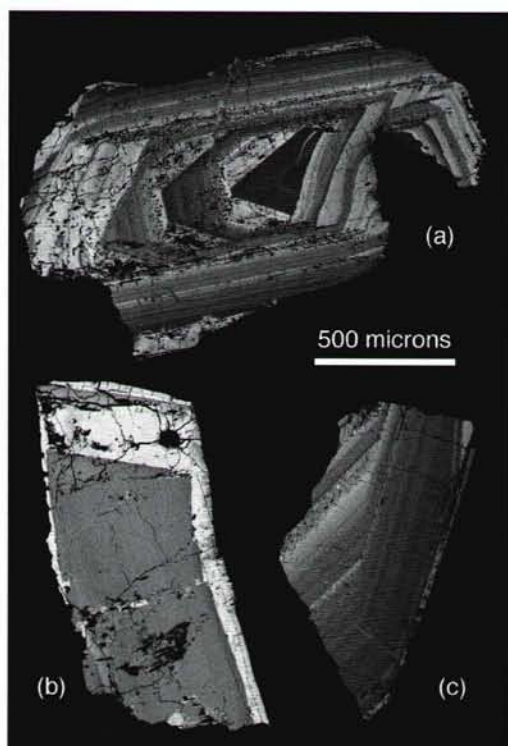


Figure 1. Backscattered electron images of ferrocolumbite from Chywoon quarry. Grains (a) and (c) exhibit oscillatory zonation whereas grain (b) shows a simpler pattern from a Ta-poor core (medium grey) to a Ta-rich rim (light grey).

scanning facilities of the Cameca SX100 electron microprobe at the Open University revealed complex oscillatory zonation and indicated large differences in mean atomic number between zones as shown by the variation in grey levels of the images. Similar oscillatory zonation in columbite-tantalite in Canadian pegmatites has been taken to indicate primary magmatic crystallisation (Tindle and Breaks, 2000).

Minerals of the columbite-tantalite group have the general formula AB_2O_6 in which the A position is occupied mostly by Fe and Mn, and the B position mostly by Nb and Ta. The end-members ferrocolumbite $FeNb_2O_6$, manganocolumbite $MnNb_2O_6$ and manganotantalite $MnTa_2O_6$ are all orthorhombic minerals as is ferrotantalite $(Fe > Mn)(Ta > Nb)_2O_6$. The latter species however is not an end-member. The end-member composition $FeTa_2O_6$ belongs to ferrotapiolite, a tetragonal species of the tapiolite group. All these species can be represented on the columbite-tantalite quadrilateral (Fig. 2).

Previous work on columbite-tantalite species, mainly from LCT (lithium-caesium-tantalum enriched) complex rare-element pegmatites has shown that crystal fractionation often controls

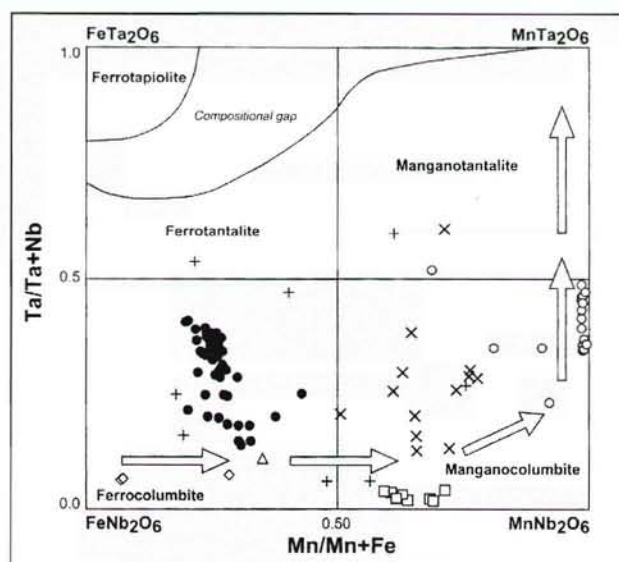


Figure 2. Columbite-tantalite compositional quadrilateral. Compositional gap separates tetragonal ferrotapiolite from orthorhombic ferrotantalite and manganotantalite and is based on a large database of columbite-tantalite analyses collected from Canadian (Ontario) REE pegmatites (Breaks *et al.*, 2003). Symbols: ● Chywoon pegmatite; ◇ Cairngorm granite (Barritt, 1983) △ Chiapaval pegmatite (von Knorring and Dearnley, 1960); ○ Meldon aplite (von Knorring and Condliffe, 1984); □ W-rich veins at Carrock Mine (Beddoe-Stephens and Fortey, 1981); + topaz granite and pegmatite, St Austell (Hodkinson and Clark, 1977, and Scott *et al.*, 1998); × Glen Gairn granite (Webb *et al.*, 1992).

