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FRONT COVER:
Pale blue fluorite cubes (to 15 mm) with minor hematite on cream dolomite. Florence Mine, Egremont, Cumbria. David Green photograph.

BACK COVER:
Paracelsian. Crystal aggregate 70 mm tall with individual crystals to 25 mm in length. Ex. G.J. Williams collection. NMW 27.111.GR.387. Photo M.P. Cooper.
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Editorial

Once again we have a ‘bumper’ issue packed with interesting articles, varied in terms of mineralogy, geographical area, and dare I say it, technical difficulty. Something for everyone’s taste I hope, reflecting the diversity of individuals’ interests within the Russell Society. Please note that I have not picked a selection of articles from a range on offer; the responsibility for this diversity lies entirely with the authors who contributed their material. To gather and scrutinise mineralogical information, and craft this material into thought-provoking and scientifically accurate articles – with the invaluable guidance of a hidden team of volunteer reviewers – is an admirable skill. It is noticeable, however, that the same author’s names are repeated in the contents lists, volume after volume. As Editor I appeal to readers who have not yet published in the Journal, or have done so very infrequently, to take the initiative and ‘put finger to keyboard’. If in doubt, consult me – or one of our ‘regular’ contributors – we will be pleased to help.

Many geology students and mineralogists, both professional and amateur, have had the memorable experience of an underground tour of the Florence Mine in Cumbria. With the closure of Florence, it is timely to review its geological and mineralogical legacy, and Brian Young presents a fascinating account. The unique legacy of another important mine, Benallt Mine on the Lleyn Peninsula, North Wales, is reviewed by Tom Cotterell who reports recent finds of rich specimens of Benallt’s type minerals such as paracelsian.

Trevor Bridges, who is always keen to develop readers’ understanding of geochemistry, has contributed a highly crafted article on the Mendips’ unique lead oxychloride assemblage. This follows on from the epic paper by Rick Turner and Mike Rumsey published in JRS Volume 13. Trevor uses geochemical principals (stability field diagrams) to demonstrate the relationships between the identified mineral species and the likely process of their formation. Importantly he concludes with a list of unsolved problems and recommendations for resolving them. This message is clear: there is always scope for more research, discovery and mineralogical insight.

Other articles in this volume describe copper mineralisation in Forcett Quarry, North Yorkshire and at Rassal Mine in the Scottish Highlands, native mercury in Derbyshire, wolframite and associated supergene minerals in the Mourne Mountains, hydrozincite from Swaledale in the Northern Pennines, and chalcoalumite from southwest England. Enjoy reading these, be inspired to make more mineralogical discoveries, and share them by contributing to Volume 16!

Norman Moles
Honorary Journal Editor
GEOLGY AND MINERALISATION AT FLORENCE MINE, EGREMONT, CUMBRIA

Brian YOUNG

Department of Earth Sciences, University of Durham, South Road, Durham DH1 3LE

The final closure of Florence Mine, the last of West Cumbria’s large hematite mines, in 2007, brought to an end an important chapter of British mining history. Known throughout its long working life as an important source of fine specimens of hematite and associated gangue minerals, the mine was also the last accessible site at which hematite orebodies of this sort could be studied in their true geological context. A detailed survey of the geological and mineralogical features, exposed within the underground workings immediately prior to closure, enabled key features of the orebody to be recorded and interpreted before being lost forever when the mine flooded.

INTRODUCTION

Florence Mine [NX 018 102] was the last working iron ore mine within the formerly important west Cumbrian iron orefield. It was one of the largest of a substantial number of mines which extracted hematite ore from huge deposits hosted mainly within Lower Carboniferous limestones. Although these deposits have been known and worked for centuries, ore production peaked in west Cumbria in the 19th century, after which a long period of decline from the early years of the 20th century culminated in the end of large-scale mining at the combined Beckermet – Florence mine complex in the late 1970s. A substantial proportion of the costs of pumping the mine water was originally met by British Nuclear Fuels Ltd. (now Sellafield Ltd.) who could use the water for their cooling processes. With the ending of this arrangement in 2007, pumping was stopped and the workings soon became flooded and inaccessible.

Mining and exploration for hematite in Cumbria has long attracted research, resulting in a very substantial technical literature that has focussed primarily upon the origins of the deposits, though few detailed descriptions of the orebodies themselves have been published.

In addition, throughout their long history of mining, these deposits have also attained international celebrity for the high quality of some of their constituent minerals, fine specimens of which figure prominently in most of the world’s major mineral collections.

In its latter years, Florence Mine was designated as a Site of Special Scientific Interest (SSSI) and a Geological Conservation Review (GCR) Site for its unique underground exposures of hematite mineralisation in their full stratigraphical and structural context (Bevins et al., 2010). With the announcement in 2006 of the intention to discontinue pumping it was clear that further mining and all access to the underground working would be impossible with the inevitable flooding of the mine on abandonment. English Nature (now Natural England) therefore commissioned the writer to undertake detailed recording of the remaining accessible geological and mineralogical features then visible in the underground workings (Young, 2007). This paper, which presents a summary of the most significant features of the deposit recorded during the study, is intended to serve as a background description to aid understanding and provide context to the many specimens held in collections from this famous locality.

BRIEF HISTORY OF FLORENCE MINE

Brief historical accounts of Florence, and nearby mines, include those by Smith (1924), Kelly (1994) and Dodd (2010). These mines exploited one of the largest groups of hematite orebodies known in the west Cumbrian orefield.

Sinking of the original shaft, the Florence No. 1 Shaft, began in 1914 and production of ore started in the early 1920s. In order to secure further ore reserves, including a substantial tonnage that would otherwise have remained sterilised within the No. 1 Shaft pillar, the Florence No. 2 Shaft was sunk to a depth of 257 m in 1947, approximately 180 metres north of the No. 1, Shaft (Fig. 1). Connections were subsequently made with the neighbouring Ullcoats and Beckermet mines, and in the 1970s the Florence workings became part of the extensive Beckermet – Florence mine complex which was finally abandoned in 1980. During its working life Florence Mine made a significant contribution to the estimated output of around 100 million tons of hematite from the west Cumbrian orefield.

Following the end of large scale mining at Florence, the Egremont Mining Company, was formed in 1980 to...
exploit remaining ore reserves from a shallow portion of the Florence orebody, known as the Lonely Hearts orebody. This had previously been developed, but only partially extracted, from both the original Florence and neighbouring Ullcoats Mine workings. An inset in the Florence No. 2 Shaft provided the original access to this orebody via the Lonely Hearts, or 1007 foot*, Level, though this was replaced during the 1980s by a 1 in 4 inclined drift, driven from the eastern end of the mine yard east of the shaft, to intersect the Lonely Hearts Level. Once completed, this drift was equipped with rope haulage and thereafter became the main access to the workings for men, ore and materials (Fig. 2). The Florence No. 2 Shaft was retained for pumping, ventilation and emergency access.

Modest tonnages of ore extracted from these workings were sold to specialised steel and pigment manufacturers. During this time, working was dependent upon pumping through the Florence No. 2 Shaft maintaining the mine water level at a few metres beneath the Lonely Hearts workings. A substantial proportion of the costs of pumping around 400 tonnes of mine water per hour was originally met by British Nuclear Fuels Ltd. who retained an option on using the mine water in their nearby Sellafield Plant. With the ending of this arrangement in 2007, pumping was stopped and the workings soon became flooded and inaccessible.

GEOLOGICAL OUTLINE OF THE WEST CUMBRIAN OREFIELD

The west Cumbrian iron orefield lies on the western margins of the Lake District and comprises an arcuate belt of country roughly 1.5 km wide, which extends from Lamplugh, south-westwards through Frizington, Cleator Moor and Egremont, almost to Calder Bridge.

The geological succession present within the orefield, and its immediately adjacent areas, is shown in Table 1.

* The elevation of this, and other, levels within the mine, is based on the Mine Datum adopted during the working of the mine, at 1000 feet (305 metres) below Ordnance Datum (OD). Thus this level lies at 1007 feet (305 m) above Mine Datum, or at 7 feet (2.1 m) above Ordnance Datum. Although recorded on the plans as the 1007 foot Level, this main haulage road was also referred to by the miners as the Lonely Hearts Level: it is henceforth referred to by that name in this paper.
Group for these rocks and this long-established group name is employed for these rocks in this paper.

Conformably overlying the Chief Limestone Group is a succession, between 50 and 110 m thick, composed mainly of rhythmically bedded mudstones, siltstones and sandstones, locally with a few thin limestones and coal seams, known as the Hensingham Group (Eastwood, et al., 1931; Mitchell et al., 1978; Young and Boland, 1992; Ackhurst et al., 1997). These rocks are in turn conformably overlain by the west Cumbrian Coal Measures which comprise up to about 400 m of mudstones, siltstones, sandstones and numerous coal seams. Coal Measures rocks are locally overlain unconformably by a succession, up to 300 m thick, of Upper Carboniferous red sandstones with minor mudstones and siltstones, collectively termed the Whitehaven Sandstone Formation.

Overlying the Carboniferous rocks, and overstepping onto the Ordovician rocks of the adjoining Lake District, is a succession of rocks of Permo-Triassic age, collectively termed the Cumbrian Coast Group, at the base of which occurs locally a variable group of conglomerates and breccias, known in Cumbria as the ‘Brockram’. Near the coast this is overlain by the St. Bees Evaporite Formation, a succession of mudstones with several beds of anhydrite. Overlying and locally overstepping this is the St. Bees Shale Formation which passes upwards into the red sandstones of the St. Bees Sandstone Formation, the local representative of the Triassic Sherwood Sandstone Group.

The west Cumbrian hematite orefield may be considered in two parts. The first comprises the so-called ‘exposed’ orefield north of Egremont. Here, limestones of the Carboniferous Chief Limestone Group, in a narrow belt extending northwards for about 10 km north-east of Egremont, contain numerous large hematite orebodies, many of which crop out at the surface. The second, or ‘concealed’ portion of the orefield extends southwards from Egremont towards Calder Bridge. Here the Carboniferous limestones and their contained orebodies are overlain unconformably by Permo-Triassic rocks. The most recent workings, including those at Florence Mine, lie within this concealed southern portion of the orefield.

The continuity of these solid rocks is considerably disrupted by numerous faults. Prominent amongst these are pre-Triassic normal faults with a predominantly NE-SW trend, known locally as the ‘Coal Faults’. Also prominent are normal faults with a predominantly NW-SE trend and which clearly exhibit both pre- and post-Triassic displacement. In addition, a number of roughly E-W trending faults are present in the Egremont area. Many of these faults have an important effect on the orebodies. Some have clearly controlled the emplacement of ore-forming fluids: some have subsequently displaced the orebodies.

Over substantial parts of the orefield, including the vicinity of Florence Mine, the ‘solid’ rocks are concealed beneath a mantle of Quaternary deposits, mainly till or boulder clay with small areas of alluvial deposits flanking the main rivers and streams.

HEMATITE OREBODIES IN WEST CUMBRIA

The west Cumbrian hematite deposits comprise a substantial part of a wider Cumbrian province of hematite mineralisation that includes deposits in south Cumbria and the central Lake District, many of which share similar mineralogies and exhibit comparable structural and stratigraphical controls (Kendall, 1873-75; Smith, 1924; Trotter, 1945; Rose and Dunham, 1977; Dunham, 1984; Shepherd and Goldring, 1993; Akhurst et al., 1997; Bevins et al., 2010).

The large west Cumbrian hematite orebodies, including those at Florence Mine, are wholesale metasomatic replacements of limestone, commonly closely associated with, or adjacent to, faults. Original features of the limestone, including some fossils, bedding planes, mudstone partings and locally stylolitic contacts, are commonly preserved in the ore (Fig. 3).

Hematite dominates the mineral assemblage. It occurs in a variety of forms, the most abundant of which is a compact massive variety, though more earthy red varieties are found in places. The deposits are famous for the very distinctive reniform fibrous crystalline variety known as ‘kidney ore’ which was locally common. The roughly conical fragments into which ‘kidney ore’ typically breaks, known as ‘pencil ore’, were sometimes employed in making haematite jewellery. The crystallised variety ‘specularite’ was common in some orebodies.

Other ore minerals recorded from the orebodies include pyrite, marcasite, chalcopyrite, galena and the manganese oxide minerals manganite and hausmannite, though these invariably comprised only very minor proportions of any individual orebody (Young, 1987; Young and Nancarrow, 1987).
1990). The deposits have long been internationally celebrated for magnificent examples of gangue, or spar, minerals, including quartz, calcite, aragonite, dolomite, baryte and fluorite, typically found in cavities or vugs within the ore or in the immediately adjacent wallrocks, though these too typically comprised only a tiny proportion of the deposits (Symes and Young, 2008). Fine examples of all of these minerals these have, over the years, been recovered from Florence Mine.

ORIGINS OF WEST CUMBRIAN HEMATITE MINERALISATION

In order to appreciate the nature of the orebodies worked at Florence Mine, and in order to understand the contributions they have made to the concepts of ore genesis, it is appropriate here to summarise very briefly the most recent views on the origins of this important suite of deposits. Much more detailed interpretations of the genesis of these ores may be found both in the references quoted and in the substantial technical literature cited within them.

The origin of the Cumbrian hematite deposits has long been the subject of speculation and controversy. Early views centred on two different potential sources of iron-rich fluids. Kendall (1873-1875) suggested a deep-seated magmatic or hydrothermal source, whereas Goodchild (1889-1890) advocated the leaching of iron by meteoric ground waters from overriding iron-rich rocks such as the St. Bees Sandstone. Rose and Dunham (1977) proposed a model whereby iron, leached by warm hypersaline fluids from the Permo-Triassic sediments of the East Irish Sea Basin, was forced up-dip towards the margins of the Lake District. More recently, Shepherd and Goldring (1993) have suggested that brines expelled from over-pressurised sediments in the East Irish Sea Basin were driven towards the Lake District. There they leached iron from the granites, before being driven upwards through fractures along the western margin of the Lake District.

Both models are consistent with the iron-rich mineralising fluids gaining access to the limestones and Lower Palaeozoic rocks of the Lake District through fractures, both faults and joints, as well as through permeable formations within the Carboniferous and Permo-Triassic sequences.

The role of the permeable Permo-Triassic rocks is of crucial importance in this mineralising process. In west Cumbria, where these rocks rest directly on Carboniferous limestones, ore bodies are commonly present; but where thick impermeable shales of Namurian, Westphalian or Upper Permian age intervene between the permeable Permo-Triassic rocks and the limestones, no orebodies are found. Young (in Jones et al., 1990) has speculated that certain west Cumbrian Coal Measures sandstones, the interstices of which contain concentrations of specular hematite, may have acted as mineralising aquifers in suitable structural settings (Young and Boland, 1992). If so, it is possible that, in suitable situations, undiscovered bodies of hematite may lie concealed west of the known orefield, beneath the Cumbrian Coalfield. Over much of west Cumbria and the Lake District the Permo-Triassic sequence is likely to have had at its base, a variable thickness of permeable breccias or ‘brockrams’, which were overlain by sandstones of the Sherwood Sandstone Group. A permeable route for mineralising fluids is thus likely to have been present over much of the area.

Shepherd and Goldring (1993) have proposed that the hematite mineralisation is the result of the mixing of sulphatic groundwaters with warm, iron-rich, relatively oxidising sulphur-poor, hypersaline brines. They advocate a downward flow of mineralising fluids to account for the distribution of orebodies within the limestones of west and south Cumbria. However, the occurrence of hematite veins within the Lower Palaeozoic rocks of the Lake District, and the distribution patterns for arsenic, barium and fluorine within the deposits suggests some upward flow of mineralising fluids. These authors favour a sedimentary source for the iron. Fluid inclusion data for quartz, fluorite and calcite within the replacement deposits in the limestones indicate formation temperatures of up to 120°C.

The age of the hematite mineralisation has also long been controversial. Shepherd (1973) favoured a middle or late Triassic age, whereas Dunham (1984) argued that the structural and stratigraphical relationships require a post-Triassic age. Using palaeomagnetic evidence a number of authors have proposed a Permian or early Triassic age (DuBois, 1962; Evans and El-Nikhely, 1982; Evans, 1986). In a palaeomagnetic study Rowe et al. (1998) have suggested that hematite mineralisation was emplaced during the Late Carboniferous and Early Permian, though this is very difficult to reconcile with the stratigraphical and structural evidence.

GEOLoGY OF FLOREncE MIInE

The geological succession penetrated by the Florence Mine workings is shown in Table 1. The form, structural and stratigraphical relationships of the orebody are depicted in Figure 4. Brief notes follow on the main geological units penetrated by the Florence workings.

Ordovician – Skiddaw Group

The Carboniferous limestone succession of the Egremont area rests unconformably upon rocks of the Buttermere Formation of the Ordovician Skiddaw Group. These rocks were not exposed anywhere in the recently accessible mine workings, though they were reached in some borings and in the Nos. 1 and 2 shafts of Ulcoats Mine.

Carboniferous – Basement Group

Little is known of these beds in the Florence workings, though clay-rich sandstones that were exposed in a crosscut beneath the Seventh Limestone in the Lonely Hearts workings may be local representatives of these beds.

Carboniferous – Chief Limestone Group

In the southern part of the west Cumbrian orefield, pre-Permo-Triassic erosion has removed all but the very lowest parts of the Lower Carboniferous succession. In the Egremont area, the Brockram rests unconformably upon the
lowest limestones of the succession, referred to as the Chief Limestone Group by Akhurst et al. (1997).

Whereas no detailed correlation of the limestones exposed in the Florence workings was attempted during the study reported here, from descriptions by Smith (1924) and other recent field observations, it seems likely that much, if not all, of the limestone exposed in the most recently accessible workings belongs to the Seventh Limestone of the classic west Cumbrian classification, recently re-named the Frizington Limestone Formation (Holkerian) by Barclay et al. (1997), with perhaps parts of the overlying Sixth Limestone (Late Asbian).

Throughout the Lonely Hearts workings these rocks are typically rather thickly-bedded, pale to medium grey bioclastic limestones in which fragments of shells, crinoids and fragments of coral may locally be seen.

Interbedded with these limestones at several places, are well-laminated pale grey to greenish grey, and locally rather purplish grey, mudstones, mostly up to about 30 cm thick (Fig. 5). These are commonly very smooth, rather slippery rocks, reminiscent of bentonites in both their appearance and physical properties. Walkden (personal communication, in Mitchell et al., 1978) noted bentonitic properties in Asbian mudstones from west Cumbria and, in support of this, Young and Boland (1992) drew attention to the evidence of contemporaneous early Carboniferous vulcanicity in the nearby Cockermouth Lavas (Courceyan). As will also be outlined below, there is evidence that these mudstones may have acted as local barriers to the passage of mineralising fluids.