compositional variation and a series of vectors plotted on Fig. 2 shows one such idealized trend for lepidolite sub-type pegmatites. Published columbite-tantalite data from the Cairngorm granite (Barritt, 1983), Chiapaval pegmatite (von Knorring and Dearnley, 1960), Carrock Fell W deposit (Beddoe-Stephens and Fortey, 1981) and Meldon aplite (von Knorring and Condliffe, 1984) all fall along this trend and although this does not mean that they are lepidolite-subtype pegmatites, it probably does mean that they represent primary compositions whose variation was controlled by crystal fractionation processes. Other published data from topaz granite and pegmatites exposed in china clay pits within the St. Austell granite complex (Hodkinson and Clark, 1977; Scott *et al.*, 1998) and greisen-related mineralisation at Glen Gairn (Webb *et al.*, 1992) clearly do not show this systematic variation, almost certainly because the columbite-tantalite has recrystallised during a later hydrothermal event. Such hydrothermal alteration is extensively developed in the case of the china clay pits. The effect of this process is to destroy any original compositional trends.

Table 1. Selected EMPA analyses of ferrocolumbite from Chywoon quarry.

Grain	a	a	a	a	a	b	b	b	b	c	c
CaO	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.70	0.01
FeO	13.45	9.20	13.53	13.79	13.21	12.94	13.94	14.06	13.03	12.07	13.08
MnO	5.99	2.80	4.87	4.30	5.72	4.68	3.53	4.13	5.11	5.19	6.35
TiO ₂	3.31	9.98	5.29	4.06	2.94	4.89	1.89	1.30	3.20	2.83	2.26
Nb ₂ O ₅	57.75	36.15	51.33	47.91	55.16	45.62	37.02	42.75	49.41	45.67	59.43
Ta ₂ O ₅	14.76	29.43	19.96	24.97	19.40	28.94	41.63	35.55	25.61	29.11	16.38
SnO ₂	0.18	0.31	0.31	0.13	0.01	0.24	0.13	0.07	0.08	0.11	0.07
WO ₃	4.62	1.67	3.27	3.47	2.26	1.80	2.21	2.89	2.32	2.68	2.22
PbO	0.32	0.36	0.21	0.19	0.21	0.26	0.15	0.15	0.31	0.23	0.25
UO ₂	0.12	3.16	0.26	0.24	0.77	0.22	0.06	0.00	0.76	0.82	0.41
Bi ₂ O ₃	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sc ₂ O ₃	0.00	0.25	0.04	0.07	0.04	0.03	0.06	0.07	0.16	0.07	0.04
Total	100.55	93.32	99.08	99.13	99.72	99.63	100.62	100.97	99.98	99.48	100.50
Number of ions based on 6 oxygens											
Ca	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.001
Fe	0.671	0.517	0.693	0.725	0.676	0.682	0.781	0.766	0.682	0.647	0.656
Mn	0.303	0.159	0.252	0.229	0.296	0.250	0.200	0.228	0.271	0.282	0.322
Ti	0.149	0.504	0.243	0.192	0.135	0.232	0.095	0.064	0.151	0.136	0.102
Nb	1.558	1.098	1.421	1.362	1.526	1.300	1.121	1.259	1.399	1.324	1.610
Ta	0.239	0.538	0.332	0.427	0.323	0.496	0.758	0.630	0.436	0.508	0.267
Sn	0.004	0.008	0.008	0.003	0.000	0.006	0.003	0.002	0.002	0.003	0.002
W	0.071	0.029	0.052	0.057	0.036	0.029	0.038	0.049	0.038	0.045	0.034
Pb	0.005	0.007	0.004	0.003	0.003	0.004	0.003	0.003	0.005	0.004	0.004
U	0.002	0.047	0.004	0.003	0.010	0.003	0.001	0.000	0.011	0.012	0.006
Bi	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sc	0.000	0.014	0.002	0.004	0.002	0.002	0.003	0.004	0.009	0.004	0.002
Total	3.006	2.922	3.011	3.004	3.008	3.005	3.004	3.003	3.004	3.011	3.005
Mn/(Mn+Fe)	0.311	0.235	0.267	0.240	0.305	0.268	0.204	0.229	0.284	0.303	0.330
Ta/(Ta+Nb)	0.133	0.329	0.190	0.239	0.175	0.276	0.404	0.333	0.238	0.277	0.142

Voltage 20kV; probe current 20nA; beam diameter 10µm; standards - a range of natural and synthetic minerals. The analysed grains a-c are embedded in a single 25mm block held at the Department of Earth Sciences, The Open University, Milton Keynes.

Analyses of columbite-tantalite from Chywoon confirms that all zones seen in Fig. 1 fall within the ferrocolumbite field (see Table 1) and define a weak trend pointing to the ferrotapiolite end-member. Individual analyses fall along this trend in a non-linear pattern consistent with oscillatory crystallisation, although grain (b) is more systematically zoned with a relatively Ta-poor core and a Ta-rich rim. Compositional variation of this nature is very unusual, though a similar pattern has been reported from the Drope Township columbite-molybdenite pegmatite in Ontario, Canada (Breaks *et al.*, 2003). These authors suggested an origin involving a pegmatite-forming melt that was contaminated by host rocks early in its history.