**Figure 4.** Simplified longitudinal section through Florence - Ullcoats orebody. The section of the Florence Mine workings described in this paper lie within the area outlined in red. After Smith (1924).

**Figure 5.** Mudstone parting within thickly bedded limestone of the Chief Limestone Group, exposed in the Lonely Hearts Drift. The limestone here is virtually unaltered: the dull red colour is due to a surface covering of hematite dust. The hammer handle is approx. 35 cm long. Photo B. Young.

### Permian – Brockram

‘Brockram’ is a Cumbrian term applied to the rather variable group of conglomerates or breccias present at the base of the west Cumbrian Permo-Triassic succession. It is commonly referred to as ‘conglomerate’ on old mine plans and records. Due to the local derivation of its component clasts, this is typically a very variable deposit, both in thickness and in clast composition. In the Lonely Hearts workings, the Brockram was exposed only in the inclined access drift, resting unconformably upon limestones of the
Chief Limestone Group (Fig. 6). Here it comprised a coarse-grained, poorly bedded and poorly sorted clast- to matrix-supported breccia composed predominantly of angular to sub-angular fragments of limestone, accompanied by a few fragments of greywacke, sandstone and siltstone derived from the nearby Skiddaw Group, together with some volcanic lithologies derived from the Borrowdale Volcanic Group, all within a sandy, silty and clay-rich matrix.

**Permian – Cumbrian Coast Group**

This Group, includes the St. Bees Shale and the St. Bees Evaporites (Akhurst et al., 1997). Although no rocks belonging to this group were seen within the most recent Florence workings, the important role of parts of this succession, most notably the St. Bees Shale, in controlling the emplacement of ore-forming solutions, has been noted above.

**Triassic – Sherwood Sandstone Group**

The St. Bees Sandstone is the local representative of the Triassic Sherwood Sandstone Group. Here in west Cumbria it normally comprises fine-grained, sporadically micaceous, reddish brown, rather silty sandstone in beds typically between 0.3 and 1.0 m in thickness, with numerous thin brown mudstone partings, mainly up to a few centimetres thick. A variety of types of cross bedding occur and good small-scale ripple marks are locally common. In places the almost universal dull red-brown colour is replaced, in small irregular lenses and patches up to a few centimetres across, by pale cream to off-white colouration, apparently reflecting localised centres of iron reduction.

Where exposed in the Lonely Hearts Drift, bedding in the St. Bees Sandstone was typically almost horizontal. Within the hangingwall zone of the Ullcoats Fault, exposed in the inclined access drift, dips of up to 40° were common (Fig. 7).

The surface plant at Florence Mine stands on the outcrop of the St. Bees Sandstone and both the No. 1 and No. 2 shafts, together with the inclined access drift, penetrate significant thicknesses of this formation.

**Quaternary deposits**

In the vicinity of Florence Mine ‘solid’ rocks are almost everywhere concealed beneath a mantle of Quaternary deposits of variable thickness. Most widespread is till, or boulder clay, which here comprises a variable assemblage of sandy and stony clays with scattered cobbles and boulders of a variety of rock types. Small and impersistent lenses and pockets of sand and gravel are also present locally within the till sequence. Narrow belts of alluvial clay, silt, sand and gravel flank the River Ehen and its tributary streams in the Egremont area.

Although there are no permanent exposures of Quaternary deposits within the immediate vicinity of the mine, till was cut in sinking the shafts and the inclined access drift. Significant quantities of water, possibly derived from Quaternary deposits, entered the mine through some of the long-abandoned shafts.
Geological structure

The main orebody at the Florence and Ullcoats mines is hosted in limestones within a graben structure bounded on the south west by the Florence faults and on the north east by the Ullcoats Fault (Fig. 4). The Lonely Hearts orebody lies on the north east, or footwall, side of the Ullcoats Fault. The fault itself was cut both in the inclined access drift and, several metres vertically beneath this, in the Lonely Hearts Level.

Evidence of post-mineralisation fracturing and shearing of the orebody, especially along or adjacent to mudstone partings, was commonly seen. Post-mining re-activation of minor faults within the orebody was also present locally (Fig. 8).

MINERALISATION AT FLORENCE MINE

As has already been noted, Florence Mine shares, with numerous other west Cumbrian iron ore mines, a considerable worldwide reputation for fine specimens both of hematite and associated gangue minerals, recovered over the long life of the workings. It is not the purpose of this paper to add to the spectacular descriptions and illustrations of some of these specimens, most notably by Symes and Young (2008) and Wilson and Moore (2010), though the fine examples of ‘kidney ore’ hematite, fluorite and quartz, illustrated in Figures 9, 10 and 11, are included as examples of some of the minerals for which Florence Mine has for so long been famous.

The account which follows describes, illustrates and wherever appropriate interprets, the nature and composition of the orebody, and its stratigraphical and structural relationships, as exposed in the accessible workings immediately before abandonment.

Alteration of limestone adjacent to the orebody

The passage from unaltered limestone to hematite ore could be observed at several places. The following features appear to characterise this transition.

More or less severe dolomitisation is known to have been common and widespread around many of the west Cumbrian hematite orebodies with, in many instances, the development of numerous cavities up to several centimetres across within the altered limestone typically lined with well-formed curved saddle-shaped rhombic crystals of white to pale cream dolomite (Smith, 1924). Such a ‘halo’ of alteration, up to several metres wide, was observed to occur around the orebody within parts of the Lonely Hearts workings. Good examples of dolomitisation, with numerous vugs lined with well-crystallised dolomite were noted in the altered limestone forming the roof of the orebody in recent workings adjacent to the Ullcoats No. 1 Shaft.

In many places the re-crystallised limestone exhibited a dark brown and locally almost black colour suggesting the presence within it of abundant iron or manganese. Irregular cavities or vugs up to about 5 cm across, lined with crusts composed of colourless to white rhombohedral calcite
crystals generally up to around 2 mm across, were locally conspicuous (Fig. 12). It was not possible to undertake chemical analyses of these rocks during this investigation. X-ray diffraction of samples collected from the western margin of the orebody in the Lonely Hearts Level, revealed only calcite: no discrete iron or manganese minerals were identified.

Large, mutually interfering, tabular crystals of white baryte up to 2 cm across were commonly seen dispersed throughout the brown altered limestone within the alteration ‘halo’ on the west side of the orebody. Baryte here appeared to be concentrated locally beneath a prominent mudstone bed within the limestone. Narrow baryte-lined veins, up to a few centimetres wide, were also locally common within the altered limestone over several metres from the western margin of the orebody. Several of these veins were observed to terminate upwards against the same mudstone bed (Fig. 13). These exposures offered clear evidence of the role of the mudstone as an impervious barrier to the local upward passage of mineralising fluids.

The passage from altered, perhaps dolomitised, limestone with conspicuous baryte crystals and calcite-lined vugs, to solid hematite appears to occur within a few centimetres. Experience in the Lonely Hearts workings revealed that the presence of baryte within the hematite was a reliable indicator of the proximity of the edge of the orebody, a feature first noted by Smith (1924, p. 76), (G. Finlinson, personal communication).

The Lonely Hearts Orebody

As noted above, and as depicted in Figure 4, the Lonely Hearts Orebody comprises an extension of the main Florence-Ullcoats Orebody close to the base of the Carboniferous limestones on the north, or footwall, side of the Ullcoats Fault. Ore was extracted via the Lonely Hearts Level, both a few metres above, and a few metres beneath, the level, around the former Ullcoats Nos. 1, 2 and 3 shafts. At the time of the survey described here, the accessible workings consisted of numerous large worked-out voids up to several metres across and up to 4 – 5 metres high, with a number of large supporting pillars of un-extracted ore (Fig. 14).

In the following description, the main characteristics of the orebody are outlined with examples of the most significant features then visible interpreted and illustrated under separate headings.

Smith (1924, p. 76) provided a brief description of the main characteristics of the ore then exposed in the main, deeper, portions of the Florence – Ullcoats orebody. According to this description the bulk of the ore comprised compact, hard blue-grey massive hematite, generally referred to in accounts of the Cumbrian deposits as the ‘hard blue’ type. Within this massive ore, loughs or vugs, typically averaging “the size of a football”, were common, though the occasional presence of much larger vugs, including one described as “ a cavern 12 feet [3.7 m] or more in height” was also noted. The vugs were typically lined with calcite, dolomite, quartz, ‘kidney’ and ‘specular’ ore. ‘Kidney ore’ was extremely common, though except for the presence of a mass of this almost 2 m across, within the large vug already mentioned, no comments were made on the nature or relationships of this variety with other forms of hematite within the orebody.

Figure 12. Dark brown altered limestone with calcite-lined vugs, close to the margin of the orebody, near the head of the Old Man’s Dib. The hammer head is approx. 10 cm across. Photo B. Young.

Figure 13. Longitudinal section through baryte vein in altered limestone close to the margins of the orebody. The vein terminates conspicuously upwards against a thin mudstone bed within the limestone. Scale is 10 p coin. Photo B. Young.

Figure 14. Ore pillars in lowest part of Lonely Hearts workings. The dark water immediately beyond the figure is the standing water level within the mine at the time of the study. Photo B. Young.
Many of the features reported by Smith (1924, p. 76) in the main Florence – Ullcoats orebody were recognisable within the Lonely Hearts workings.

An outline of the essential characteristics of, and features present within, the two predominant forms of hematite within the orebody, massive hematite and ‘kidney ore’, is followed below by a review of the main minerals found within vugs.

**Massive hematite, Fe₂O₃**

The majority of the ore exposed in the Lonely Hearts Orebody comprised massive fine-grained hematite, much of which was characterised by a smooth, or in places almost sub-conchoidal, fracture. Whereas subtleties of colour are difficult or impossible to distinguish underground, samples brought to the surface revealed that the colour varied between mid-grey or bluish grey and rather reddish grey. This is the form commonly referred to as the ‘hard blue’ type of earlier descriptions. A number of samples of this ore contained colourless glassy quartz, apparently disseminated as small pockets or veinlets <1 mm across.

Clear remnants of original bedding were extensively preserved in the ore throughout the accessible workings. These were especially obvious where beds of unaltered mudstone remain within the hematite (Figs. 15 and 16). Good examples of such relic mudstone beds, up to roughly 30 cm thick, were conspicuous locally, notably in the walls of several working places near the position of the Ullcoats No. 1 Shaft (Fig. 17). Although no mineralogical investigations of the associated mudrocks was undertaken during this investigation, they appear to remain essentially unaltered by the hematite mineralisation, save for the development of a strong brownish red colouring, no doubt due to impregnation with hematite. Intense red to purplish staining of these mudstone beds and partings was found to be very conspicuous for many metres beyond the margins of the orebody, with the adjoining limestone commonly showing little or no reddish colouration.

Vertical joints in the massive hematite which exactly match those in the original host limestone were seen locally. In a few places, particularly near the margins of the orebody, these were seen to be lined with conspicuous coarsely crystalline baryte, suggesting that they acted as significant conduits for fluids during at least part of the mineralising process.

Throughout large parts of the workings, the massive hematite contained very conspicuous small, usually horizontally flattened, vugs, typically around 10 cm across. These were commonly found in roughly horizontal, or

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*Figure 15. Original widely spaced limestone bedding planes preserved in massive hematite, near Old Man’s Dib. The hammer handle is approx. 35 cm long. Photo B. Young. (The pale discs on the right of the picture are due to water droplets)*

*Figure 16. Original limestone bedding replaced by massive hematite. An original, and unaltered, thin shale parting is conspicuous to the left of the hammer. Old workings near foot of Ullcoats No. 1 Shaft. The hammer handle is approx. 35 cm long. Photo B. Young.*

*Figure 17. Unaltered mudstone partings in massive hematite. Note ‘kidney ore’ lined vugs in massive hematite below lowest mudstone. Near foot of Ullcoats No.1 Shaft. The hammer handle is approx. 35 cm long. Photo B. Young.*
sub-horizontal, bands apparently developed parallel to the bedding of the original limestone. Excellent examples, lined with ‘specularite’ were numerous in the working place adjoining the former Ullcoats No. 1 Shaft (Fig. 18). Smith (1924, p. 76) likened similar vugs to the cavities commonly found in dolomitic limestones, a description that seems entirely appropriate, as their origin due to the replacement of limestone by hematite has close parallels with the origins of many such dolomitic rocks.

These vugs were typically seen to be lined with a variety of minerals, most conspicuous and widespread of which appears to be well crystallised, ‘specularite’. The mineralogy of vug fillings is considered more fully below.

‘Kidney ore’, Fe₂O₃

Florence Mine was one of numerous west Cumbrian mines long famous for the quality of specimens of this variety of hematite (Figure 9). ‘Kidney ore’ consists of reniform, or kidney-like, masses of hematite composed of fine-grained radiating fibrous crystals elongated perpendicular to the c-axis (Bradshaw and Phillips, 1967). A layered structure, at right angles to the fibrous crystals, is characteristic of most examples, commonly causing the ‘kidney ore’ to break into concentric, dish-shaped fragments (Fig. 19). This layering, and associated tendency for concentric fracturing, may be due to discontinuities in the growth of successive bands of crystalline hematite, perhaps associated with the deposition of extremely thin layers of poorly crystallised, micaceous or earthy, hematite between successive layers of ‘kidney ore’. When broken parallel with the constituent fibrous crystals, ‘kidney ore’ typically fractures into roughly conical tapering masses, known to the miners as ‘pencil ore’. When very fine grained this is capable of taking a very high polish and was formerly much in demand for making hematite, or ‘bloodstone’, jewellery and ornaments.

Reniform surfaces of ‘kidney ore’ were typically seen to be composed of mutually interfering spheroidal masses which ranged from a few millimetres up to masses at least 10 cm or more across. ‘Compound kidneys’ consisting of large rounded surfaces composed of aggregates of smaller ‘kidneys’ were also common. The ‘kidney ore’ surfaces varied in colour from reddish grey to brownish or purplish red. They may be very smooth with a moderate to high lustre, though dull or rather rough surfaces were also common. Broken surfaces were usually grey in colour with a sub-metallic or silky lustre. A faint colour banding in shades of grey was observed in some samples of ‘kidney ore’. The cause of this is not clear, though it may simply reflect slight differences in the coarseness of the constituent haematite crystals.

Smith (1924, p. 76) noted the abundance of ‘kidney ore’, in the Florence – Ullcoats orebody then being worked. The recently accessible exposures reveal that it was a common and widespread variety of hematite within the Lonely Hearts section of the deposit. ‘Kidney ore’ appears to have occurred in two rather distinct situations within the orebody: as bands within the otherwise massive hematite, and as a distinct component of vug linings within this ore. The former will be described here; the latter will be discussed below with other vug linings.

Throughout the Lonely Hearts orebody, ‘kidney ore’ was widely present as crudely horizontal bands, commonly around 30 cm thick, within otherwise massive hematite. In many instances these bands appeared to lie parallel to the bedding of the original limestone. In a number of locations, roughly horizontal bands of ‘kidney ore’ could be traced laterally for two to three metres. In most of these examples the ‘kidney ore’ occurred as crusts on the upper and lower margins of stiff brown clay partings up to around 4 cm thick. These appear to be relics of original mudstone partings (Fig. 20). The reniform surfaces above the clay partings faced downwards, those beneath the clay parting faced upwards. In most instances the characteristic smooth reniform surfaces of the ‘kidney ore’ were best developed in the uppermost, downward facing, layers. This relationship suggests that the impervious original clay partings may have played an important role in the development of ‘kidney ore’ and that formation of the reniform surfaces may have been facilitated by growth into the comparatively soft and yielding clay rather than into an open void.

Although rather widespread throughout the orebody, such bands of ‘kidney ore’ were generally of rather limited
extent, rarely exceeding 0.5 m in thickness and generally persisting laterally for no more than a very few metres. However, an especially striking example of ‘kidney ore’ exposed at the time of this investigation, was in the large partially worked-out area a few metres above the water level in the area of workings then known as the foot of the ‘Old Man’s Dib’ (Fig. 21). The remaining pillars, walls and roof in these workings exposed faces of ore up to at least 3 m high and at least 15 m across composed almost entirely of ‘kidney ore’. In these exposures the ‘kidney ore’ occurred as spectacular concentric bands, mostly up to about 5 cm thick, with individual rounded spheroidal masses up to at least 10 cm across. In many places the ‘kidney ore’ layers appeared to encrust cores of massive hematite. Rounded reniform surfaces were especially well-developed in numerous open vugs, typically up to 30 cm across. Whereas generally smooth reniform surfaces lined many of these, the ‘kidney ore’ was in places overgrown by thin crusts of ‘specularite’ and a little colourless quartz. In many places the ‘kidney ore’ bands appeared to exhibit a crude sub-horizontal banding, perhaps parallel to original bedding, though no relics of original mudstone beds were found within this large body of ‘kidney ore’.

It is, however rather difficult to reconcile the very extensive developments of ‘kidney ore’ seen here with comparatively simple replacement of limestone. It is also difficult to envisage the circumstances whereby sufficiently large open voids were available for the formation the extensive occurrences of ‘kidney ore’ seen in such occurrences. The circumstances of this extensive development of ‘kidney ore’ remain unresolved.

Fracturing and brecciation of ‘kidney ore’ was seen to be common. Such fracturing varied from narrow, discontinuous cracks up to a centimetre or so long, which in some instances appear to have been ‘healed’ by overgrowth of later hematite or spar minerals, to severely crushed breccias or gouges.

Much of the brecciated ‘kidney ore’ comprised dish-shaped fragments of ‘kidney ore’ layers up to several centimetres across in a matrix of friable hematite, that appeared to consist of crushed ‘kidney ore’, accompanied by smaller quantities of ‘specularite’ and white calcite. Some examples of this material exhibited rather flattened, quartz crystals, commonly with a red colour, deposited on the inner surface of the ‘kidney ore’ crust. A few specimens have been seen in which similar quartz crystals occur between individual concentric layers of ‘kidney ore’. Such specimens suggest that at least some of the quartz mineralisation may have been coeval with the formation of ‘kidney ore’. A few blocks of brecciated ore, when removed from the mine and cleaned, revealed a matrix-supported breccia composed of dish-shaped fragments of ‘kidney ore’ crusts embedded in a dark brown matrix composed mainly of calcite and earthy ‘limonite’. Small cavities up to 5 cm across in this material were seen to be lined with fine-grained white calcite and, in places, colourless to very faintly ice-blue fluorite cubes up to 4 mm across.