The origin of the Chywoon ferrocolumbite must remain enigmatic for the time being. Ferrocolumbite forming euhedral crystals in miarolitic cavities attached to and partially overgrown by large euhedral alkali feldspar crystals is an extremely rare occurrence and there are no other examples with which to directly compare it. However it almost certainly formed under late magmatic conditions as one of the final episodes in the crystallisation of the Carnmenellis granite pluton.

The authors wish to thank the management of Lawer Bros., the operators of Chywoon quarry for allowing one of them (DM) to collect specimens there. They would also point out that access is no longer normally permissible.

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COTUNNITE FROM PENRHYN DU MINE, GWYNEDD, WALES

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Cotunnite, PbCl_2 , is a rare mineral which typically forms as an alteration product of galena in arid saline environments or as a volcanic sublimate in fumeroles (Anthony *et al.*, 1997). It was first identified in the British Isles during a survey of the minerals of the Leadhills-Wanlockhead mining district undertaken in the

1950s by A.K. Temple (Temple, 1954; 1956). Two locations for cotunnite were noted: High Pirn Mine, Wanlockhead, Dumfries and Galloway, and Hopeful Vein, Leadhills, South Lanarkshire. To the author's knowledge, cotunnite has not been found by subsequent researchers in the Leadhills district and the whereabouts of Temple's original

specimens is unknown, but the original X-ray films were present at Leeds University in the 1980s. Cotunnite has recently been identified at Clevedon Beach, North Somerset (Bridges, 2003). It has also been recorded as an artefact growing on fused lead recovered from the wreck of the fire-ship 'Firebrand' in the harbour at Falmouth, Cornwall (Russell, 1920).

Penrhyn Du Mine near Abersoch, Gwynedd was worked sporadically for lead and silver from about 1630 until 1870 (Bennett and Vernon, 2002). The mine was operated via four adits and a number of shafts on a near-vertical east-west trending fissure vein known as the Main Lode, and two adjacent NNW-SSE trending veins. These cut Ordovician mudstones of Arenig age and the underlying Cambrian sediments (Cattermole and Romano, 1981). The Main Lode, which can be traced west of Penrhyn Du for over three kilometres, was also worked by the Assheton, Tan-y-Bwlch, Pantgwyn, Daugoch and Port Nigel mines. At its western end it is exposed in coastal cliffs near the headland of Penrhyn Du, and the two smaller unnamed galena-bearing veins, crop out a little further south.

Cotunnite was collected in situ from below the High Water mark from the most southerly of the two unnamed veins described above (NGR SH 326 261). It was found as whitish translucent tapering bladed crystals to 4 mm in a cavity in oxidised galena associated with a few tiny sulphur crystals. Identification was by XRD (X-ray reference number MANCH:XRD727). Nearby cavities contained the lead chloro-carbonate phosgenite which also occurs in loose blocks of vein material from around the outcrop of Main Lode approximately 100 m further north (Hubbard, 1991).

At Penrhyn Du Mine, which is the first reported Welsh locality for cotunnite, the environment in which the mineral formed is closely similar to that described at Clevedon Beach (Bridges, 2003). Theoretical data together with years of fieldwork show that cerussite or phosgenite rather than cotunnite are the minerals that would normally be expected to crystallise when galena veins oxidise in this environment. Cotunnite is only able to form if the chloride ion activity is increased a little by evaporation and other common ions are buffered (Bridges, 2003). This requires a relatively unusual set of conditions, which probably accounts for the rarity of cotunnite compared to cerussite and phosgenite in coastal lead vein exposures.

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AN UPDATE OF THE SUPERGENE MINERALOGY OF HILTON MINE, SCORDALE, CUMBRIA

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Eight supergene minerals, including the first reliable reports of the arsenates adamite and mimetite in the Alston Block of the Northern Pennine Orefield, are described from Hilton Mine, Scordale, Cumbria. They occur as small and generally inconspicuous crystals and crusts in cavities in iron-stained quartz-fluorite veinstone.

INTRODUCTION

Hilton Mine is situated near the head of the Scordale valley on the western escarpment of the Pennine Hills, Cumbria in the vicinity of NY 762 228. The geology, mineralogy and structural setting are described by Dunham (1990). Hilton Mine exploited vein mineralisation and metasomatic replacement deposits in the Melmerby Scar and Robinson limestones (Dinantian), which proved especially rich at or near the base of the overlying Whin Sill. The mine is internationally famous for beautiful golden-yellow penetration-twins of fluorite and large groups of tabular baryte. It is one of the few places in the Alston Block of the Northern Pennine Orefield where baryte and fluorite occur together in significant amounts. An unusual assemblage of nickel minerals, including nickeline, gersdorffite, minor millerite and good small crystalline specimens of annabergite, was found in pods and pockets just below the Whin Sill in 1978/79 (Bridges, 1982). Bridges also noted the presence of cerussite and possible anglesite and erythrite. Erythrite was later confirmed by Bridges and Young (1998) and they also reported aurichalcite, amorphous cadmium sulphide, pyromorphite and gypsum.