Much more intense brecciation of ‘kidney ore’ was observed locally producing a rather loose friable mass of comminuted ‘kidney ore’ fragments in which slickensided surfaces were common. Such areas of intense brecciation appear to have resulted from post-mineralisation movement along the comparatively weak mudstone or clay partings and their associated layers of ‘kidney ore’.

**Vug linings and fillings**

As noted above, open cavities or vugs, were common throughout much of the Lonely Hearts Orebody. They were typically lined, or in some instances almost completely filled, with a number of minerals, including varieties of hematite or a small range of gangue, or spar, minerals.

Examination of the contents of vugs exposed within the present workings, together with specimens from the mine in mineralogical collections, suggests that a general paragenetic order of deposition of these minerals may be discerned. The paragenetic diagram (Table 2, see p. 14) attempts to represent the most significant observed relationships of vug-filling minerals, though it should be regarded as extremely tentative.

The west Cumbrian hematite deposits have long been known for superb specimens of ‘kidney ore’ and magnificently crystallised specimens of ‘specularite’ and a
variety of gangue or spar minerals, recovered from them (Young, 1987; Symes and Young, 2008; Wilson and Moore, 2010). Fine examples are to be seen in most of the World’s major mineralogical collections. The Florence – Ullcoats orebody is known to have been a source of many such specimens, especially during its earlier years of working. However, excellent examples of many of these minerals were also recovered during the recent working of the Lonely Hearts orebody.

‘Specularite’, Fe₂O₃

Most conspicuous of the vug linings within solid massive hematite was well crystallised hematite, or ‘specularite’ (Fig. 18). This occurred as highly lustrous black tabular crystals, most commonly ≤1 mm across though, exceptionally, crystals up to over 7 mm across have been obtained. In most instances, the ‘specularite’ occurs as continuous, or almost continuous, crusts composed of a single layer of crystals. Where ‘specularite’ was the main vug lining, it was almost invariably separated from the massive hematite by a layer of ‘kidney ore’, usually up to only a few millimetres thick, and in places so thin as to be inconspicuous or almost imperceptible to the naked eye.

‘Kidney ore’, Fe₂O₃

As noted above, the numerous ‘specularite’-lined vugs within the massive ore, typically exhibited a very thin layer of small-scale ‘kidney ore’ separating ‘specularite’ vug linings from massive hematite. This was normally small ‘kidney ore’, the constituent spheroids of which were typically no larger than 2 to 3 mm across.

Less abundant, though common locally, were vugs within the massive ore in which ‘kidney ore’ comprised the main lining. In such instances, well-developed masses of typical ‘kidney ore’ locally formed masses many centimetres across (Figs. 17 and 22). The mass of ‘kidney ore’ almost 2 m across, referred to by Smith (1924, p. 76) may be an example of this form in such a situation. Every gradation appeared to exist between vugs with almost imperceptibly thin ‘kidney ore’ linings, overlain by conspicuous ‘specularite’, to vugs in which ‘kidney ore’ appeared to be the main, in many instances sole, lining.

Within vug fillings, the reniform surfaces of ‘kidney ore’ varied from dull and lustreless to smooth, bright and glossy.

‘Kidney ore’, Fe₂O₃

Figure 22. Large vug lined with ‘kidney ore’ in massive hematite, near foot of Ullcoats No. 1 Shaft. The hammer head is approx. 10 cm across. Photo B. Young.

Quartz, SiO₂

Quartz was seen to be an extremely common mineral within vugs. It was observed to be the main mineral forming a complete lining within many vugs, but was also commonly noted as isolated crystals or groups of crystals, associated with other vug lining minerals. Indeed, examination of a large number of vugs in situ, and a large number of specimens recovered from them, suggests that quartz is rarely completely absent.

Quartz usually occurred as well-developed, doubly terminated crystals which typically exhibited very prominent pyramid faces, commonly with less prominent prism faces. Crystals around 1 to 2 cm across appeared to be most common, though much smaller, and occasionally much larger examples were also seen. Colourless ‘rock crystal’, or occasionally very slightly milky white quartz, was most common.

Many of the most transparent, and apparently colourless, crystals were distinguished by a more or less smoky brown appearance, often rather unevenly distributed through the crystal. Specimens of a comparatively uniform deep smoky brown colour, typical of ‘smoky quartz’, are known in many collections from Florence Mine (Fig. 12), though comparatively few good examples of this variety were seen during this investigation.

Table 2. Provisional paragenetic diagram for the main vug-filling minerals within the Lonely Hearts Orebody.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Diagram</th>
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<tbody>
<tr>
<td>Dolomite</td>
<td>─────</td>
</tr>
<tr>
<td>‘Kidney ore’</td>
<td>──────</td>
</tr>
<tr>
<td>‘Specularite’</td>
<td>──────</td>
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<tr>
<td>Quartz</td>
<td>────</td>
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<tr>
<td>Fluorite</td>
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<td>Baryte</td>
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<tr>
<td>Calcite</td>
<td>────</td>
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<tr>
<td>Goethite</td>
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</table>

Figure 22. Large vug lined with ‘kidney ore’ in massive hematite, near foot of Ullcoats No. 1 Shaft. The hammer head is approx. 10 cm across. Photo B. Young.
In addition to forming the main lining in many vugs, quartz was commonly observed as scattered crystals within the crusts of ‘specularite’ that line many vugs. Such crystals were usually colourless and transparent, and most were only a few millimetres across, though larger examples were also common. Crusts of transparent colourless quartz crystals were also found locally as coatings on the reniform surfaces of ‘kidney ore’.

More rarely, quartz crystals coloured red or pink by the presence of finely disseminated red hematite were found. Fine examples of these from west Cumbrian mines, including Florence and Ullcoats, feature conspicuously in numerous mineral collections. These were commonly known by the miners as ‘tomato quartz’, and are sometimes referred to in mineralogical texts as ‘eisenkiesel’. Small examples of such red crystals, up to about 3 mm across, many with the colour rather unevenly dispersed throughout the crystal, were recovered from small vugs in massive hematite in an old working place near Ullcoats No. 1 Shaft. Like the colourless and smoky varieties, these are typically doubly terminated and directly encrust massive hematite, and were associated in some specimens with perfectly colourless quartz crystals.

Where quartz formed the dominant vug lining in massive hematite it appeared to grow directly on the massive ore, without a layer of ‘kidney ore’, as in the ‘specularite’-lined vugs.

Fluorite, CaF<sub>2</sub>

Florence Mine has long been known for well-developed crystals of beautiful sky-blue fluorite, though yellow, green and purple varieties have also been reported (Trotter, 1945; Young, 1987; Symes, and Young, 2008; Wilson and Moore, 2010). Very fine examples of the pale blue form, usually associated with pale cream, saddle-shaped crystals of dolomite, are to be seen in many mineral collections (Fig. 10). These were mined many years ago and are understood to have been recovered from the margins of the orebody at deeper levels of the workings that have long been inaccessible. However, a number of fine specimens of clear deep blue fluorite in well-crystallised interpenetrant cubes up to 5 mm across, on a matrix of ‘specularite’ lining vugs in massive hematite, were recovered during the 1980s from parts of the Lonely Hearts workings.

A number of fluorite samples obtained during this investigation, together with a handful of specimens collected in previous years, both from the Lonely Hearts workings and from deeper levels within the mine, exhibit very weak purple fluorescence under long wave ultra violet radiation. This is consistent with Dunham’s (1952) observation of very feeble violet fluorescence on samples of fluorite from both Florence and Ullcoats mines.

During the present investigation, very pale ice-blue fluorite cubes were noted locally within several samples of brecciated ‘kidney ore’. A few examples of small fluorite cubes, from near the Ullcoats No. 1 Shaft position, appeared colourless when collected, though after a few days exposure to daylight had assumed a very faint pale ice-blue tint.

Close examination of a number of specimens of ‘specularite’-rich vug linings from several places throughout the Lonely Hearts workings revealed the presence of isolated tiny, >1 mm, cubic crystals of colourless fluorite. These were difficult, or impossible to detect underground and are extremely easily overlooked. It seems likely that fluorite of this type may be widespread in tiny amounts throughout the orebody. Goldring and Greenwood (1990) drew attention to fluorite-hematite-dolomite mineralisation along the Ullcoats Fault, suggesting that such fluorite mineralisation may be widespread in west Cumbria, where it has hitherto been overlooked due to its generally inconspicuous appearance.

Baryte, BaSO<sub>4</sub>

Baryte is a common gangue mineral in many of the west Cumbrian hematite orebodies, from several of which some spectacularly fine crystallised specimens have been collected (Young, 1987; Symes and Young, 2008; Wilson and Moore, 2010 Wilson and Moore (2010). Although a comparatively common gangue mineral within the Florence – Ullcoats orebody, Florence Mine seems not to have yielded specimens of the striking quality seen from other west Cumbrian mines. However, in the present workings baryte was abundant and conspicuous in several places within the Lonely Hearts orebody as linings of vugs within massive hematite (Fig. 23). In these, an outer layer of rather compact crystalline salmon pink baryte commonly lined the vug. This was almost invariably overgrown by a later, inner, crust of pure white baryte forming thin tabular crystals up to several centimetres across (Fig. 24, see p. 16). In places, where vug filling was incomplete, euhedral terminated crystals were found, commonly in the form of typical ‘cockscomb’ aggregates. In places baryte occurred as groups of pure white tabular crystals and crystalline aggregates filling, or almost completely filling, the centre of ‘specularite’- and quartz-lined vugs up to about 15 cm across within massive hematite. In both of these occurrences the baryte was clearly the last mineral to have crystallised within the vugs. In common with such ‘specularite’-lined
vugs seen elsewhere in the orebody, these occurred in roughly horizontal bands, almost certainly parallel to, and determined by, the bedding of the original limestone.

As noted above baryte was also conspicuous as masses of thin tabular crystals within cavities in the altered limestones within a few metres of the western margin of the orebody exposed in the Lonely Hearts Level. It also occurred here forming roughly vertical veins up to a few centimetres wide within these altered limestones. Some of these veins terminated upwards against thin mudstone partings, suggesting that these impervious layers had acted as barriers to the upwards passage of mineralising fluids (Fig. 13).

Baryte is a deleterious constituent of hematite ores and, where in abundance generally rendered the ore unworkable. Experience at Florence Mine suggested that baryte was normally abundant close to the margins of the orebody (G. Finlinson, personal communication).

Calcite, CaCO₃

Vugs in massive hematite, lined with crusts of small white rhombic crystals of calcite, typically around 2 to 3 mm across, were common locally close to the margins of the orebody, notably in the area near the Ullcoats No. 1 Shaft (Fig. 12). Colourless to black prismatic crystals up to a few millimetres long, the latter probably coloured by minute inclusions of manganese oxides, were also seen very locally. Similar vugs were also locally conspicuous in the altered limestone within a few metres of the margins of the orebody. Calcite was generally uncommon or absent from most of the vugs in the main parts of the orebody. The observed distribution of calcite is consistent with Smith’s (1924, p. 76) observation that the abundance of calcite within the ore was generally taken as a sign that the margin of the orebody was close.

Dolomite, CaMg(CO₃)₂

Although very fine examples of well-crystallised dolomite are known from the older Florence Mine workings, few good examples of the mineral were visible in the Lonely Hearts workings examined during this study. However, good examples of typical saddle-shaped curved rhombic crystals of a pale cream colour were found to be common in vugs up to several centimetres across in the altered, presumably dolomitised, roof rock exposed in the working place adjacent to Ullcoats No. 1 Shaft.

Goethite, FeO(OH)

Bright yellowish brown earthy crusts, identified by X-ray diffraction as goethite, were seen locally coating massive hematite exposed in a few places in the Lonely Hearts Level.

The origin of these small amounts of goethite within the orebody is not clear, though they may represent post-mining deposits, possibly derived from the oxidation, in the oxygen-rich mine atmosphere, of traces of an iron sulphide mineral such as pyrite. Although recorded from a number of the west Cumbrian hematite orebodies (Young, 1987), pyrite is not known to have been reported from the Lonely Hearts Orebody and none was seen during the present investigation.

Goethite was never a significant member of the mineral assemblage present within the orebody or within the adjacent wallrocks.

EPILOGUE

The closure of Florence Mine brought to an end a long history of iron ore mining in Cumbria. Moreover, its abandonment and flooding have rendered inaccessible the remaining significant exposure of this important suite of mineral deposits. A small number of sites within Cumbria still offer very limited opportunities to study examples of hematite mineralisation, though the few remaining accessible exposures of such mineralisation are virtually restricted to vein deposits within the Lower Palaeozoic basement rocks: no good exposures of the widespread replacement ores within Carboniferous limestone host rocks remain.

Fine specimens of all of the minerals for which Florence and nearby mines were justly celebrated feature prominently in mineral collections throughout the UK and beyond and will forever remain as permanent legacies of the mineralogical importance of these deposits. However, a true understanding of mineral deposits depends not solely upon glamorous cabinet specimens but, more significantly, from descriptions of the orebodies and their associated wallrocks as well as upon access to examples of the component of the orebody.
minerals in their more usual and apparently mundane form, ideally in situ, or where this is no longer possible as suites of representative specimens. Immediately prior to the mine’s closure, a representative suite of specimens of typical ore and associated minerals was recovered. These have been deposited in the collections of Tullie House Museum, Carlisle where they remain as a permanent record which, it is hoped, will help to augment the spectacular specimens more commonly encountered in many collections.

Fortunately, most of the Cumbrian hematite mines worked since the introduction of the statutory requirement to maintain and preserve accurate plans of workings. Of particular importance in this respect are the numerous abandonment plans compiled on the final closure of individual mines. Together with the substantial technical literature dealing with these deposits, of which this paper is a small contribution, a very significant archive exists for these formerly important deposits.

ACKNOWLEDGEMENTS

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REFERENCES


A GEOCHEMICAL STUDY OF THE LEAD OXYCHLORIDE MINERAL ASSEMBLAGE OF THE MENDIP HILLS, SOMERSET, UK USING A STABILITY FIELD MODEL

Trevor F. BRIDGES
1 Mill Court, Waddingham, Lincolnshire DN21 4SD

Rick TURNER
The Drey, Allington Track, Allington, Salisbury SP4 0DD

Michael S. RUMSEY
Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD

A computer-based model of the geochemistry underpinning lead oxy/hydroxy chloride (hereafter shortened to oxychloride) mineral formation in the Mendips has been used to investigate the conditions required for their formation, the results being presented in a series of stability field diagrams. The study shows quite clearly that there has to be a steady source of at least a moderately strong base while the oxychloride minerals are forming. It is suggested that the mechanism proposed by Alabaster (1976, 1982, 1989) offers a reasonable hypothesis for pod formation: erosion of nearby Upper Carboniferous strata resulted in the formation of hydrous oxide colloids of iron and manganese which adsorbed negative and positive ions respectively on their surfaces and transported them into karstic fissures in limestone to form pods of mineralisation. Of particular importance is the transport of lead into the fissures and it is suggested that as the colloids flocculated at least some of the lead formed oxides.

Low pCO₂ and, in most cases, high pH are essential for oxychloride formation. The most probable mechanism for this seems to be reaction of heavy metal oxides, particularly lead oxide, with calcite in solution to form cerussite, hydrocerussite and Ca(OH)₂, the latter being a moderately strong base capable of raising pH to the level required for formation of all the minerals found in the manganese pods. The model predicts several mineral associations which observations show actually do occur in the pods. It also predicts that paralaurionite (and laurionite) are most likely to have formed by alteration of mendipite. However, this mechanism cannot be regarded as a complete answer to pod mineralisation, since there are several unexplained problems. Further work is required to solve these and suggestions for this are made.

INTRODUCTION

There is a long history of lead and zinc mining in the Mendip Hills, the source veins generally being considered to be Mississippi Valley type (MVT). However, the Mendips are unique due to the mineralogy of ‘manganese pods’, which were often mined in the past and are now exposed from time to time in quarries. Some of these pods contain an assemblage of lead oxychloride minerals with numerous accessory elements giving a wide range of rare and interesting species. In addition to the oxychloride minerals,
the pods contain numerous other interesting species, such as wulfenite and cuprite, which do not contain chlorine. Over the past five years or so an extensive amount of research has been carried out on the Mendips by various workers and Turner and Rumsey (2010) have summarised progress so far in a major paper in the Journal of the Russell Society. In addition to discussing well known minerals, many new findings are summarised and several minerals, thought to be present, have been disproved. The paper also includes an extensive and useful bibliography.

Several papers on the deposits containing lead oxychloride minerals have suggested mechanisms for their formation, but no consensus has been reached, so this seemed to be a convenient time to attempt a re-appraisal of the geochemistry of the deposits.

- Alabaster (1976) suggested the pods were filled with surface water streams of hydrous oxides of iron and manganese as colloids and carrying metallic and other ions with them.
- Symes and Embrey (1977) modified this model suggesting that the pods were initially filled with hydrothermal deposits of galena, baryte and minor chalcopyrite and that these reacted with iron and manganese oxide/hydroxide suspensions in brine.
- Alabaster (1982) enlarged his original mechanism, pointing out the importance of positive and negative charges on iron and manganese colloids respectively, but then in a paper on the Wesley Mine, (which is situated on the west side of the Mendips), he modified his original mechanisms to include a hydrothermal component (Alabaster, 1989). At the Wesley Mine a late stage lead-copper (MVT) vein intersects the manganese pods, a feature which has also been noted elsewhere (Turner and Rumsey, 2010). Alabaster’s Wesley Mine paper gives fluid inclusion geothermometry data on pod minerals, including calcite, mendipite and laurionite, with formational temperatures of 60 to 68°C.
- Turner (2006) proposed a mechanism based on oxidation of galena in the pods combined with the accumulation of the less common elements by a seawater scavenging process related to the formation of deep sea manganese nodules. In this paper, Turner also pointed out that the presence of minerals such as kentrolite and melanotekite indicates that hydrothermal activity had raised temperatures at an early stage in the process.
- Finally, Turner and Rumsey (2010), in their paper on the Mendips as a whole, summarised the above and, most importantly, disproved the presence of some of the minerals originally thought to be in the pods including blixite.

In addition to the above papers on the mineralogy of the pods, three theoretical papers provide physical constants for the main lead oxychloride minerals; constants which can be used in the construction of stability field diagrams. The papers are Humphreys et al. (1980), Abdul-Samad et al. (1982) and Edwards et al. (1992). These papers include theoretical stability field diagrams, showing mineral relationships, but do not demonstrate relationships in real situations in the pods.