With the assistance of the Ministry of Defence, a further underground visit to the mine was made in 1988. It was quite apparent that significant further oxidation of the primary nickel minerals had taken place in the 10 years since the first visits, giving rise to excellent

specimens of annabergite. In 2003 the dumps were inspected as part of a survey of mine dump GCR sites in northern England. There had been significant flooding and as a result some fresh spoil was available for examination. A few blocks of vein material, almost certainly derived from a dump at NY 7637 2271, were collected from the bed of the Great Augill Beck. Detailed examination of the specimen material collected on these visits has revealed a number of supergene minerals new to this mine. These include adamite and mimetite, which have not previously been reliably recorded from the Alston Block.

THE SUPERGENE MINERALS

Eight minerals of supergene origin, which are previously unreported from Hilton Mine are described below. The first three minerals listed came from a single specimen (maximum dimension 10 cm) collected from the nickel deposit in the Dow Scar level flats, which subsequently broke into four pieces. The specimen is porous and is mainly a mixture of quartz and fluorite, heavily iron-stained and encrusted with limonite. Minor galena, pyrite and gersdorffite are present in the matrix, the last partly oxidised to green annabergite. There are numerous small cavities, lined with small quartz and fluorite crystals and occasional small crystals of baryte. The adamite, mimetite and smithsonite described below occur in these cavities. Minor cerussite is also present on this specimen.

ADAMITE, $\text{Zn}_2(\text{AsO}_4)(\text{OH})$

Adamite is an uncommon mineral which is typically found in the oxidation zones of zinc-rich orebodies in which primary arsenic minerals are also present. On the above specimens, the adamite occurs in cavities mainly as white to pale yellow subhedral crystals to 0.5 mm. The surfaces of most of these crystals are at least slightly etched, indicating some remobilisation of zinc and arsenate. However, in one cavity, the crystals are lustrous and pale yellow. Identification was by XRD (X-ray reference number MANCH:XRD905) supported by SEM EDAX which showed zinc and arsenic to be the only elements present with an atomic number greater than ten. This is the first report of adamite from the Alston Block of the Northern Pennine Orefield. Associated minerals are mimetite and smithsonite. A micromount specimen is preserved in the Manchester Museum mineralogy collection under the accession number N18020.

MIMETITE, $\text{Pb}_5(\text{AsO}_4)\text{Cl}$

Mimetite is commonly found in the supergene oxidation zones of lead and arsenic-rich orebodies. Brief mention of mimetite at a number of localities in the Northern Pennines is made in Greg and Lettsom (1858), but subsequent research has failed to uncover any specimens (Bridges and Young, 1998). It seems likely that the early references to mimetite in the area refer in fact to pyromorphite.

At Hilton Mine, mimetite has been identified as an inconspicuous white encrustation in some of the cavities in two fragments of the above specimen. Under a stereomicroscope at high magnification, the crusts are seen to be composed of interlocking masses of minute acicular crystals up to 0.2 mm in length. Examination by SEM EDAX revealed the presence of lead, arsenic, and chlorine in the crystals, but no phosphorus. The crusts were subsequently identified by XRD as mimetite (X-ray reference number MANCH:XRD906). This is the first positive report of mimetite from the Alston Block of the Northern Pennine Orefield. A micromount specimen is preserved in the Manchester Museum mineralogy collection under the accession number N18021.

SMITHSONITE, ZnCO_3

Smithsonite is fairly common in the Northern Pennines (Bridges and Young, 1998). There are numerous white crystals on the largest of the fragments of the above specimen, all in small

cavities. These are usually irregular and rounded, but some are three and six-sided prisms up to 1.5 mm long, many resembling a common form of pyromorphite. Smithsonite has also been found on specimens from elsewhere in the Dow Scar level flats and also in material from the surface spoil heaps. Identification was by SEM EDAX and XRD (X-ray reference number MANCH:XRD967).

ANGLESITE, PbSO_4

Anglesite occurs in small quantities at many sites in the Northern Pennine Orefield (Bridges and Young, 1998). It has now been confirmed from Hilton Mine where it occurs as typical colourless elongated prismatic crystals up to 2 mm in length associated with partly oxidised galena and fluorite from the Dow Scar level and from specimens collected from the bed of the Great Augill Beck. Identification was by XRD (X-ray reference number MANCH:XRD827).

CALCITE

While mainly a primary mineral, calcite also occurs as complex lustrous clear 'nailhead' crystals to 2 mm across in cavities in a well-oxidised iron-stained fluorite and galena matrix. These crystals are almost certainly supergene in origin.

HYDROZINCITE, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$

Hydrozincite is common in the Northern Pennine Orefield as white crusts which form as a result of post-mining oxidation on the walls of abandoned mines and on rocks in zinc-rich mine dumps (Bridges and Young, 1998). At Hilton Mine, hydrozincite occurs as bright fluorescent white amorphous looking crusts and masses in cavities in zinc-rich ore. Identification was by XRD (X-ray reference number MANCH:XRD833).