There are problems with all of the above mechanisms, which will be discussed later (see Discussion), and it is for this reason that this study has been undertaken to attempt to clarify the relationships of the main lead oxychloride minerals with each other and the factors controlling their formation. However, it must be stated from the outset that this paper does not propose a definitive mechanism for oxychloride mineral formation; it just outlines essential factors in their formation, shedding light on how it might have happened and is intended to promote further debate and, hopefully, research. The work reported is the result of an investigation into relatively low temperature mineral relationships in the manganese pods using a computer-based stability field model of the chemically simpler lead oxychloride minerals in the system. The geochemistry underpinning the model is kept as simple as possible and is mostly included as an appendix at the end of the paper.

THE CONSTITUENTS OF THE SYSTEM

It is generally accepted that the manganese pods are hosted in karstic cavities, along the line of minor fissures in Carboniferous limestone, some partly filled with Perno-Triassic rubble. Similar cavities are common in limestones elsewhere, such as the Pennines.

The cavities containing the oxychloride minerals are usually filled with an outer layer of hydrated iron oxides, often associated with quartz, and an inner core of manganese oxides. The Perno-Triassic Dolomitic Conglomerate of the Mendip region contains numerous deposits of similar iron oxides and deposits of manganese mineralisation are often, but not always, associated with these. The manganese mineralisation is always associated with the iron; never on its own. Calcite is always present in the deposits and also sometimes baryte. All this mineralisation is considered to result from the erosion of overlying Coal Measure sediments and the similarity between all the deposits, including those bearing the oxychlorides, does suggest a common origin.

A source of chloride ion is required and there are three possibilities:

- Seawater associated with the incursion of the Jurassic sea.
- Partly evaporated seawater associated with the formation of the Perno-Triassic deposits.
- Hydrothermal brines.

Hydrothermal brines would be expected to have deposited sulphide minerals, particularly galena and sphalerite, throughout the pods and there is no evidence that this happened. Sulphides have been noted at the bottom of the manganese pods at Merehead Quarry (Symes and Embrey, 1977), but these could be the result of ponding of later hydrothermal brines at the base of the pods, which failed to break right through. The known oxychloride-bearing pods are situated to the south and west of the main Mendip upland and were on the original edge of the Jurassic sea, which does indicate that seawater is the most likely source (Turner and Rumsey, 2010).

The wide range of minerals present in the manganese pods require numerous elements for their formation, of
which the most important are lead and copper, but others include magnesium, boron, chromium, molybdenum, vanadium and arsenic. These are present as cations such as Pb^{2+} (lead) and Cu^{2+} (copper) and anions such as MoO_{4}^{2-} (molybdate) and AsO_{4}^{3-} (arsenate). The source of these elements is the subject of much debate and is discussed later.

EXPLANATORY INFORMATION

The computer-based stability field model used for this paper is very flexible. It does not presume any source for any of the minerals and elements in the pods. It just shows the relationships of the simpler lead oxychlorides to each other and other common relevant species over a wide range of conditions. If better data for any of the physical constants are produced, the model can be updated immediately. However, in order to produce the stability diagrams that follow, simple assumptions have had to be made which are outlined below.

The models are based on the assumption of relatively low temperatures of formation, in keeping with the geothermometry measurements of Alabaster (1989). This assumption is discussed later, since some of the minerals recorded from Merehead Quarry could be interpreted as indicating higher temperatures of formation.

Even the simplest model for the formation of the main lead oxychlorides requires four variables to be considered: pH, concentrations of chloride and sulphate ions expressed as activities (aCl^{-} and aSO_{4}^{2-} respectively) and the partial pressure of carbon dioxide (pCO_{2}) in equilibrium with the system, this also in effect being a concentration. For seawater, which is nearly saturated with calcium carbonate and calcium sulphate, the aCl^{-} is 10^{-0.5} (-0.5 on the ‘y’ axis of Figures 1-5) and aSO_{4}^{2-} is 10^{-2.7} (Garrels and Thompson, 1962). Note also that the pH of seawater only varies slightly around 8.2 and the relevant atmospheric pCO_{2} is 10^{-3.52} (0.0003 which is 0.03 %v/v CO_{2}).

To interpret the diagrams it is necessary to have an understanding of the relationship between pH and pCO_{2}. In the presence of calcium carbonate, which can be solely in solution or present as solid calcite or limestone, there is an imprecise inverse relationship between pH and pCO_{2}. If the pH of an orebody falls below neutral, pCO_{2} can increase well above atmospheric and rarely can approach a value of 1 (100 %v/v CO_{2}), usually due to the reaction between sulphuric acid, released by the oxidation of iron-bearing sulphides, with calcium carbonate. This accounts for the formation of minerals such as azurite which requires a very high pCO_{2} in order to form. Equally, however, in the absence or near absence of calcium carbonate, pCO_{2} can remain low permitting the formation of minerals such as leadhillite. This relationship will become clearer as the stability diagrams are explained. At pH above neutral, the inverse relationship becomes tighter and the very low pCO_{2} required for the formation of some of the lead oxychlorides only occurs at high pH. Finally, it should be noted that if acid is added to seawater the pH will fall, but CO_{2} will be generated. In a closed or nearly closed environment, such as a manganese pod or a cavity in a vein, pCO_{2} will increase.

THE STABILITY FIELD DIAGRAMS

The stability field diagrams shown in Figures 1-5 show a progression from a pCO_{2} a little above atmospheric to very low pCO_{2} and relatively high pH, and therefore cover the conditions of formation for a wide range of lead minerals including the main oxychlorides. Except where otherwise stated, they are based on seawater. However, if evaporated seawater was the source of chloride ion, the only affect on the diagrams would be to raise log aCl^{-} a little above -0.5 on the diagrams, which would not alter the conclusions.

At every stage in constructing the diagrams, ion balances were used to ensure impractical assumptions were not being made, i.e. the sum of the cations in solution must always equal the sum of the anions to maintain electrical neutrality and the solubility product of none of the possible minerals must be greatly exceeded.

Considering the diagrams in turn, Figure 1 is for a pCO_{2} of 10^{1.195} (1.12 %v/v) and aSO_{4}^{2-} of 10^{2.7}. Under these conditions, the only minerals in the stability field are cotunnite, PbCl_{2}, anglesite, PbSO_{4}, phosgenite, Pb_{2}(CO_{3})Cl_{2} and cerussite, PbCO_{3}. If pCO_{2} is increased further, the stability fields move en bloc to lower pH.

![Figure 1. Stability field diagram at pCO_{2} of 10^{1.195} and aSO_{4}^{2-} of 10^{2.7}.](image1)

![Figure 2. Stability field diagram at pCO_{2} of 10^{2.32} and aSO_{4}^{2-} of 10^{2.7}.](image2)
without changing their form. Below a pCO\textsubscript{2} of $10^{-9.5}$ a leadhillite, Pb\textsubscript{4}(SO\textsubscript{4})(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{2}, field starts to open up between anglesite and cerussite and gradually widens as pCO\textsubscript{2} becomes lower (see Figures 2-4).

Figure 2 shows the situation for a pCO\textsubscript{2} of $10^{-3.52}$ (0.115 %v/v). At this point phosgenite and paralaurionite, Pb(OH)Cl, coexist at equilibrium and below this value paralaurionite replaces phosgenite as the stable mineral in this part of the diagram. Leadhillite now has a significant stability field. Note that this pCO\textsubscript{2} is still above the atmospheric level of CO\textsubscript{2}. Ion balances on the system show that at no point can phosgenite and paralaurionite coexist at equilibrium with solid calcite, because, in the presence of calcite, cerussite and not phosgenite or paralaurionite, would form. Note also that laurionite will occupy a nearly identical field to paralaurionite since they are polymorphs.

Figure 3 is a diagram for a pCO\textsubscript{2} of $10^{-3.52}$ (0.03 %v/v), the atmospheric level of CO\textsubscript{2}. At this value mendipite, Pb\textsubscript{3}O\textsubscript{2}Cl\textsubscript{2}, has a small, but significant field of stability at the aCl\textsuperscript{-} of seawater (10\textsuperscript{-0.5}), but the pH of seawater (8.2) is still too high for it to form. Note that mendipite requires a temperature of over 30°C to form (Edwards et al. 1992), but based on the geothermometry values quoted above, this is not a problem.

The next significant change is for a pCO\textsubscript{2} of $10^{-3.85}$ (0.0142 %v/v) and is illustrated in Figure 4. At this point cerussite and hydrocerussite, Pb\textsubscript{3}(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{2}, can coexist based on the preferred data of Taylor and Lopata (1984) (see Appendix). Below this value, hydrocerussite replaces cerussite as the stable lead carbonate phase in this part of the diagram.

As pCO\textsubscript{2} continues to decrease and pH to increase, first mendipite is able to form from seawater and then at a pCO\textsubscript{2} of $10^{-4.2}$ (0.0053 %v/v) the mendipite field increases, to the point where calcite and mendipite can coexist at equilibrium at the aCl\textsuperscript{-} of seawater, thus satisfying mineralogical observations. Note that to reach these conditions, the system requires the addition of at least a moderately strong base. More base is required to proceed to higher pH and to further lower pCO\textsubscript{2} and also calcite would have to crystallise out or the solutions become diluted by freshwater.

The next calculable significant change in the system occurs at high pH and a pCO\textsubscript{2} of $10^{-7.49}$ when, based on the data determined by Taylor and Lopata (1984), hydrocerussite and plumbonacrite can coexist. Below this pCO\textsubscript{2} plumbonacrite replaces hydrocerussite in this part of the diagram, until eventually PbO would replace the plumbonacrite. Unfortunately, there has been some doubt about the precise chemistry of plumbonacrite and it is not currently accepted as a mineral species, but it undoubtedly occurs at Merehead Quarry and work in progress, to be presented soon by the Natural History Museum, London (NHM), shows it is Pb\textsubscript{5}O(OH)\textsubscript{3}(CO\textsubscript{3})\textsubscript{3}.

At one time blixite, Pb\textsubscript{8}O\textsubscript{5}Cl\textsubscript{4}, was thought to occur at Merehead Quarry and potentiometric work on the system PbO-H\textsubscript{2}O-HCl by Edwards et al. (1992) gave thermochemical data for the mineral which shows it should have a narrow stability field at a pCO\textsubscript{2} of $10^{-7.49}$. However, much of the material originally thought to be blixite is now known to be mereheadite, Pb\textsubscript{5}O\textsubscript{4}(OH)\textsubscript{2}(CO\textsubscript{3})(BO\textsubscript{3})\textsubscript{2}, (Turner and Rumsey, 2010) for which thermochemical data are not available, but the ratios of Pb to O to Cl are similar for the two minerals, with mereheadite having some substitution of CO\textsubscript{3}\textsuperscript{2-} and BO\textsubscript{3}\textsuperscript{3-} for the O\textsuperscript{2-} and OH\textsuperscript{-} in blixite. It is therefore likely that mereheadite will form under fairly similar conditions to blixite and Figure 5 (see p. 22), which shows the system for a pCO\textsubscript{2} of $10^{-7.49}$, includes a tentative field for mereheadite (shown in dashed lines), which assumes it to be slightly more stable than blixite, thus accounting for its presence at Merehead Quarry instead of blixite. It must be emphasised this is only an approximation, but it is supported by the mineralogical evidence (see later).

A further complication arises from the ion balances which show that at the mereheadite fence and at the aCl\textsuperscript{-} of seawater, the solutions would be significantly super-saturated with calcium carbonate, and calcite would have had to crystallise out for the fence to be reached. While this could easily occur, alternatively mereheadite could form at a lower aCl\textsuperscript{-} than $10^{-7.49}$ and this is illustrated in Figure 5 where pCO\textsubscript{2} is still set at $10^{-7.49}$ and an ion balance shows the calcite problem
would not occur below an $aCl^-$ of $10^{-2.3}$. Mereheadite should still have an adequate stability field at these conditions.

Small adjustments to pH and pCO$_2$ as well as the assumed thermochemical data for mereheadite, could expand the field in which mereheadite can form. The reduction in $aCl^-$ requires dilution of the seawater by a substantially calcium carbonate free source of water such as rainwater. Figure 5 assumes this situation and $aSO_4^{2-}$ is reduced in proportion to the dilution to an $aSO_4^{2-}$ of $10^{-5}$, but the findings would be the same as for an $aSO_4^{2-}$ of $10^{-2.7}$.

**INTERPRETATION OF THE DIAGRAMS**

The above diagrams make no assumptions about the source of the minerals and elements in the pods, beyond seawater as the source of chloride ion, but as will be shown, they do place constraints on mechanisms for the formation of the oxychlorides. As far as possible this part of the paper is kept factual within the constraints of the available data.

Figure 1 shows the situation that arises when a mineral vein carrying primary sulphides outcrops on a foreshore. At the pH (8.2) and $aCl^-$ ($10^{-0.5}$) of seawater, it can be seen that cerussite is the stable supergene lead mineral. Reaching the phosgenite stability field requires acidification, which in a nearly closed cavity, can be achieved by the oxidation of pyrite with the concomitant formation of sulphuric acid and goethite. However, this will increase pCO$_2$, and means that the situation shown in Figure 2, where paralaurionite becomes stable, can only be reached if the system can lose CO$_2$, which is unlikely in the manganese pods. Figure 2 also shows that if a lowering of pH could be achieved without a change in pCO$_2$, leadhillite, a mineral not found in the manganese pods, would form. Paralaurionite really requires a different mechanism to simple acidification and probably forms from mendipite (see later). These two diagrams show why cerussite and phosgenite dominate the lead mineralogy at sites such as Clevedon Beach, Avon (Starkey, 1984) and Lossiemouth, Moray (Starkey, 1988).

Figure 3 shows the stability fields at the atmospheric pCO$_2$ of $10^{-3.32}$ (0.03 %v/v). Mendipite has a significant stability field, but slight acidification of sea water would still be needed to reach the field and this will increase pCO$_2$, which will shrink the mendipite field, preventing it from being reached.

Ion balances now show that further lowering of pCO$_2$ can only be achieved by addition of a moderately strong base to the system and without this the mendipite field cannot be reached from seawater.

Cerussite and hydrocerussite are both common in the pods and Figure 4 shows that, given a source of Pb$^+$ and a base, both minerals can form from seawater. As pCO$_2$, continues to fall, mendipite can also form from seawater, initially requiring a rim of cerussite and/or hydrocerussite to protect it from contact with calcite, but eventually being able to coexist with calcite. Both situations occur on specimens from the pods and Figure 6 shows a small specimen of mendipite in calcite with no protective rim. However, Figures 3 and 4 also show that if mendipite comes in contact with seawater (or groundwater containing minor carbonate) without addition of a base to the system, it will be unstable and will gradually change firstly to hydrocerussite and then cerussite, which could also explain the rims of these minerals around mendipite. This is also true of all the other lead oxychloride minerals. These rims are worthy of further study.

As pCO$_2$ falls further, mineralogical evidence from the study of specimens suggests that initially mereheadite will form at least a small field before, at a pCO$_2$ of $10^{-7.49}$, hydrocerussite and plumbonacrite can coexist. Figure 5 illustrates this situation which probably explains why mereheadite has been observed in association with both
hydrocerussite and plumbonacrite. Figure 7 shows a small area of plumbonacrite crystals marked ‘>’, together with hydrocerussite and mereheadite (and also rickturnerite). As inferred previously, mereheadite and calcite should be able to coexist and Figure 8 is an example of this association. Figure 5 also predicts the observed association between mereheadite and mendipite.

A mechanism for the formation of paralaurionite (and laurionite) requires some speculation. It is theoretically possible for it to form from seawater if this can be acidified with loss of some of the CO₂ formed. However, there is no obvious source of acid in the pods and losing CO₂ is unlikely in the confined situation that would have prevailed there. Alternatively, if mendipite formation was well established, fluctuations in the amount of base and CO₂ available could allow conditions to move left to lower pH on Figures 4 and 5, through the mendipite field to reach the paralaurionite field. This latter mineral could then form at the same time as mendipite or even partly or wholly replace it. A close association of paralaurionite with mendipite would usually be expected and examination of specimens shows this is born out in practice. Figure 9 shows a typical specimen of paralaurionite with mendipite. It is also worth noting that Alabaster (1975) comments that a specimen in the collections of the University of Bristol appears to show alteration of mendipite to paralaurionite. Note that as stated previously, paralaurionite (and phosgenite) cannot coexist with calcite. In the presence of calcite at least a thin shield of cerussite and/or hydrocerussite is required around the paralaurionite and examination of specimens shows this is indeed the case.

**OTHER RELEVANT MINERALS**

The pods contain a wide range of other minerals, some of which shed light on the processes related to oxychloride formation. Considering these in turn:

**CHLOROXIPHITE, Pb₃CuO₂(OH)₂Cl₂**

**DIABOLEITE, Pb₂Cu(OH)₄Cl₂**

As can be seen from Figure 5, as pCO₂ falls and pH rises, mendipite eventually occupies a very large stability field and is able to form under a wide range of conditions and at much lower aCl⁻ than seawater. It is not surprising, therefore, that small amounts of other elements in the system, such as copper, give rise to minerals such as chloroxiphite and diaboleite, which are often closely associated with mendipite. Work by Abdul-Samad *et al.* (1981) shows these minerals will tend to form at the higher pH end of the mendipite field. Rarely chloroxiphite occurs in contact with calcite, which again indicates high pH, low pCO₂ conditions of formation. Figure 10 (see p. 24) shows an excellent specimen of well-formed blades of chloroxiphite in mendipite from Merehead Quarry.

The presence of other ions in the fluids has given rise to several other lead oxychlorides, e.g. the Mg in rickturnerite
and the Mo in parkinsonite. In view of the abundance of sulphate in seawater, symesite, $\text{Pb}_10(\text{SO}_4)O_7\text{Cl}_4\cdot\text{H}_2\text{O}$, might be expected to be more common than thought previously and current research indicates this could well be the case.

**CALCITE, CaCO$_3$**

Calcite is abundant in the pods, occurring in a wide range of habits, including massive crystalline material showing good cleavage, radiating columnar forms and crystals in cavities, which are usually variations on scalenohedra. Colour varies from white to grey, shades of orange to lustrous transparent colourless crystals in some cavities. Much of the calcite is associated with the iron stage of the mineralisation and is often overcoated with goethite, showing that some formed during the deposition of the iron mineralisation. However, cavities in the manganese deposits also contain crusts of calcite and some glassy scalenohedral crystals, demonstrating a lengthy period of calcite deposition. Finally, many of the cavities containing the oxychloride assemblage are lined with calcite showing that calcite formation preceded that of the oxychlorides. It is possible that at least some of the calcite in cavities, particularly the colourless transparent crystals (Fig. 11), is the result of the elevation in pH that occurred during oxychloride formation.

**CERUSSITE, PbCO$_3$**

**HYDROCERUSSITE, Pb$_3$(CO$_3$)$_2$(OH)$_2$**

These minerals have been discussed several times above. In addition to rims around the oxychlorides, they commonly form excellent crystals in cavities, usually on calcite, often showing typical hexagonal structures. However, on some specimens there is clear evidence that black manganese oxides have partly over-coated cerussite, which may indicate some of the cerussite formed before manganese deposition had finished, since remobilisation of earlier manganese oxides seems unlikely.

**QUARTZ, SiO$_2$**

Quartz is of common occurrence in the pods, where it is mainly associated with the iron mineralisation. Crystals are normally hexagonal prisms with pyramidal terminations and are generally colourless, but often incorporate needles of dark brown goethite, which would seem to indicate the quartz formed at the same time as the formation of the goethite. Calcite is also commonly found on quartz specimens.

**DISCUSSION**

The Discussion is divided into two parts: the first considering the assumption of relatively low temperatures during oxychloride formation and the second the implications of the geochemistry study above.

**Temperature**

The only published data for the temperature of formation of the mineralisation in the pods is the 60 to 68°C measured on calcite, mendipite and laurionite from the Wesley Mine (Alabaster, 1989). Since all these minerals have a strong cleavage, it is possible these temperatures are a little higher than actual due to inclusion stretching (Jonathan Naden, personal communication). It has to be said that the geology and mineralogy of the deposits all suggest a relatively low temperature of formation. However, the above temperatures are high for mineral formation in pods no more than a few 10s of metres below the surface, suggesting a minor external source of heat at the Wesley Mine, possibly the start of the hydrothermal mineralisation that later intersected the deposit. It is regrettable that no geothermometry has been carried out on specimen material from Merehead Quarry for comparison, since this would be of considerable interest.

Despite the above comments, there are six minerals that have been reported from Merehead Quarry that need addressing, since they could be interpreted as requiring much higher temperatures than 60 to 68°C in order to form. These are best considered in pairs:

**GALENA, PbS**

**CHALCOPYRITE, CuFeS$_2$**

These two minerals were reported by Symes and Embrey (1977) as occurring with baryte in the lower levels of the No. 1 Vein at Merehead Quarry, below the main part of the iron and manganese mineralisation in the vein. The
most likely explanation is that this was late stage MVT mineralisation, similar to that at Wesley Mine, except that it failed to break right through the iron and manganese deposits. In common with other examples of MVT mineralisation, the temperature of deposition of the sulphides is likely to have been between 100 and 200°C.

**Aphophyllite**, probably **Aphophyllite-(NaF)**, NaCa$_2$Si$_3$O$_9$F·8H$_2$O

**Datolite**, CaBSiO$_4$(OH)

These two minerals were reported as occurring at Merehead Quarry by Symes (1977). They were found in the goethite-rich lower part of the No. 1 Vein, encrusting botryoidal goethite and associated with baryte and calcite. Aphophyllite group minerals and datolite are related to the zeolites and like them are commonly associated with late stage hydrothermal activity in volcanic rocks, particularly basaltic lavas. However, Nicholson and Black (1998) report the formation of aphophyllite (with calcite and several zeolites) at temperatures <50°C in basalts of the Tangihua Complex of Northland, New Zealand and zeolites are known to occur in deep sea manganese nodules again at warm rather than hot temperatures. No similar data are available for datolite, but it is possible that a high temperature mechanism is not necessary for the formation of either of these minerals. However, the site where the aphophyllite and datolite were found was in the vicinity of the MVT mineralisation reported above (Bob Symes, personal communication) and it is possible this elevated the temperature at the site where these two minerals formed. On balance, the presence of these two minerals at Merehead Quarry is unlikely to mean that the low temperature hypothesis is wrong.

**Kentrolite**, Pb$_2$Mn$_2$Si$_2$O$_9$

**Melanotekite**, Pb$_2$Fe$_2$Si$_2$O$_9$

These two minerals, which form a series, have been associated with high temperatures due to their occurrence in the metamorphic skarn deposit at Långban, Sweden. Lindqvist and Charalampides (1987), used them for geothermometry at Långban by synthesising them over a wide range of compositions, including impurities, using high pressure and temperatures above 200°C. They concluded that the Långban skarn formed at temperatures above a minimum of 575°C. However their starting points were oxides of the component elements, presumably quartz in the case of silicon. Quartz is extremely inert and the situation in the manganese pods is very different, in that the silicon (and other elements) would have been in the form of much more reactive ions, silicate in the case of silicon (see later). In this situation it is not unreasonable to presume that a low temperature route to melanotekite and kentrolite exists. In the case of melanotekite this is supported by a specimen recently acquired by the NHM from Su Elzu Ozieri, Sardinia (an old lead mine) which consists of melanotekite on willemite (Zn$_2$SiO$_4$) with associated cerussite and has clearly formed in a supergene environment. The image of kentrolite featured on the cover of Volume 13 (2010) of the Journal of the Russell Society also has a distinctly supergene appearance.

Considering all of the above in conjunction with the geology and mineralogy of the manganese pods, there is no reason to believe that temperatures in the pods exceeded the 60 to 68°C determined by Alabaster (1989), except where there could be localised effects due to later hydrothermal activity. However, some geothermometry research on minerals from Merehead Quarry, including the quartz associated with the iron mineralisation, is highly desirable. Some analysis on inclusions in the quartz would also be of considerable interest.

**Geochemistry**

While this study does not provide a definitive mechanism for the formation of the oxychlorides, it does demonstrate a number of conditions which must be met for the minerals to be able to form, these being:

- There must be no addition of acid stronger than carbonic acid to the system, since this will raise pCO$_2$, destabilising the oxychlorides and preventing their formation.
- Galena does not make a good source for the lead, because its oxidation results in the formation of sulphate. Figures 2 and 3 both show that only a slight increase in aSO$_4^{2-}$ would result in the formation of leadhillite, a mineral not found in the pods. At higher pH values, because seawater is nearly saturated with calcium sulphate, the formation of SO$_4^{2-}$ would result in the precipitation of gypsum, another mineral which has not been found in the pods. Galena is also very resistant to oxidation, particularly at high pH, and if this was the source of the lead, relict galena would be expected in the pods.
- In addition to only forming at relatively high pH, all the oxychlorides require a steady supply of a moderately strong base to the solutions to elevate pH and provide the hydroxyl ions (OH$^-$) needed to form some of the minerals, e.g. mendipite requires four OH$^-$ groups per molecule, the equation being:

$$\text{Pb}^{2+} + 4\text{OH}^- + 2\text{Cl}^- = \text{Pb}_2\text{O}_2\text{Cl}_2 + 2\text{H}_2\text{O}$$

mendipite

- There has to be a mechanism for the production of significant quantities of a suitable base and this is another problem for any mechanism that assumes the source of the lead is galena, since its oxidation does not produce hydroxyl ions. Finding a suitable source of a base is one of the more difficult problems to solve.
- Finally, there must be a source for the extensive range of elements and ions found in the minerals in the pods. The complete range of the mineralogy is not typical of any normal hydrothermal deposit.

The current known chemistry of the pods does not indicate a definite source of a suitable base, but one possibility stems from the fact that the hard hydrous manganese oxides still contain significant amounts of lead of unknown composition at present. If this lead was originally in the form of a lead oxide, such as PbO, then this would solve the problem of the source of an adequate base as well as providing the lead required to form the oxychlorides. While PbO is a weak base in itself, it will react with calcite to form the much stronger calcium hydroxide, Ca(OH)$_2$ and cerussite
(or hydrocerussite depending on pCO$_2$), the reaction forming cerussite being:

$$\text{PbO} + \text{H}_2\text{O} + \text{CaCO}_3 = \text{PbCO}_3 + \text{Ca}^{2+} + 2\text{OH}^-$$
cerussite

In a simple experiment by one of us (TFB), litharge and crushed calcite were mixed in water in a sealed flask and left for a week. The Ca(OH)$_2$, formed by this reaction raised the pH to over 11, which is quite adequate for the formation of even the brucite, Mg(OH)$_2$, reported by Alabaster (1977) and plumbonacrite, the minerals in the pods requiring the highest pH for their formation. Moreover, once the pH and pCO$_2$ have reached the mendipite (or other oxychlorides, excepting paralaurionite) stability field, self sustaining reactions set in provided there is an adequate supply of PbO, i.e.

$$3\text{PbO} + 2\text{Cl}^- + \text{H}_2\text{O} = \text{Pb}_3\text{O}_2\text{Cl}_2 + 2\text{OH}^-$$

mendipite

In theory, this and similar reactions for other oxychlorides such as mereheadite, could drive pH up through the plumbonacrite stability field until that for PbO is reached. However, it is unlikely that PbO would be the sole source of lead in the system and the reaction would be moderated if some of the lead was derived from cerussite or hydrocerussite, which are the other probable sources of lead. However, apart from a little coronadite (PbMn$_4$O$_6$), the presence of lead oxides does not seem to have been confirmed in the pods. It is interesting to note that at several quarries elsewhere in the Mendips, where calcite veins intersect manganese pods, lead and copper sulphides have formed in the veins in the immediate vicinity of the pods, but not further away. Good examples were seen at Coombe Farm, Whatley and Holwell quarries (Chris Alabaster, personal communication). This indicates that reasonably mobile lead and copper were present in all manganese pods, not just those associated with the oxychloride assemblages, and that this reacted with reduced sulphur (S$^{2-}$, HS$^-$) in the solutions depositing the calcite. A better understanding of the lead-containing compounds in the pods is definitely worthy of research, but even if PbO was originally present, it may have reacted to form carbonates by now.

For the above hypothesis to be correct, there has to be a mechanism for PbO to occur in the pods, together with the manganese oxides, and this requires consideration of how the iron and manganese minerals were emplaced. Alabaster (1976, 1982) suggested the iron and manganese minerals were transported into the pods as colloidal suspensions and this process does offer potential answers to some of the problems.

Colloidal particles are stabilised by an electrical charge on their surface, negative in the case of manganese and positive in the case of iron. Hydrous manganese oxide colloids adsorb cations such as Pb$^{2+}$ and Ba$^{2+}$ on their surface while similar iron-based colloids adsorb anions such as borate, BO$_4$$^{3-}$, and silicate, SiO$_4$$^{4-}$. The colloids would have to flocculate to allow the iron and manganese minerals to solidify in the pods (in the mineralogical equivalent of curdling milk), although once started this process tends to be auto-catalytic. Possibly a change in pH caused by the limestone could account for this. The ability of hydrous iron colloids to transport silicate ions is significant. Once the colloid has flocculated, the silicate would initially form the very weak acid - silicic acid (H$_4$SiO$_4$). This in turn readily breaks down to form quartz and this could explain why the quartz in the pods is mainly associated with the iron mineralisation. Although silicic acid is weaker than carbonic acid, it could result in the observed silicification of some of the limestone adjacent to the pods. It is possible that the flocculation of the manganese-based colloids could result in at least part of the heavy metals forming oxides, which would be trapped in the manganese deposits until mobilised by warm seawater.

Alabaster, (1976, 1982), suggested the source of the colloids was erosion of the overlying upper Carboniferous strata, now present to the north and east of the manganese deposits, but possibly overlying the fissures at one time. The Coal Measures, in particular, consist of layers of fine sediments, silts and sandstones with coal seams. Below the surface of deposition of such sediments, the environment is highly reducing and readily converts heavy metals to sulphides. The fine sediments also form a trap for numerous other elements, even those not dependant on reducing conditions to become insoluble. In the Mendips, the Coal Measures seem to have trapped large amounts of iron, which would be held as pyrite (or marcasite). This is common to all coal fields and accounts for the need to scrub coal fired power station flue gases to remove sulphur oxides. It is also quite common for the Coal Measures to contain significant amounts of lead and zinc and some copper, as well as small amounts of many other elements. Figure 12 shows an image of galena, with sphalerite and pyrite from a site typical of coal deposits, in this case from Co. Durham.

Effluent from old coal mine workings often precipitates iron and manganese oxides/hydroxides into water courses and it is interesting to note that the iron precipitates out first as the usual orange ochres followed further downstream by black manganese oxide/hydroxide deposits. The reason for this is that even very low concentrations of Fe$^{3+}$ (<1 mg.l$^{-1}$) prevent relatively soluble Mn$^{2+}$ compounds from oxidising to the highly insoluble higher valency states (Nairn and

Figure 12. Galena, with sphalerite from Priors Close North Opencast-site, Great Lumley, Co. Durham. Field of view, 40 mm. Specimen and photo T.F. Bridges.
Hedin, 1993). This provides a possible explanation for the structure of the pods. Weathering of Coal Measures close to karstic cavities could result in deposition of hydrous iron oxides such as goethite on the walls of the cavities, while the manganese remains in solution and is lost to the water table. Later, as the weathering front moves further away, the iron could be deposited on the surface above the fissures and cavities, while the manganese can now reach and deposit on the iron in the cavities. Finally it is known that as these coal mine effluents become less acid they do result in the formation of colloidal suspensions of the hydrous iron and manganese oxides.

The above can also be extended to explain the oxidation of galena which, as stated previously, is very resistant to oxidation under most conditions. However, at low pH the Fe$^{2+}$/Fe$^{3+}$ couple has a strong catalytic effect on the oxidation of sulphides including galena. Galena, caught up in the oxidation of typical Coal Measure deposits could easily be oxidised to lead sulphate, the iron then removing the sulphate while the manganese adsorbs the lead.

The above assumes that the galena was already present in the Coal Measures. However, if early MVT mineralisation had penetrated the Coal Measure deposits (or ponded up below them) and deposited galena, then this could still have been involved in the weathering in exactly the same way.

**CONCLUSION AND RECOMMENDATIONS FOR FURTHER WORK**

This study shows that infilling of karstic cavities by colloids of oxy/hydroxy iron- and manganese-based minerals, carrying numerous other elements, derived from the erosion of Upper Carboniferous sediments, followed by inundation with warm seawater, is a reasonable hypothesis for the formation of the lead oxychloride assemblage, provided there is a source of moderately strong base. It is suggested that if at least some of the lead is present as an oxide, then this would be an adequate source of the required base. In addition, this hypothesis provides an explanation for the internal structure of the pods. However, there are gaps in the mechanism which need resolving to provide a complete explanation of pod mineralisation. Useful further research would include:

- Determining the precise form of the lead ad/absorbed on to the manganese oxides.
- Some fluid inclusion geothermometry and analysis on quartz and oxychloride minerals from Merehead Quarry to see whether the Wesley Mine data applies elsewhere.
- Studying the nature of the wall rock silicification. Is the limestone replaced or just impregnated with quartz?
- Studying the form of the rims of cerussite/hydrocerussite that often separate oxychlorides from calcite or manganese oxides. Do they form before the oxychlorides are deposited or are they the result of alteration of the oxychlorides? It is possible that both mechanisms occur and on one specimen in the NHM, corrosion of mendipite is evident at one end, while the rest of the mendipite is firmly embedded in hydrocerussite.
- Determining the thermochemical data for merrheadite and possibly other rare minerals in the pods.

**APPENDIX**

The construction of stability field diagrams requires knowledge of thermochemical data for each of the minerals being considered, normally expressed as the Gibbs free energy of formation ($\Delta G^\circ$). There is often considerable variation in values in the literature, due to the difficulty in determining $\Delta G^\circ$, possibly compounded by problems with the most common method, which is to dissolve the mineral in water and then to analyse the solution for its constituents. Having done this, the values need to be corrected for non-ideality. However, a possible problem with this technique is that oxy and hydroxy minerals can become less soluble as they ‘dry out’, so the method can give false high stabilities.

There are several references giving relevant thermochemical data, e.g. Humphreys et al. (1980) and Abdulsamad et al. (1982), but the most useful are Edwards et al. (1992) and Näsänen et al. (1962). These authors used potentiometry to determine $\Delta G^\circ$ values for the oxychlorides and phosgenite respectively, which is in effect carrying out the determinations as the minerals precipitate. Their data are therefore used in this study, with values for most of the other species taken from the compilation of Robie et al. (1978). However, the relationship of hydrocerussite and cerussite is a problem, with significant variations in $\Delta G^\circ$ for both minerals. Williams (1990) argues that hydrocerussite is the stable phase in equilibrium with the atmosphere (pCO$\text{CO}_2$) of 10$^{-3.25}$ and quotes data to support this. However, the authors’ experience with cerussite from well-ventilated mine dumps, which show no signs of alteration, and the frequency with which hydrocerussite, from the Leadhills-Wanlockhead mining field, the Calbeck Fells and the Mendips, is pseudomorphed by cerussite, leads to the conclusion that it is cerussite that is stable under atmospheric conditions. Taylor and Lopata (1984) published good data supporting this and their data was used in preparing the model.

The technique used was to derive solubility products for the minerals from the $\Delta G^\circ$ data, to develop equations for the ‘fences’ between mineral species and fence intersection points and then to programme these onto a computer. The solubility product data were held centrally and the equations written algebraically, so that in the event of better data emerging in due course, the model could be updated immediately. As an example, the mendipite-hydrocerussite equilibrium reaction and its related fence equation are shown below:

$$\text{Pb}_3\text{O}_2\text{Cl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 2\text{H}^+ + 2\text{Cl}^- \text{ mendipite} \text{ hydrocerussite}$$

$$a\text{H}^+ = (K_{md})^{0.5} \times a\text{H}_4\text{CO}_3^\circ \times 10^{-2.69}$$

$$a\text{Cl}^- \times (K_{hc})^{0.5}$$

where $K_{md}$ and $K_{hc}$ are the solubility products of mendipite and hydrocerussite, $a\text{H}^+$ is obtained from pH and $a\text{Cl}^-$ and $a\text{H}_4\text{CO}_3^\circ$ are the activities of chloride ion and undissociated carbonic acid respectively. The last is derived from pCO$\text{CO}_2$.

Following construction of the diagrammatic section of the model, ion balance equations were set up to enable any point on a diagram to be investigated to ensure that no unrealistic assumptions were being made inadvertently.
and in particular to investigate the degree of saturation with calcite.