LIMONITE

Uncharacterised hydrated iron oxides are abundant in the mine and on the spoil heaps and are best referred to as limonite.

ROSASITE, $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$

Rosasite is a rare mineral in the Alston Block of the Northern Pennine Orefield. It has been reported only from Closehouse Mine, Lunedale and West Pasture Mine, Stanhope (Bridges and Young, 1998). At Hilton Mine rosasite has been identified as blue-green crusts made up of spherulitic masses to 0.3 mm across on iron-stained fluorite matrix (X-ray reference number MANCH:XRD1001).

CONCLUSION

The dumps and underground exposures where the minerals described above were collected are part of the Scordale Mines GCR site. Examination of a relatively small number of specimens from the site has revealed the presence of eight previously unrecorded minerals including two arsenates which are new to the Alston Block. This demonstrates the value of fieldwork and the systematic examination of well curated mineral collections. The discovery of adamite and mimetite increases the number of supergene arsenates known from Hilton Mine to four.

Representative specimens of the adamite and mimetite have been placed in the collections of Manchester University Museum.

ACKNOWLEDGEMENTS

We would like to thank the Department of Earth Sciences at the University of Manchester for access to analytical equipment. DG would like to thank the landowners and English Nature for permission to visit the Scordale mines and collect representative specimens in 2003.

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Journal of the Russell Society, **8**(2) 110-111 (2005).

KEGELITE, A FIRST BRITISH OCCURRENCE, FROM WANLOCKHEAD, DUMFRIES AND GALLOWAY, SCOTLAND

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Kegelite, $\text{Pb}_8\text{Al}_4\text{Si}_8\text{O}_{20}(\text{SO}_4)_2(\text{CO}_3)_4(\text{OH})_8$, is a rare mineral which was first reported from Tsumeb in Namibia (Medenbach and Schmetzer, 1976; Dunn *et al.*, 1990). It is thought to consist of alternating layers of a smectite and a leadhillite group mineral (Braithwaite, 1991). The name honours Friedrich Wilhelm Kegel who was director of mining at Tsumeb between 1922 and 1938. Kegelite occurs as colourless to white aggregates of flexible pseudo-hexagonal crystals with a perfect basal cleavage in the deep oxidation zone of the Tsumeb orebody. It is found with other lead-rich supergene minerals including alamosite, anglesite, fleischerite,

leadhillite, mimetite and melanotekite. There are two other known occurrences of the mineral in lead-zinc orebodies at the Oceana Mine, Zeehan, Tasmania and at Minge, Ostfold, Norway (Brian Jackson, *personal communication*).

Kegelite has recently been identified on a specimen collected from the Leadhills-Wanlockhead mining field, in southern Scotland. It was found on a small area of fenced-off waste tips which are specifically set aside for mineral collectors on the Glencrieff Mine site at the foot of Whytes Cleuch (NS 866 134). The site is well known to collectors for hemimorphite, which

occurs as hand specimens displaying white to eggshell-blue and green crusts. Many other supergene species occur as microscopic crystals. The mouth of Whytes Cleuch Low Level, a cross-cut that intersected numerous veins beneath Wanlock Dod, is near to the dump, but it is uncertain whether this level was the source of the spoil.

Kegelite was identified on an equant block about 60 mm across. The exterior comprised weathered drusy bladed hemimorphite encrusted with abundant euhedral yellow-brown descloizite crystals up to 0.2 mm long together with a few grey hexagonal tabular vanadinite crystals up to 0.7 mm across. The interior of the specimen revealed kernels of residual galena and bleached light grey mudstone surrounded by irregular cleavages of leadhillite (identified by XRD, reference no. MANCH:XRD1080) generally less than 10 mm across, massive granular cerussite and granular quartz. Kegelite was identified as small patches up to 5 mm across embedded in leadhillite and intimately associated with cerussite. Each kegelite-rich patch comprised numerous tiny coalescing rosettes, 0.2 to 0.3 mm in diameter, made up of radiating pale greenish-yellow fibres. None of these was developed within a cavity so the crystal habit is unknown.

Kegelite was identified by a combination of energy dispersive X-ray analysis (SEM EDAX) and X-ray diffractometry (XRD). Qualitative chemical analysis by SEM EDAX showed the presence of the elements lead, silicon, aluminium and sulphur with an atomic number greater than 10. Subsequent examination by XRD suggested the presence of both kegelite and cerussite in a small fragment which was ground and applied in solvent suspension to a glass slide (XRD reference number MANCH:XRD750).