The minerals investigated by the model are; mendipite, Pb₃O₄Cl₂; mereheadite, Pb₂O₃(OH)₃Cl; paralaurionite, Pb(OH)Cl; and cotunnite, PbCl₂, together with the more common species anglesite, leadhillite, cerussite and hydrocerussite. However, thermochemical data for mereheadite are not available, but are for the related mineral blixite, Pb₂O₃(OH)₃Cl and it is assumed that mereheadite is slightly more stable than blixite in the models. This is obviously an approximation, but the two minerals have similar ratios of Pb to O to Cl and the work by Edwards et al. (1992) shows they would form at similar alkalinity. Laurionite is assumed to occupy the same field as paralaurionite, which is reasonable since they are polymorphs, with the same chemical composition, so again any error should be negligible.

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INTRODUCTION

The Benallt Mine (Figs. 1 and 2), situated near to the village of Rhiw, on the southern end of Pen Llŷn (Lleyn Peninsula) in North Wales was the largest producer of manganese ore in the British Isles, particularly during the Second World War. Through its operation by the Ministry of Supply it produced 62,000 tons of ore (Groves, 1952). Combined with production from earlier pre-1913 operations and those of the adjoining Rhiw Mine, incorporated as part of Benallt during the Ministry of Supply operations in the 1940s, a total well in excess of 100,000 tons of manganese ore was extracted. Unfortunately, discrepancies in the published data (Dewey and Dines, 1923; Groves, 1952; Down, 1980) prevent a precise figure being obtained.

Benallt is, undoubtedly, one of the most important mineralogical sites in Wales, displaying an incredible diversity of mineral species. The mine is the type locality for three of the eleven species first discovered in Wales: banalsite, cymrite and pennantite, and is the source of the world’s finest crystals of celsian and paracelsian, demonstrating that barium also plays an important role in the complex mineralogy of this unusual manganese deposit.

Research at Amgueddfa Cymru – National Museum Wales has identified examples of all three of the type mineral species originally described from Benallt Manganese Mine, samples of which had long remained absent from the national collection. Specimens of cymrite collected during fieldwork are amongst the best ever discovered, with two distinct crystal forms observed. The situation regarding the official type locality for bannisterite is explained and evidence is put forward to suggest that the Benallt Mine should be considered as the type locality for paracelsian. Many other unusual species have been identified at the Benallt Mine, bringing the total number of recorded species to over sixty.

GEOLOGY

The geology and mineralogy of the Benallt Mine has been much studied on account of its complexity and strategic importance during times of war and has been summarised by Bevins and Mason (2010). The orebodies, which are irregular in shape, occur as lenses in highly faulted and folded metamorphosed Ordovician mudstones showing...
imbricate structures. The ore-bearing tuffs and mudstones are Arenig in age (Matley, 1932; Woodland, 1939; Beckly, 1988; Brown and Evans, 1989; Gibbons and McCarroll, 1993) bounded above and below by basic igneous rocks. The upper of these, the Lower Clip Lava (Groves, 1952), is a basalt interpreted as having been intruded into wet sediments just below the sea floor (Brown and Evans, 1989). The lower, or Footwall Sill, is doleritic in composition (Groves, 1952). A further cross-cutting intrusion, the Ty Canol Dyke encountered during wartime operations (Groves, 1952), is probably Tertiary in age (Bevins and Mason, 2010).

The orebodies, which vary considerably in size (Groves, 1952) were considered by Matley (1932) to be metasomatized tuff, but metasomatized chamositic mudstone formed a major part of the ore at Benallt Mine (Groves, 1952). The largest, the No. 1 Orebody, produced 30,000 tons of ore, but many more much smaller lenses of ore were reported as comprising only a few tons (Groves, 1952). The nearby and geologically similar Nant Mine (Fig. 2) worked a single much larger orebody some 60,000 tons in size (Groves, 1952). A third mine, Rhiw, adjoined Benallt to the north and worked the same ore ground, but the workings were incorporated into the Benallt Mine during the Ministry of Supply operations in the 1940s and the whole site now tends to be referred to as the Benallt Mine for simplicity.

Mineralogically the ore consists of silicates and oxides of manganese and iron (Bevins and Mason, 2010). Early reports suggested that manganese carbonates were dominant in the undecomposed ore, with a small proportion of silicate, but that weathering resulted in hydrated black oxides of manganese at outcrop (Dewey and Bromehead, 1915; Dewey and Dines, 1923). This view of the primary mineralogy was maintained by Matley (1932) and to some degree modified by Woodland (1939). Groves (1947), however, demonstrated that the ore at Benallt Mine consists of dominant manganese silicates with very little carbonate. Discussions ensued from Groves’ (1947) paper with Woodland claiming that he had identified significant carbonate mineralisation, but Groves countered this by demonstrating that the manganese content quoted in Woodland’s 1939 analyses from Nant Mine could not possibly represent the true ore and was more likely waste rock.

Groves (1952) considered that the ore at the Benallt Mine had formed by the metasomatic alteration of chamositic mudstone. The ore displays stromatolitic, pisolitic and oolitic textures and is occasionally phosphatic and chamositic (Groves, 1952). Indeed it was the gradation from chamosite (Fe-rich chlorite) to pennantite (Mn-rich chlorite) on all scales down to the microscopic level which led Groves (1952) to conclude that metasomatism by manganese-bearing solutions played an important part in the formation of the ore. Groves (1952) suggested that the neighbouring igneous intrusions were the probable source of thermal metamorphism.

Woodland (1956) realised that the ore bed between Nant and Benallt mines must have varied considerably in its original constitution. In the south, at Nant, the ore has the appearance of a coarse keratophyric tuff, the accumulation of which was interpreted by Woodland (1956) to have taken place subaqueously accompanied by the deposition of mudstone with chemical precipitation of iron and manganese oxides and clay minerals. Further north, at Benallt, the volcanic components died away allowing the original rock to assume a chamositic mudstone character, but still with chemical precipitation of iron and manganese (Woodland, 1956).

In assessing the economic potential for new ore discoveries at Benallt and Nant, Brown and Evans (1989) interpreted the ore as likely to have been of exhalative origin, formed subaqueously, accompanied by the deposition of mudstones. According to Brown and Evans (1989) differences in the chemical composition between the ores at Benallt and Nant mines are attributed to their position with respect to the exhalative centre. This view is very similar to that proposed by Woodland (1956), but does not take into account the lithological differences between ores at Benallt and Nant reported by Groves (1952) and
Woodland (1956). It also does not account for the small scale gradational differences in ore composition witnessed by Groves (1952) at the Benallt Mine.

Following precipitation, alteration of the ore was probably pene-contemporaneous and caused by the circulation of hydrothermal solutions (Woodland, 1939; Brown and Evans, 1989). Thus it was postulated that in the Nant Mine area the fluids must have carried more CO$_2$, giving rise to the formation of rhodochrosite (Woodland, 1956; Brown and Evans, 1989). Groves (1947) demonstrated that the dominance of carbonate in ore at Nant Mine was erroneous because the content of manganese reported (Woodland, 1939) was not appreciable enough to be considered as being of ore grade. However, even if the majority of carbonate is not in the ore its presence does suggest a chemical difference between the deposits.

Bevins and Mason (2010) reviewed the earlier interpretations and concluded that, similar to Brown and Evans (1989), the ores were originally deposited from hydrothermal brines onto the early Ordovician seabed during an episode of volcanism, but that modification by both intense deformation and by metamorphic remobilisation of manganese and other elements had taken place.

HISTORICAL CONTEXT

During early mining at Benallt, Griffith John Williams, in his capacity as Assistant Inspector for Metalliferous Mines and Quarries for the North Wales and Ireland Division, collected some superb crystallized mineral specimens which he sent to Arthur Ian Edward Montague Russell (later Sir Arthur Russell) for identification. Russell took them to Leonard James Spencer at the British Museum (Natural History), now the Natural History Museum London, who identified them as a barium-felspar, celsian (Figs. 3, 4 and 5) and a second, possible dimorphous form (shown by Spencer, in 1942, to be paracelsian – Figs. 6 and 7). The richest specimens were collected in 1911 (Russell, 1911). Unfortunately, in 1911, an accident in Court Shaft led to its premature abandonment (Groves, 1952). It appears from the lack of specimens recorded after 1911 that the source was probably accessed via Court Shaft. Mining continued until 1913, but with production then focussed at the nearby Nant Mine, where the geology was far simpler, with one large orebody.

In 1927 Williams’ private mineral collection was acquired by Amgueddfa Cymru. Staff at the Natural History Museum London, maintained an interest in Benallt Mine, largely in the hope that if it ever reopened crystallized celsian and paracelsian may once more be encountered. The
mine did reopen, during the Second World War from 1940 to 1945, but no new crystallized celsian and paracelsian was found. What was discovered was far more important: three minerals new to science.

Under the leadership of Dr Walter Campbell Smith several researchers systematically carried out detailed X-ray and chemical analyses of the ore and gangue minerals from Benallt Mine provided largely by Dr Arthur William Groves, Chief Geologist to the Home Ore Department, Iron and Steel Control of the Ministry of Supply. During his periodic examinations of the workings at Benallt Mine Groves kept watch for unusual minerals, sending anything of interest to the Natural History Museum London (Bannister et al., 1955). It was during this work that several new minerals came to light, including banalsite, cymrite and pennantite. The type materials (holotype and cotypes) were deposited in the Natural History Museum London, where the studies were carried out, but with cotype and topotype specimens lodged in major institutions in France and the USA. Amgueddfa Cymru received no samples of the type species.

Consequently, the only specimens of cymrite (named after the Welsh word for Wales, Cymru) in the Amgueddfa Cymru collection were purchased specimens, from Pacheco Pass, Merced Co., California, USA and Långban, Värmland, Sweden. Banalsite and pennantite were not represented in the Amgueddfa Cymru collection whatsoever. Indeed, up until the start of this millennium no examples these species from the type locality had come up for sale in mineral dealer lists and so there was never the opportunity for Amgueddfa Cymru to acquire them.

The acquisition of new XRD equipment in 2005, combined with existing energy dispersive X-ray spectroscopy (EDS) and FTIR facilities, allowed rapid analyses of mineral samples to be made at Amgueddfa Cymru. The author took the opportunity to carry out a comprehensive study of mineral specimens from the Benallt Manganese Mine in the collection of Amgueddfa Cymru, and to undertake additional fieldwork and analyses. Further specimens were provided for study by Richard Taylor and more recently by Ian Dossett and Dr David Green. All three type mineral species have been identified in material collected during the last decade.

Analytical data indicate that some of the type species are more common than was originally thought, but are inconspicuous. This explains why for so many years these species have been so elusive for mineral collectors. During the course of this study several other rare species were discovered for the first time in the British Isles bringing the total number of species known from the Benallt Mine to over sixty (Cotterrell, 2008; Cotterrell and Tayler, 2012a). One major highlight was the discovery of euhedral crystals of cymrite. An article describing the full mineralogy of the Benallt Mine is in preparation by the author.

**TYPE MINERAL SPECIES**

The Benallt Manganese Mine is officially recognised as the type locality for three mineral species: banalsite, cymrite and pennantite (see Catalogue of Type Mineral Specimens at http://www.snmp.net/IMA-CM/ctms.htm). It was for a short time the type locality for “grovesite” (Bannister et al., 1955), but this was later shown to be a polytype (Ia) of pennantite (Bayliss, 1975; Bayliss, 1983; Bailey, 1988). The Benallt Manganese Mine has also been listed as the type locality for bannisterite in several major publications (Clark, 1993; Bevins, 1994; Gaine et al., 1997; Tindle, 2008), but the International Mineralogical Association (IMA) catalogue of type mineral specimens records Franklin, New Jersey, USA as the type locality.

**BANALSITE, BaNa$_2$Al$_4$Si$_4$O$_{16}$**

This mineral was discovered in July 1943 in ore on the footwall side of the No. 1 Orebody by No. 1 Chute, 50-60 feet west of the main band (Benallt No. 1 Shaft) and some 10-20 feet above the 130 foot level, and named for its composition Ba, Na, Al, and Si (Campbell Smith et al., 1944a,b). Banalsite represents the first alumino-silicate of barium containing sodium as the dominant alkali to be discovered.

In the original find banalsite forms a 1.5 cm wide, compact and rather coarsely crystalline band in dark, spotted manganese ore with additional narrow, white veins running parallel to the main band (Campbell Smith et al., 1944a). Calcite and minor baryte occur in association with banalsite in the main vein and dark, narrow, bladed crystals of tephroite and alleghanyite up to 2 cm in length cross-cross the banalsite (Campbell Smith et al., 1944a). Angular fragments of opaque, black jacobsite occur as inclusions in the vein.

Further specimens were discovered in separate sections of the mine. Campbell Smith et al. (1944a) reported banalsite forming a thin (less than 1 cm) opaque white layer between ‘bedding planes’ of the No. 2 Orebody towards the foot wall side. This ore body lies 40 to 80 feet west of the Court Shaft, and dips east at about 60°. In that occurrence baryte occurs in association with banalsite with a few small tephroite crystals. In places a thin coating of minute harmotome and baryte crystals is present on the banalsite layer. Additional specimens collected from the No. 2 Orebody in November 1943 revealed pearly cleavages of banalsite among cleavage plates of baryte which pervade the ore.

The first distinct crystals were described by Campbell Smith (1945) on material collected from the No. 5 Orebody by Dr A.W. Groves. The crystals are 0.5 to 1 mm in length, although one rather rough crystal was 2 mm long. The crystals are colourless with a pearly lustre on some faces and occur in a small cavity in a thin mineralised band of a blackish brown chloride, described by Bannister et al. (1955) as grovesite, but shown by Bayliss (1983) to be pennantite-(Ia), partially coated by a film of baryte. A second thin platy band of massive banalsite with a crust of pale brown mica (probably ganophyllite) coated by numerous, minute, harmotome crystals is separated from the chloride band by a narrow slip of ore (Campbell Smith, 1945).

According to the catalogue of type mineral specimens, holotype material is housed at the Natural History Museum.
London, as specimens BM 1944.420-423. Topotype material was donated to the National Museum of Natural History (NMNH), Washington, USA by the Natural History Museum London in 1949 (now registered as No. 105854). Cotype material was donated to the Musée de Minéralogie de l’École Nationale Supérieure des Mines de Paris (ENSM), France by the Natural History Museum London, in 1965 and cotype material was donated to Muséum National d’Histoire Naturelle (MHN), Paris, France, by “WC Smith” (presumably Walter Campbell Smith), date unknown (registered as 146.20).

Liferovich et al. (2006) demonstrated that banalsite from Benallt Mine conforms to end-member composition. It is particularly interesting that no strontium was detected by Liferovich et al. (2006), given that significant strontium occurs at Benallt in the form of strontianite (Bevins, 1994), piemontite-(Sr) and epidote-(Sr) (Cotterell and Tayler, 2012a).

The present study has identified many specimens of banalsite at Benallt, all with subtly different forms. Specimens have been collected from the long dump at SH 2224 2804 which appears to be derived from the earlier Rhiw Mine workings and from partially excavated dumps in a field at grid reference SH 2210 2813. Examples include fudge-coloured masses (Fig. 8) consisting of massive, intergrown banalsite, cymrite and andradite (NMW 2002.3G.M.1: XRD NMW X-1495), relatively pure cream-coloured, massive to sugary crystalline masses (Fig. 9) with minor baryte in association (NMW 2007.20G.M.1: NMW X-1515), pinkish crystallized masses (Fig. 10) of pure banalsite showing discrete, blocky micro crystals (NMW 2006.15G.M.4: NMW X-1406), white, massive, sugary, veinlets of analcime intergrown with banalsite with traces of harmotome and edingtonite in massive cream-coloured analcime containing minor intergrown banalsite (NMW 2007.20G.M.6: NMW X-1608-1611), minor banalsite intergrown with cream-coloured, pseudohexagonal cymrite crystals (NMW 2008.2G.M.1: NMW X-1743), massive clove brown banalsite intergrown with calcite and minor baryte (D.I. Green specimen, NMW X-2364), and massive, dark brown banalsite containing hematite-rich pisoliths with later surface coatings of gorceixite as described by Cotterell and Tayler (2012b).

**Figure 8.** Banalsite. Fudge coloured massive banalsite intergrown with cymrite and andradite. Specimen approximately 6 cm across. NMW 2002.54G.M.1. Photo D.I. Green.

**Figure 9.** Banalsite. Cream coloured sugary banalsite. Field of view 15 mm across. NMW 2007.20G.M.1. Photo D.I. Green.

**Figure 10.** Banalsite. Relatively pure crystallized pinkish banalsite. Field of view 15 mm across. NMW 2006.15G.M.4. Photo D.I. Green.
The variety of forms and the fact that it occurs intimately intergrown with a number of other phases suggests that banalsite may be relatively common, but may have been overlooked by mineral collectors due to its inconspicuous appearance. In this regard it is worth recording that the vast majority of banalsite identified during this study is cream to brown in colour rather than the colourless to white material described by Campbell Smith et al. (1944a,b) and Campbell Smith (1945). Perhaps more importantly banalsite usually exhibits bright pink fluorescence under short wave UV light similar to, but not quite as dark as, that observed for paracelsian. This should not, however, be used as the main method of identification because white calcite from Benallt also fluoresces pink in UV light (Campbell Smith, 1948); however, it is a useful indicator.

Banalsite has recently been identified (NMW X-2657 and NMW X-2665) in cream- to beige-coloured lenses in massive, dark, chocolate-brown tephroite collected at the nearby and geologically similar Nant Mine by Dr Austin Woodland during the 1930s (specimen no. NMW 37.676. GR.14), suggesting that it is quite widespread in the Woodland during the 1930s (specimen no. NMW 37.676. GR.14), suggesting that it is quite widespread in the different orebodies.

**PENNANTITE, \( (\text{Mn}_2\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8 \)**

Pennantite was described by Campbell Smith et al. (1946) as manganese-rich chlorite and named after the famous Welsh naturalist and travel writer Thomas Pennant (1726-1798). Bayliss (1975; 1983) showed that two polytypes of pennantite exist at the Benallt Mine, including the Ia type, represented by the mineral formerly known as “grovesite” (Bannister et al., 1955) and the Ib type, the original pennantite of Campbell Smith et al. (1946).

Pennantite (now pennantite-Ib) forms the dominant constituent of the ore at the Benallt Mine (Groves, 1952), where it is orange-coloured. It is often intergrown with other manganese silicates and oxides, which makes identification difficult. Manganese-rich chlorite was suspected as one of the ore minerals by Dr H.F. Hallimond during examination of some sections of ore, and Matley (1932) and Woodland (1939) identified a yellow manganese-rich chlorite as an important secondary mineral in the manganese ore at the nearby and geologically similar Nant Mine.

The opportunity to characterize this new mineral came with the discovery of discrete veins traversing massive manganese ore from the Ty Canol Incline section of the Benallt Mine (Campbell Smith et al., 1946). Pennantite occurred as small (0.5 mm), orange-brown, micaceous flakes lining the walls of thin, white to pink, veins consisting of analcime, paragonite and banalsite with occasional ganophyllite, pyrophanite, calcite and tephroite (Campbell Smith et al., 1946).

According to the catalogue of type mineral specimens, cotype material is housed at the Natural History Museum London, as specimens BM 1947,295 and 296. Topotype material was donated to the Musée National d’Histoire Naturelle (MHN), Paris, France by the Natural History Museum London (part of specimen no. BM 1944,50) and to the National Museum of Natural History (NMNH), Washington, USA, also by the Natural History Museum London in 1949 (now registered as no. 105855).

The second structural type, pennantite-Ia, was originally described by Bannister et al. (1955) under the name “grovesite”, as the manganese-rich analogue of berthierine. It seems appropriate here to mention that “grovesite” is named in honour of Dr Arthur William Groves (see above). It was due to him that the Natural History Museum London received the material in which the new minerals banalsite, cymrite, pennantite and “grovesite” were discovered (Bannister et al., 1955; Beard, 1956).

Bannister et al. (1955) based their identification on XRD as chemically “grovesite” is almost identical to pennantite. It occurs as dark brown rosettes in a thin crust on manganese ore from the No. 5 Orebody at Benallt on Natural History Museum London, specimen no. BM 1944,35 (Bannister et al., 1955). However, Peacor et al. (1974) established that “grovesite” is actually a one-layer manganese chlorite and not a member of the serpentine group. Subsequently Bayliss (1975) recommended that the name “grovesite” be discarded because it is a polytype of a previously described species, pennantite. Thus it was recommended that pennantite-Ia be used as the name for specimens previously described as “grovesite” and pennantite-Ib for the original two-layer structure type (Bayliss, 1983).

This study has identified pennantite in dump material, but has also revealed that, although it is probably widespread, definitive identification of pennantite at Benallt is not practical by XRD alone due to the similarities in structure between chlorite group phases. Compositions ranging from near end-member pennantite to manganese-rich clinochlore have been found by EDS of material collected recently, but Groves (1952) implied that much chamosite is also present. All recent analyses have shown a deficiency in iron. Realistically, XRD data will determine whether the material in question is a member of the chlorite group, but chemical data is required in order to assign accurate species status.

A useful starting point in identification is that pennantite is orange to orange-brown when fresh (Fig. 11), compared...
with the typical dark green colour of clinochlore or chamosite, and alters to a darker, purplish-brown colour (Fig. 12) while maintaining its chlorite-like appearance. It should, however, be stressed that the colour is only a guide to the presence of manganese as manganese-rich chamosite also weathers to a brown colour.

Several examples of pennantite have been definitively identified during this study, almost invariably associated with celsian. Patches of a dark reddish-brown ‘chlorite’ (Fig. 12) associated with masses of crystalline celsian in specimen NMW 2006.15G.M.5 collected by the author from grid reference SH 2220 2812 near to the old Main Shaft at the Rhiw Mine, produced an XRD pattern (NMW X-1405) consistent with several chlorite group minerals. EDS data show that no iron is present and that manganese is dominant over magnesium by a factor of 2.7.

Discrete, small, brown, hexagonal, mica-like 'books' in bladed baryte in veins cutting massive celsian in specimen NMW 2006.4G.M.3 collected from the field dumps at SH 2210 2813 by Richard Tayler is identified as a chlorite-group phase by XRD (NMW X-1498) with the presence of a chlorite group phase suspected.

**CYMRITE, BaAl₂Si₂(O,OH)₆H₂O**

Campbell Smith et al. (1949) described cymrite on the basis of specimens collected in 1944 by himself and Dr A.W. Groves from the 60 foot level in the No. 1 Orebody and from the No. 5 Orebody. Two crystal habits are described by Campbell Smith et al. (1949): colourless plates up to 7 mm across and 0.5 mm thick on dark, compact manganese ore from the No. 1 Orebody, and white, satiny, prismatic crystals, hexagonal in form, exceptionally to 1 mm long with a fibrous structure parallel to their length associated with ganophyllite in thin veins traversing manganese ore.

According to the catalogue of type mineral specimens the Natural History Museum London is the only institution that holds type material. The holotype is no. BM 1944,36 and cotype no. BM 1944,48.

However, in December 2010, the mineral dealer Rob Lavinsky offered for sale an ex. American Museum of Natural History specimen, No. T29124H, described as from the No. 1 Orebody and part of the cotype specimen BM 1944,48. To the author’s knowledge this is the only specimen of cymrite from the original discovery at Benallt Mine to ever come up for sale. Unfortunately the specimen was sold before Amgueddfa Cymru was made aware of its existence.

Fieldwork and analyses by the author have identified both crystal forms, usually in association with prismatic celsian crystals. Cymrite has also been identified (NMW X-1495) as a minor phase, intergrown with banalsite and andradite in massive, beige-coloured material on Amgueddfa Cymru specimen no. NMW 2002.3G.M.1 (see Figure 8 for comparison), collected by Richard Tayler from dumps at SH 2210 2813.
Well-crystallized specimens displaying small spherical cymrite masses (typically <4 mm diameter) containing a massive, pale grey to white core (Fig. 13) and coated by sheaf-like clusters of small, colourless to white, prismatic cymrite crystals (to 0.8 mm long) (Figs. 14 and 15), were discovered on overgrown dumps at SH 2220 2812 derived from the Rhiw Mine. The spherical aggregates, which have a passing resemblance to cockscomb baryte, are occasionally aggregated to form layers in celsian-rich Mn ore. In this material cymrite is paragenetically later than celsian, often lining cavities with prismatic celsian protruding through the layers of spherical cymrite and occasionally with thin surface coatings of soft black manganese oxides. Identification was made by XRD (NMW X-1436) on specimen NMW 2006.15G.M.1. This form of cymrite exhibits faint greenish-white fluorescence under short wave UV light.

In 2007 an entirely different habit of cymrite was identified in material collected from inside an old walled enclosure between the Macelllan Shaft and the old Main Shaft at the Rhiw Mine. Beige-coloured masses (to small cabinet size) comprising aggregated, colourless to beige, platy, pseudo-hexagonal crystals (Fig. 16) to several mm across with minor banalsite intergrowths and occasional prismatic celsian crystals were recovered. Identification of cymrite was confirmed by XRD (NMW X-1743 and NMW X-1744) on specimen NMW 2008.2G.M.1.

**BANISTERITE, (K,Ca)\(_{0.5}\)(Mn,Fe,Zn)\(_4\)(Si,Al)\(_7\)O\(_{14}\)(OH)\(_8\)**

Also rediscovered during this research was the rare manganese silicate bannisterite. Confusion exists over the exact type locality for this species. Some publications list the Benallt Mine as the type locality (Clark, 1993; Bevins, 1994; Gaines et al., 1997; Tindle, 2008; Cotterell, 2008), but others (Dunn, 1995; Dunn et al., 1981; Blackburn and Dennen, 1997) describe Franklin, New Jersey as the type locality. Mindat.org prefers to list both localities (http://www.mindat.org/min-509.html). The International Mineralogical Association (IMA) catalogue of type mineral specimens records Franklin, New Jersey, USA, as the type locality, with no mention of the Benallt Mine whatsoever. It is worth setting out the background to this confusion.

Bannisterite was named by Lindberg Smith and Frondel (1968) in honour of Dr Frederick Allan Bannister.
(1901-1970), former Keeper of Mineralogy at the British Museum (Natural History), whose X-ray work helped to establish the existence of the new mineral in material from the Benallt Mine (Campbell Smith, 1948). Lindberg Smith and Frondel (1968) described bannisterite from Franklin, New Jersey, USA, and the Benallt Mine, Wales, on the basis of chemical and crystallographic data obtained from material from Franklin Furnace, New Jersey, USA. The material was earlier studied and analysed by Foshag (1936). Foshag had, however, described the very coarse, platy, brown mineral as a form of ganophyllite on the basis of optical and chemical properties, not knowing that it differed crystallographically to lath-like ganophyllite crystals.

Campbell Smith (1948) demonstrated that two forms of ganophyllite were present in material from the Benallt Mine using XRD and detailed optical studies. Lindberg Smith and Frondel (1968) acknowledged the work done by Campbell Smith (1948), confirmed their observations, and established that two different minerals occur in the Benallt and Franklin specimens. The original ganophyllite described was from Harstig, Sweden, and for the new form they proposed the name bannisterite. No new chemical data were presented for the Benallt bannisterite by Lindberg Smith and Frondel (1968), but the optical properties recorded by Campbell Smith (1948) were quoted. Lindberg Smith and Frondel (1968) also highlighted the fact that the new mineral had been independently identified by a separate group of researchers in specimens from the Ananai Mine, Kochi, Japan.

Later, Dunn et al. (1981) produced new chemical data for bannisterite using material from Franklin, New Jersey, USA, and Broken Hill, Australia, but failed to mention the occurrence at the Benallt Mine. In 1995 Dunn described the history of bannisterite, but again failed to recognise the occurrence at the Benallt Mine. The reason for this is probably because all of the registered type specimens are from Franklin, New Jersey.

According to the catalogue of type mineral specimens, the holotype and cotype specimens are housed at the National Museum of Natural History (NMNH), Washington, USA (numbers 145728 and 145729), donated by Harvard University (through Dr Carl Francis) in 1979. Cotype material is stored at Harvard Mineralogical Museum (HMM), MA, USA, numbers 91862-3, 108571 and 128253. It was from material from the Harvard Mineralogical Museum that the original description was made by Lindberg Smith and Frondel (1968). Cotype material is also present in the Natural History Museum London (BM 1967,321).

The original Benallt Mine bannisterite was collected by Dr Groves from the No. 5 Orebody in 1944 and is registered as B.M. 1944,36 (Campbell Smith, 1948). This is also the holotype specimen of cymrite, but neither bannisterite or ganophyllite is recorded on the Natural History Museum London online database. Another specimen, B.M. 1945,110, was obtained from Stope 84 (Campbell Smith, 1948), but is still registered as ganophyllite on the Natural History Museum London online database. The only specimen of bannisterite from the Benallt Mine listed is one acquired recently from Richard Tayler and was identified in this study.

Cinnamon brown masses cementing quartz and calcite (Fig. 17 and 18) on specimen NMW 2007.7G.M.1 collected by Richard Tayler have been identified as bannisterite (NMW X-1719). EDS analyses of bannisterite from the Benallt Mine show it to be barium-rich (up to 0.38 wt% Ba), similar in composition to material from Japan described by Matsubara and Kato (1989). Bannisterite is one of the hardest species to identify at Benallt, particularly visually, and it requires a combination of XRD and accurate EDS to be certain of its identity.

**THE TYPE LOCALITY FOR PARACELSIAN?**

In discussing the type species discovered at Benallt Mine, it is perhaps worth covering the history of paracelsian. This is the name applied to describe a dimorph of celsian, adopted in 1911 (Spencer, 1942). Tacconi (1905) had earlier used the name to describe grains and granular masses of a mineral in impure marble at Candoglia, Piedmont, Italy. Spencer (1907), in abstracting Tacconi’s (1905) paracelsian as a new mineral, described it as being compositionally...
and optically near to celsian, differing by possessing only poor cleavage. Subsequently, Tacconi (1908) found a single minute (0.5 mm) crystal, which when tested gave goniometric measurements agreeing with those of celsian reported by Strandmark (1903). Tacconi (1911) concluded that his “paracelsian” was identical with celsian (Spencer, 1942).

In 1911, Griffith John Williams sent Arthur Russell some superb crystallized specimens of barium feldspar from the Benallt Mine (Russell, 1911). Russell suggested that celsian and a separate dimorphous form was present, but he did not know what it was. Many years later Spencer (1942) produced a full account of this occurrence, describing monoclinic crystals of celsian and pseudo-orthorhombic paracelsian.

Paracelsian is much rarer than celsian at the Benallt Mine and has only been recorded from three localities (www.mindat.org; http://minerals-of-the-carpathians.eu/). At Benallt paracelsian crystals exceptionally reach 5 cm in length (Fig. 7), but anything over 1 cm is considered rare. One interesting observation is that paracelsian from Benallt displays strong pink-red fluorescence under short wave UV light while celsian does not fluoresce. This fact is very useful for identification, particularly when paracelsian is poorly crystalline.

Spencer (1942) suggested that it is probable that at Candoglia, as at Benallt, both celsian and paracelsian occur together, but no indisputable paracelsian has been recorded at Candoglia despite it still being recorded as the type locality (www.mindat.org). An occurrence at the Iacobeni Mine, Suceava district, Suceava County, Romania, is listed (www.mindat.org), but the fact that no description, image, or analytical details are provided (http://minerals-of-the-carpathians.eu/) it must be considered unconfirmed. The Benallt Mine remains the only known locality for crystalline paracelsian. The catalogue of type mineral specimens (www.smmp.net/IMA-CM/ctms.htm) does not record a type locality for paracelsian. This raises an interesting question: should Benallt Mine be considered as the type locality? In the author’s opinion it should.

All modern technical data for paracelsian is derived from material from the Benallt Mine. Spencer (1942) produced the first detailed description of paracelsian based wholly on specimens collected at the Benallt Mine in 1911, and the structure of paracelsian was investigated by Chiari et al. (1985) using crystals from the Benallt Mine. Chemical data quoted in Anthony et al. (1995) relates to the Benallt Mine.

**DISCUSSION**

It is clear from earlier research (Spencer, 1942; Campbell Smith et al., 1944a; Campbell Smith et al., 1946, 1949; Groves, 1952; Bevins, 1994; Bevins and Mason, 2010) that the Benallt Mine is a fascinating mineralogical site. This study has demonstrated that, despite much of the surface remains of mining being covered by vegetation, all of the type mineral species first recorded from Benallt can still be found through diligent searching.

Very few of the rarer species found at Benallt Mine are aesthetic in nature and the vast majority occur only as fine-grained masses which require sophisticated analytical equipment in order to identify them correctly. This study was made possible through the museum investing in new XRD equipment. Anguaedda Cynru now holds a full suite of type species from the Benallt Mine and a fine representative collection of many of the other rare and unusual species recorded from the mine. The collection already contained world-class examples of celsian crystals including unusual twinned forms (Figs. 3 and 4) and some of the world’s largest crystals of paracelsian (Figs. 6 and 7). These are now complemented by rich specimens of banalsite, cymrite, pennanite and bannisterite. Many mineral species that had not previously been recorded from the mine have been identified both in recently collected material (Cotterell and Tayler, 2012a,b) and through the study of older specimens (Cotterell, 2008). Over sixty different mineral species are now known to occur at the Benallt Mine, making it one of the most diverse mineralogical sites in Wales. Research is continuing into the identification of a number of uncharacterised manganese silicates at Benallt and a complete review of the mineralogy of this unusual deposit is in preparation.

**ACKNOWLEDGEMENTS**

The author is extremely grateful to Richard Tayler, Ian Dossett and David Green for providing many specimens from the Benallt Mine for analysis. The author would also like to thank staff at Anguaedda Cynru, including Amanda Valentine-Baars, for producing polished blocks of material from the Benallt Mine, Lin Norton for drafting the location map, and Michael Lambert, formerly of Anguaedda Cynru, for assistance with EDS analysis and SEM imaging. David Green is thanked for his excellent photography of specimens and Lynda Garfield for providing the location photograph.

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Tungsten and bismuth minerals, including russellite, within greisen veins in the western Mourne Mountains, Northern Ireland

Norman R. Moles
School of Environment and Technology, University of Brighton, Brighton BN2 4GJ

Andy G. Tindle
Centre for Earth, Planetary, Space and Astronomical Research, The Open University, Milton Keynes MK7 6AA

Primary and secondary W-Bi minerals are minor components of two greisen veins associated with the Palaeocene Mournes Granite Complex in Northern Ireland. The primary mineral, ferberite ( wolframite with Fe>Mn), forms 2-3 mm crystals associated with well-crystallized quartz in a vein through greisened granite. Associated with the ferberite crystals is a suite of secondary Fe-W-Bi-Mo minerals that formed during late-stage hydrothermal or supergene alteration. These comprise bismutite, russellite, a Bi-bearing hydrated Fe-W mineral similar to hydrokenoelsmoreite (formerly ferritungstite), and an intergrowth of scheelite with an unknown Ca- and Mo-bearing mineral. This is the first record of these secondary minerals (apart from scheelite) from Ireland. Microprobe analyses and back-scattered electron images reveal a range of mineral compositions and replacement textures that help to explain the mineral forming processes. The occurrences are comparable to W-Bi-Mo mineralisation in SW England and the English Lake District.

Introduction

Tungsten and bismuth mineralisation associated with granitic intrusions is known from several areas in Britain notably Cornwall, Cumbria and the Grampian region, but has not been described previously from Northern Ireland. We report mineralogically interesting though economically insignificant occurrences of W-Bi minerals in greisen veins associated with the Western Centre of the Mournes Granite Complex in County Down. The main occurrence on the flank of Wee Roosley is a granite-hosted quartz-mica greisen vein containing black, stumpy prisms of ‘ wolframite’ that upon analysis proved to be ferberite with associated secondary species including bismutite, russellite and a scheelite-like mineral. A similar assemblage occurs in greisen veins in granite and porphyry at Gruggandoo about 2 km to the northeast. This suggests that a late-stage magmatic-hydrothermal W-Bi mineralising event followed intrusion of the western Mournes granite.

Geological Background

The Mournes Granite Complex (Meighan et al., 1984; Cooper and Johnston, 2004) comprises five overlapping plutonic intrusions, named G1 to G5, of Palaeocene age (around 56 Ma) emplaced into Silurian greywackes and shales (Fig. 1). Several features such as porphyritic, granophyric and drusy textures suggest a level of emplacement perhaps as shallow as 3-4 km below the contemporary land surface, although there is no evidence of associated volcanicity. The mechanism of emplacement was previously regarded as
cauldron subsidence (Richey, 1928), but Stevenson et al. (2007) and Stevenson and Bennett (2011) dispute this and propose a blister-like, laccolithic intrusion mechanism for the Eastern and Western Centres with magma emanating from a deep source to the south of the present outcrop.

Surrounding the Eastern Centre granites (G1 to G3) is an annular dyke-like intrusion of quartz feldspar porphyry which is regarded as a cone sheet (Richey, 1928). Although shown on published geological maps as a continuous sheet, the original Geological Survey field mapping shows that it comprises multiple discontinuous dyke segments (Fig. 1). As the porphyry ‘cone sheet’ is truncated against the G4 granite at Gruggandoo (Figs. 1 and 2), its intrusion must predate the Western Centre granites G4 and G5 (Emeleus and Preston, 1969).