The interpretation of the XRD pattern was complicated by the perfect cleavage of the mineral, which meant that the scattering intensity of lattice planes lying parallel to the cleavage direction was greatly enhanced while other planes were greatly reduced or absent. This preferred orientation effect is well known in diffractometers which use planar sample holders (e.g. Bish and Post, 1989). Only three reflections which could unambiguously be attributed to kegelite were present in the diffractogram (XRD750), corresponding to the [200], [300] and [700] planes (using the XRD assignments of Dunn

et al., 1990). The intense [100] plane which was outside the scanned area was detected separately. The potential [600] reflection was masked by a cerussite peak but since this was much more intense than it ought to be for pure cerussite it was taken to indicate a combination of both cerussite and kegelite. This accounts for all the expected kegelite reflections of the type {h00} (Dunn *et al.*, 1990). No reflections of the type {0kl} were detected. The pattern was checked against all known lead minerals containing silicate and sulphate together with the carbonates cerussite, hydrocerussite and dundasite. In combination with the SEM EDAX results the XRD data indicates a mixture of kegelite and cerussite. However the dataset is relatively poor due to massive preferred orientation and is not suitable for publication.

The specimen is lodged in the TN collection under registration number 7330.

ACKNOWLEDGEMENTS

We would like to thank the Department of Earth Sciences at the University of Manchester for continued access to analytical equipment.

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EPIMORPHS OF QUARTZ AFTER FLUORITE FROM THE RAMPGILL, COALCLEUGH AND BARNEYCRAIG MINE SYSTEM, NENTHEAD, CUMBRIA, ENGLAND - AN UPDATE

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Figure 1. Epimorph of fluorite in the corner of a fluorite cast from Bounder End Cross vein, Rampgill, Nenthead, Cumbria, specimen width 6 cm.

Bridges and Wilkinson (2003) reported interesting epimorphs after a cubic mineral, presumed to be fluorite, from the Bounder End Cross vein system above the Rampgill Horse Level (NY 782 435) at the High Flat horizon of the Great Limestone. They offered evidence that the original mineral was indeed fluorite on the basis of cubes of fluorite re-growing in perfect alignment with the faces of similar epimorphs from elsewhere in the Nenthead area. Since writing the original note, further interesting specimen material has been found.

An excellent small example of a cube of fluorite growing in the corner of a cast, and in perfect alignment with it, has now been found in the floor of a short level SE of the North String associated with the Bounder End Cross vein (Fig. 1). Some epimorphs from the floor of another cavity in the wall of the same level contained fluorite which is believed to be original, since

there is no sign of fluorite regrowth on empty casts from the same place. The quartz from the base of the cavity is thicker than that from the roof and this may have protected the fluorite from dissolving. Another epimorph (now in the R.A. Sutcliffe collection) consists of very corroded residual fluorite under the quartz surface. While known to be from the Bounder End Cross vein, the precise location is not known. However, the thickness of the quartz suggests it is probably from the flats on the SE side of the horse level. It is considered that these recent finds prove the epimorphs are indeed all after fluorite.

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A TIN-LEAD ALLOY FOUND IN A ZEOLITIC AMYGDALE AT CARSAIG BAY ON THE HEBRIDEAN ISLE OF MULL

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Mull, the second largest island in the Inner Hebrides, is dominated by two lava flow sequences each approximately 1km thick. These were erupted in the Palaeocene during opening of the North Atlantic and were subsequently intruded by acid and basic magmas from the central igneous complex. The Central Group (Richey, 1961) occurs in central and southeast Mull and on Ulva, and formed mainly in a subsidence caldera with three concentric zones. It overlies the Plateau Group which consists of the Pale and Main Suites of Ben More, and the Staffa Suite of southeast Mull and the adjacent islands.

Zeolite minerals are abundant in the Mull lavas and G.P.L. Walker (Walker, 1970) suggested, for the purpose of mapping, that five discrete amygdale mineral assemblages can be recognised in the basalts of Mull and the adjacent mainland (Morvern). The assemblages are named as "carbonate", "mesolite", "laumontite", "prehnite" and "epidote" based on the presence of an index mineral. Walker pointed out that the localities containing these assemblages are not randomly distributed, as each can be seen in well-defined areas. On the basis of his records of some 520 localities, he constructed the map reproduced here as Figure 1.

The Plateau lavas, which are mainly olivine-rich basalts, are evident in Carsaig Bay on the south coast of Mull, and the Walker assemblage at this locality is the laumontite assemblage containing mesolite, thomsonite, analcime, chabazite, heulandite, laumontite with some gyrolite, apophyllite and tobermorite. In the early 1980s an unusual sample was collected by one of us (BT), in the presence of two of the other authors (AD, CDW), from this locality at grid reference NG 534 213. An amygdale



Figure 1. Zones of amygdale minerals in Mull and Morvern showing localities on which they are based. Figure reproduced from Walker (1970). Localities-•.

was broken open to reveal three, ~1mm diameter, near-perfect spheres of silvery appearance. These were resting on zeolite crystallites, visually identified as analcime, rather than the host basalt. Figure 2 shows one of these spheres selected for further study.

Viewed on an illuminated microscope stage the sphere is solely silver in appearance, and of high surface reflectance. This reflectance is the source of the colours in Figure 2. The brown colour is reflected from the underlying stained analcime. This staining is probably caused by iron oxide but is perhaps from a coating of lead oxide - this was not confirmed. The other tones come from the background against which the photograph was taken.

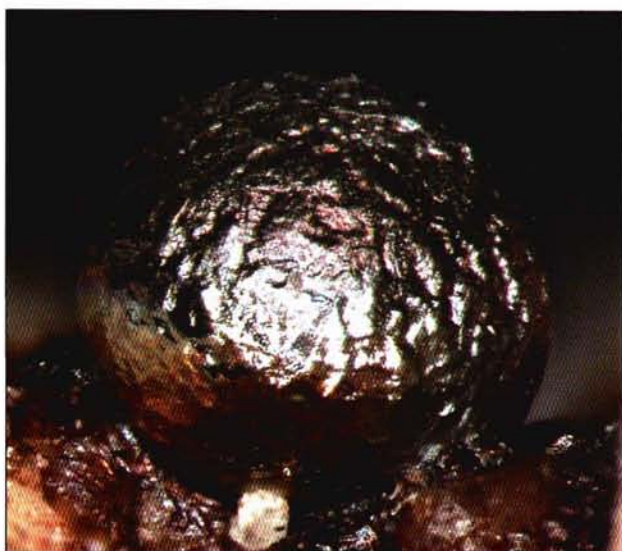


Figure 2. Near-perfect spherical ball of silvery tin-lead alloy from Carsaig Bay, Mull. Diameter 1mm.

The nature of the sample was such as to require a non-destructive analysis and this has delayed examination of this unusual find. With recent developments in scanning electron microscopy such a non-invasive examination became possible at the University of Wolverhampton. Tests used a Zeiss EVO 50 EP, which carries out scanning electron microscopy at ambient temperature coupled with elemental analyses. Analyses performed at 66 Pa and 20KeV, with a working distance of 8.5mm, showed the sphere chosen for examination to be composed only of elemental tin and lead, in near equal proportions. This mirrors the proportions used in commercial solders that have a melting temperature of about 216°C (Handbook of Chemistry and Physics, 1974/5).

We are not aware of any mineralisation involving tin or lead minerals on Mull, although there are unconfirmed reports of a silver occurrence, or silver mine, somewhere near Carsaig (Hedde, 1901).

Our attention has been drawn to the work of Dekov et al. (2001) who have identified particles of metal alloys in samples from the Mir hydrothermal field obtained from a gravity core taken as part of the Trans-Atlantic Geotraverse. They carried out detailed chemical analyses of the particles and compared them to similar particles found in alluvial placers from the Central Urals and in basic rocks from the Siberian platform. Amongst the Mir samples some 20% were said to be spherical. These workers have provided an extensive discourse in which possible genesis mechanisms were considered. This included a considered rejection

that they might be anthropogenic or technogenic in origin. Their conclusions were that the particles were of natural origin and one possible formation route was that of reduction from a silicate melt formed magmatically during the evolution of ridge crest systems. Another possible route was from hydrothermal seepage. They suggest that Sn-Pb alloy could crystallise out as "stannian lead" at temperatures near 183°C.

When considering zeolite genesis in Icelandic geothermal zones, Kristmannsdottir and Tomasson (1978) suggest that analcime can be formed at temperatures up to 300°C. This would be consistent with its prior formation in the Mull Plateau lavas to the stannian lead phase via either of the routes suggested by Dekov *et al.*, with a hydrothermal seepage route, perhaps, being favoured.

ACKNOWLEDGEMENT

Our sincere thanks are due to Dr Norman Moles for drawing our attention to the work of Dekov and co-workers.

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Book Reviews

Minerals: Their Constitution and Origin
by Hans-Rudolf Wenk and Andrei Bulakh.
Cambridge University Press, Cambridge,
2004, pp 646.
ISBN: 0 521 52958 1 (paperback);
0 521 82238 6 (hardback)
Price: paperback £35, hardback £95

The authors describe this book as an "introduction to mineralogy for undergraduate students and graduate students in all fields of geology, materials science, and environmental sciences, and for those with a general interest in the subject" (my italics). Knowledge of basic high school physics and chemistry is assumed, and the text includes highlighted boxes of additional technical, enrichment, or mathematical details. The book is divided into five parts subdivided into chapters. Each chapter ends with self-assessment questions and suggestions for further reading.

The first part commences with a brief historical background to mineralogy, and then goes on to deal with structural features of minerals. This starts by explaining how elements create bonds as part of the process of forming minerals, and then builds to a detailed exposition of crystallography that includes the unit cell concept, lattices and simple symmetry. The chapter then goes on to considerations of crystal morphology related to space groups, followed by crystal growth and habit, twinning and crystal defects.

The second part covers the many methods employed to identify minerals and their internal geometries. This is wide ranging and, of necessity, succinct. Despite the wide coverage the authors have provided a sound introduction for students, to emphasize the tools that are available to the modern mineralogist.

There are some criticisms to be made. One would have hoped that the authors might have explained the "luck" needed to complete an identification by using the three strongest lines in a powder x-ray diffractogram can now be aided by computer search. They mistake the technique of nuclear magnetic resonance for the more specialized branch involving magic angle spinning NMR, and it is spectra from this

technique that are displayed in the text. Smaller criticisms are the omission of tin as a Mössbauer active element, and the absence of any coverage of thermal analysis techniques.

The third part introduces the wide variety of existing minerals, with their classification and also describes natural mineral-forming processes. Its depth of coverage is varied. A simple chapter relates to the identification of mineral hand specimens, in sharp contrast to the earlier sophistication of the instrumental techniques in the previous part – but essential to the beginner in the field. Other chapters go to greater depth in introducing the importance of thermodynamics, phase diagrams and crystallization from melts to the study of mineral systems.

Part four, comprising close to 50% of the book, is a systematic review of mineral groups which approaches the various groups from a mainly mineralogical perspective. This has the result that, to this reviewer, the logical progression from silica to silicates is disrupted. The authors have included feldspars in a new class of minerals namely "alumosilicates as opposed to aluminosilicates in which at least some Al^{3+} is in octahedral coordination". This can only lead to confusion in a student mind, particularly as it is reversed in a later section!

It would have been expected that a book of this standard should include the IMA reclassification in 1998 of leucite as a zeolite and the inclusion of framework structures composed of elements other than aluminium and silica as part of the zeolite group.

The section detailing this mineral group contains several errors. Mazzite, a zeolite that is only known at one locality, is described as a common framework mineral. Zeolites are said to lose cations on heating which can subsequently be regained by ion exchange – which is quite incorrect, and discussion of these highly useful minerals makes no distinction between those uses for which natural zeolites are employed and those which require their synthetic analogues – some, but by no means all, are known in nature. The authors also state that all zeolites are originally white! These errors detract from what is otherwise a good coverage of minerals, common and more obscure, and the reader will benefit from the clear diagrams and photographs that supplement the textural coverage.

The last part of the book is devoted to applied mineralogy. This part gives an overview of metalliferous deposits, their geological setting, and metal production round the world. Gemstones are given a separate section which includes their synthesis. Likewise cement minerals are covered - with their problems - although high alumina cement is not mentioned. The wide-ranging nature of this final part is illustrated by discussion of minerals in the body, with health hazards, followed by the mineral composition of the solar system. The final chapter deals with the mineral composition of the Earth.

Despite the unfortunate errors mentioned above, and several typographical errors, there is much of value in this book. Most of the text is clear and appropriate to the level intended. The interested non-student reader can ignore some of the deeper treatments (as the authors suggest) and still gain knowledge over the wider range of mineralogy to further their interests. The cost of the paperback version should not be too costly for those "with a general interest the subject" - or as an acceptable present?

Alan Dyer

Minerals and their Localities, by Jan Bernard and Jaroslav Hyrsl.

Hardcover, 807 pages, 2004.

Published by Granit, s.r.o.

ISBN 80-7296-039-3.

Price: £70-90, depending on source.

This is a heavyweight tome in more than one sense of the word - as well as spanning some 4200 minerals, 8500 localities, and 807 pages, it weighs in at around 3 kg so is not a book to consider taking on holiday as your in-flight reading material. The book is in two parts, and - unsurprisingly given the title - the major portion of the book (some 680 pages) is given over to mineral descriptions, and the bulk of the remainder to locality lists.

The main text is organised alphabetically, and covers all species known up to the end of 2003 or thereabouts. A short addendum on p806 adds a few minerals published early in 2004. As a result, it is current for all but the most determined of species collectors.

The entry for each species gives the chemical formula, the crystal system, space group and axial data, the strongest XRD lines, and standard information about physical characteristics such as colour, habit and cleavage. This is followed by a useful descriptive section covering where and how the species occurs. Finally, there is a reference to the mainstream professional journals for those seeking further information.

Perhaps 10% of species have a colour photograph. Unusually, these are of typical specimens rather than museum quality 'one-offs' and so they are relevant to material that a collector will see. The photographs are of good quality, and essential information about field of view or specimen size is given. Most of the examples featured are in the 2-5cm size range so again are typical of material that is available on the market.

Localities are also listed alphabetically, and for each is given a list of the species found there. Unfortunately these lists are far from complete. For example, the page on 'richest localities' states that there are 241 species from Tsumeb, but only 136 are listed by name under the locality entry. Some of those missing are not excessively rare there, e.g. gartrellite and susannite.

Perhaps inevitably in a book of this nature, there is the odd typo, but I was disappointed to see that some of the information is quite old. Using Tsumeb as an example again, the 'richest localities' entry references a 15 year old book, and recites 15 year old data, apparently ignoring more recent works.

Despite the problems with locality data, this book is well worth having as a reference if you are an advanced systematic collector or a micromounter like me, but given the relatively low number of UK localities mentioned it may be of less interest to the specialised collector of British minerals.

Rick Turner

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.

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