The last major magmatic event was emplacement of the G5 granite largely within the pre-existing G4 granite sheet, such that G5 underlies G4 in much of the western Mournes. The resulting geometry is a sill-like body of G4 around 200-300 m thick sandwiched between the overlying Silurian greywacke country rock and the underlying G5 granite. Minor dykes of intermediate to mafic composition intrude all the granites. In the western Mournes, faulting created a graben structure and crush zones that have been exploited by weathering and glacial erosion to form prominent NNE-trending valleys through the mountains.

The Mournes Granites are well known for beautiful crystals of smoky quartz, feldspars, topaz, beryl and other pegmatite-association minerals within drusy cavities (e.g. Green et al., 2005). Cassiterite has been reported in the eastern-central Mournes occurring in drusy cavities (Seymour, 1903) and in thin quartz veining associated with greisen alteration at Pollaphuca and the Miners Hole (Fig. 1) (Arthurs and Earls, 2004). Cassiterite is common and locally abundant in heavy mineral concentrates derived from stream sediments in the western Mournes (Warner et al., 2010). Alluvial gold is also found in stream sediments in the western Mournes. This gold is undoubtedly derived from local bedrock sources (Chapman et al., 2000; Warner et al., 2010), and although in situ mineralisation has not been found, this is likely to be located in the Silurian country rock near contacts with the granite (Moles et al., 2013). Some of the alluvial gold is relatively enriched in copper and contains inclusions of bornite, chalcocite and hessite. Minor occurrences of chalcopyrite and galena, in veins and vug fills, are known in the Silurian country rocks, for example at Aughrim Quarry in the central southern Mournes (Moreton et al., 2012).

Tungsten and bismuth minerals have not previously been described from the Mournes area. The occurrences described here were found while one of the authors (NRM) was supervising undergraduate geology mapping and prospecting for potential bedrock sources of cassiterite and gold (these were not discovered).

LOCATION AND MINERALISATION

The greisen occurrences are in the upper Leitrim River valley south of Hilltown on the flanks of hills named Gruggandoo and Wee Roosley (Figs. 1 and 2).

The Wee Roosley locality is a small disused quarry, about 15 m wide, from which granite kerbstones were produced probably in the late 19th or early 20th century. The quarry exposes G4 granite that is underlain by G5 at a depth of around 15-20 m below the level of exposure.
At the south side of the quarry face is a sheared greisen vein approximately 0.7 m wide, trending NNE (Fig. 3), in which white mica and kaolinite replace the original feldspars. The sample analysed is a vein of vuggy, well crystallized milky quartz within greisen from the east margin of the main structure. The sample contains minor topaz and mica (based on XRD and optical microscopy; not fully characterized) and small stubby prisms of a sub-metallic black mineral, provisionally identified as wolframite, partially altered to a brittle, pale yellow mineral. Examination of a polished thin section of this sample using EMPA revealed the presence of ferberite (wolframite with Fe>Mn) along with secondary minerals namely bismutite, russellite, a Fe-W-Bi-oxide species similar to ferritungstite, and a scheelite-like mineral occurring in intimate association within the black prismatic crystals.

The Gruggandoo locality is a bracken-clad hillside with scarce exposures of bedrock close to the contact of the G4 granite with hornfelsed Silurian greywacke and shale. At this site, Emelues and Preston (1969) described a quartz feldspar porphyry cone sheet truncated by the G4 intrusion. Greisen alteration of the porphyry was observed by one of us (NRM) in a distinctly banded exposure (Fig. 4) located about 25 m up slope (west) of the inferred contact. The banding is due to parallel, dark-coloured alteration zones about 1 cm wide that cut through pale coloured, relatively unaltered porphyry. Similar greisen veining was found within the G4 granite nearby. The alteration comprises topaz and chlorite (identifications based on XRD and optical microscopy), akin to greisen alteration described by Emelues and Preston (1969) from south of Lindsay’s Leap quarry in the eastern Mournes and observed by us at the Miners Hole (Fig. 1). In samples from the Gruggandoo locality, metallic minerals were not obvious from visual inspection although tiny crystals of metallic minerals were found in polished thin section.

In the following account of the minerals and their chemical composition, the description relates to the Wee Roosley greisen unless specified otherwise.

TUNGSTEN AND BISMUTH MINERALS

FERBERITE, Fe²⁺WO₄

Ferberite is the principal primary tungsten mineral and forms a series with hübnerite, MnWO₄. Without analyses, these species are not readily distinguished and in such circumstances the more inclusive term wolframite is commonly used. Electron microprobe analyses of wolframite crystals from many localities in SW England show core to rim and/or oscillatory zonation with zones of intermediate...
composition between ferberite and hübnerite end members (Tindle, 2008). Rarely, crystals of the ferberite-hübnerite series contain major amounts of niobium, as in the vein occurrence at Glen Gairn, Grampian, Scotland (Tindle and Webb, 1989).

At Wee Roosley, ferberite occurs as black prismatic crystals typically 2-3 mm in length and 0.5-1.0 mm wide within quartz (Figs. 5 and 6). Table 1 presents representative microprobe analyses which show variations in the Fe and Mn contents. Fifteen analyses of three crystals of ferberite show a range in Mn/(Mn+Fe) ratios from 0.09 to 0.48, averaging 0.20, i.e. some compositions are close to hübnerite in which the ratio is >0.5. Niobium was occasionally detected with values up to 0.51% Nb$_2$O$_5$ whereas tantalum was not detected. These compositions are similar to wolframite from SW England and localities in the Lake District (e.g. Young et al., 1986) but contrast with the composition of zoned wolframite crystals from Glen Gairn which range from pure hübnerite to transitional hübnerite-ferberite containing major amounts of Nb and Ta (Tindle and Webb, 1989; Webb et al., 1992).

**BISMUTITE, (BiO)$_2$CO$_3$**

Bismutite is a rare secondary bismuth mineral that typically forms as a result of the alteration of Bi-bearing minerals. In Britain, it has been described from a number of Cornish tin mines, such as South Crofty (Anthony et al., 1990), from the Carrock Fell Tungsten Mine in Cumbria (Tindle, 2008), and in a supergene alteration assemblage associated with a Cu-W-bearing vein in the Eskdale Granite (Young et al., 1986). Bismutite has not been recorded previously from Ireland.

Bismutite occurs as microscopic, prismatic crystals typically less than 300 µm in length associated with ferberite in the Wee Roosley greisen (Fig. 6) and as isolated crystals of similar or smaller size in the Gruggandoo greisen. Representative microprobe analyses are given in Table 2. Low oxide totals in some analyses may be due to undetermined H$_2$O or may be a consequence of uneven

![Figure 6. Colour enhanced back-scattered electron image of a prismatic crystal of ferberite (yellow) with associated bismutite (orange-red) and a zoned scheelite-like mineral (turquoise-blue) in the Wee Roosley greisen. The matrix of quartz and altered feldspar appears black. Width of view 1.5 mm.](image)

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**Table 1.** Electron microprobe analyses of typical ferberite in the Wee Roosley greisen. Values in weight %.

**Table 2.** Electron microprobe analyses of bismutite in the Gruggandoo and Wee Roosley greisens. Values in weight %. CO$_3$ not determined; the value of 8.63 wt% is a representative figure from Anthony et al. (1990). Analysis HA10 may represent bismutoferrite or a mixed material (see text p. 44).
surfaces as bismutite does not polish well. Fifty analyses of Wee Roosley bismutite showed compositional ranges with maximum wt% values of: 0.79 MoO$_3$; 7.58 WO$_3$; 0.56 ThO$_2$; 1.84 UO$_2$; 0.79 CaO and 0.33 FeO. From 26 analyses of bismutite in the Gruggandoo greisen, the corresponding maximum wt% values are: 0.18 MoO$_3$; 0.19 WO$_3$; 0.15 ThO$_2$; 2.58 UO$_2$; 0.50 CaO and 19.14 FeO. One possibility is that Gruggandoo bismutite compositions are transitional to bismutoferrite, Fe$^{3+}_2$Bi(SiO$_4$)$_2$(OH). A more likely explanation is the presence of nanoparticulate iron oxides or oxyhydroxides, such as schwertmannite or goethite, in the Bi-rich material (Cornell and Schwertmann, 1996).

We speculate that the absence of ferberite in the Gruggandoo greisen may have encouraged iron to be accommodated in bismutite, whereas at Wee Roosley iron was preferentially taken up by the Fe-rich secondary material that replaced ferberite. In Gruggandoo bismutite, uranium and iron concentrations show a mutual positive correlation with higher amounts of UO$_2$ in the Fe-rich analyses. This supports the hypothesis that nanoparticulate iron oxides may be present, since actinides commonly sorb to such particles. Molybdenum and tungsten concentrations are relatively higher in the Wee Roosley bismutite, although the abundance of Mo and W is not correlated.

### Unidentified Fe-W-Bi mineral pseudomorphing ferberite

In the Wee Roosley greisen, some of the ferberite crystals are pseudomorphed by a dull grey-black mineral. Microprobe analysis showed that the pseudomorphs are iron-rich and contain significant tungsten and minor bismuth (Table 3). Low oxide totals suggest the presence of undetermined H$_2$O or (OH). This mineral was initially considered to be the common alteration product of ferberite, ferritungstite, Fe$^{3+}_2$(WO$_4$)(OH)$_4$4H$_2$O, which is now regarded as a ferric iron-rich variety of hydrokenoelsmoreite, □$W$O$_6$(H$_2$O) (Atencio et al., 2010). However, as the amounts of FeO exceed 50 wt% and WO$_3$ does not exceed 21 wt%, the mineral cannot be ferritungstite in which by definition W>Fe (Ercit and Robinson, 1994). Therefore the identity of this mineral has yet to be determined. The pseudomorphs may well comprise an intimate mixture of minerals with ferritungstite (hydrokenoelsmoreite) as one component (David Green, personal communication).

Viewed with an electron microscope in back-scattered electron mode (BSE), the crystals show internal heterogeneity with dark and light areas and bands: bright areas are relatively W-rich with higher oxide totals, and darker areas are relatively W-poor with lower oxide totals. The bands or zones transgress across the original cleavage and crystal growth zonation (Fig. 7) and are in places

<table>
<thead>
<tr>
<th>Wee Roosley</th>
<th>Comparisons</th>
</tr>
</thead>
<tbody>
<tr>
<td>3e</td>
<td>4b</td>
</tr>
<tr>
<td>MnO</td>
<td>1.21</td>
</tr>
<tr>
<td>FeO</td>
<td>58.25</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>0.04</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>0.04</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>12.46</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>1.95</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.36</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.24</td>
</tr>
<tr>
<td>CaO</td>
<td>0.10</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Total 76.65 80.24 78.86 99.75 95.91

Table 3. Electron microprobe analyses of Fe-W-Bi pseudomorphs of ferberite in the Wee Roosley greisen. Values in weight %. For comparison are analyses of ferritungstite from Kalzas Mountain, Yukon Territory, Canada (Ercit and Robinson, 1994) and from the hydrokenoelsmoreite type locality, the Germania Tungsten Mine, Adams Mountain Stevens County, Washington, USA (Bernard and Hyrstl, 2004).
symmetrical around cracks, suggesting that Fe and W were redistributed during pseudomorphic replacement of the original ferberite. Bismuth was presumably introduced during this process, as Bi is absent from unaltered ferberite elsewhere in the sample.

**RUSSELLITE, Bi$_2$WO$_6$**

Russellite generally occurs as an alteration product of previously formed bismuth minerals in Sn-W-bearing hydrothermal, pegmatite or greisen mineralisation. It was originally characterized from the Castle-an-Dinas wolfram mine in Cornwall by Hey and Bannister (1938) who remarked upon the variability in russellite compositions. Subsequently russellite has been described by Young et al. (1991) from Buckbarrow Beck, Cumbria, and by Webb et al. (1992) from Glen Gairn in the Grampian region, Scotland. It remains a very rare mineral.

In the Wee Roosley greisen, russellite occurs as inclusions within the pseudomorphs of ferberite crystals.

The inclusions are tens of microns in size (Figures 7 and 8) and clearly cut across pre-existing grain boundaries within the host mineral (Fig. 8). Microprobe analyses indicate compositions are close to stoichiometric with some substitution of iron for tungsten (Table 4). A similar composition for russellite, 69.5% Bi$_2$O$_3$ and 30.5% WO$_3$, was calculated by Hodge (1970) from a wet chemical analysis of impure material from Poona, Western Australia. In contrast, russellite from Glen Gairn (Webb et al., 1992) has more Bi and less W than the formula would indicate. Russellite compositions reported by Young et al. (1991) from Buckbarrow Beck have less W than the Wee Roosley analysis, but contain significant amounts of V, Cu, As and U which were not observed in detectable amounts in the Wee Roosley material.

**SCHEELITE, CaWO$_4$ and unidentified Ca-W-Mo mineral**

Scheelite is a relatively common calcium tungstate found in high-temperature hydrothermal veins and greisens, and also in granite-related skarn and contact metamorphic mineralisation. Commonly a primary mineral, scheelite is also found as an alteration product of wolframite, often associated with the appearance of a carbonate phase in the paragenesis (King, 2005). King notes that wolframite containing 10-20% Mn is often not homogeneous and is more liable to alteration than Fe-dominant wolframite. Supergene dissolution cavities in the cores of wolframite crystals are often where secondary tungstate crystals are found (Sahama, 1981).

Trapezoidal crystals, typically 100-200 µm across, of a brightly fluorescent mineral were observed in cavities within some ferberite crystals in the Wee Roosley greisen (e.g. Fig. 6). This blue-fluorescent mineral was initially presumed to be scheelite. However, microprobe analyses show that this mineral is actually a Ca-W-Mo scheelite.

<table>
<thead>
<tr>
<th></th>
<th>Wee Roosley</th>
<th>Buckbarrow Beck</th>
<th>Glen Gairn</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1a</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>64.16</td>
<td>62.13</td>
<td>63.95</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>29.04</td>
<td>20.21</td>
<td>20.01</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>2.30</td>
<td>1.15*</td>
<td>1.37*</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>-</td>
<td>1.07</td>
<td>1.02</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>1.76</td>
<td>1.95</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>-</td>
<td>0.93</td>
<td>1.02</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>-</td>
<td>3.19</td>
<td>3.40</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>2.50*</td>
<td>3.25*</td>
</tr>
<tr>
<td>Total</td>
<td>(96.42)</td>
<td>(93.93)</td>
<td>(96.40)</td>
</tr>
</tbody>
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**Table 4.** An electron microprobe analysis of russellite in the Wee Roosley greisen. For comparison, analyses are included of russellite from Buckbarrow Beck, Cumbria (Young et al., 1991) and from Glen Gairn, Grampian (Webb et al. 1992). – not determined; * wt% Fe$_2$O$_3$; ^ wt% SO$_3$. Totals in brackets include <0.5 wt% Al$_2$O$_3$ and SiO$_2$. 

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of the fluorescent crystals showed a variable deficiency in tungsten and enrichment in calcium, coupled with enrichment in molybdenum and low oxide totals (Table 5). Back-scattered electron images show pronounced growth zonation in the crystals with dark and bright bands giving the appearance of oscillatory zonation (Fig. 9). The bands are narrower than the resolution of the microprobe beam and therefore all analyses are mixtures of the compositions of the bright and dark bands. Transects of analyses from core to rim across individual crystals (an example is shown in Fig. 10) indicate that the bright bands have relatively higher tungsten and lower molybdenum than dark bands. Figure 11 is a scatter plot of W against Mo oxide values in a set of 24 analyses from three crystals. There is a systematic trend of increasing Mo with decreasing W, although an undetermined component must account for most of the weight change as the WO$_3$ content decreases. Analyses with the highest W and lowest Mo approach the composition of scheelite, calculated from the formula as 80.5 wt% WO$_3$ and 19.5 wt% CaO. Scheelite forms a series with powellite, CaMoO$_4$, for which the calculated composition is approximately 72 wt% MoO$_3$ and 28 wt% CaO. However, in the Wee Roosley crystals the Mo content is far too low, even in the most Mo-rich laminae, to be powellite (Table 5). EMPA alone is unable to elucidate the identity of the Ca-W-Mo mineral that is forming micron-wide bands alternating with scheelite, and this mineral has yet to be determined.

<table>
<thead>
<tr>
<th>Wee Roosley</th>
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<tbody>
<tr>
<td>MoO$_3$</td>
</tr>
<tr>
<td>WO$_3$</td>
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<tr>
<td>SiO$_2$</td>
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<tr>
<td>ThO$_2$</td>
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<tr>
<td>UO$_2$</td>
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<tr>
<td>CaO</td>
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<tr>
<td>MnO</td>
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<tr>
<td>FeO</td>
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<tr>
<td>Total</td>
</tr>
<tr>
<td>AK</td>
</tr>
<tr>
<td>0.16</td>
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<tr>
<td>71.19</td>
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<td>0.23</td>
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<tr>
<td>0.03</td>
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<tr>
<td>0.15</td>
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<tr>
<td>20.41</td>
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<tr>
<td>0.00</td>
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<tr>
<td>0.03</td>
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<tr>
<td>92.20</td>
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Table 5. Electron microprobe analyses of scheelite (AK) and of scheelite intergrown with an unidentified Ca-W-Mo mineral in the Wee Roosley greisen. Values in weight %.

Figure 9. Back-scattered electron image of an oscillatory zoned crystal of a scheelite-like mineral within ferberite in the Wee Roosley greisen. Light zones are W-rich, dark zones are W-poor with low oxide totals indicating undetermined components such as water or hydroxyl ions. The red line indicates the EMPA traverse shown in Figure 10. Long axis of the crystal is 100 µm.

Figure 10. Line graph of EMPA analyses taken at 4 µm intervals across an oscillatory zoned crystal of a scheelite-like mineral, Wee Roosley greisen. Values are weight % oxides; values for MoO$_3$ multiplied by 10 to enhance visibility. Low totals are explained by an undetermined component such as water or hydroxyl ions.

Figure 11. Scatter plot of tungsten against molybdenum contents, expressed as weight % oxides, in EMP analyses of Wee Roosley scheelite-like mineral. The best fit line indicates the trend of increasing Mo with decreasing W, although an undetermined component must account for most of the weight change as the WO$_3$ content decreases. Analyses with the highest wt% WO$_3$ and lowest MoO$_3$ are close to the composition of scheelite.
DISCUSSION

The Mournes W-Bi mineral occurrences are similar in mineralogy and geological setting to the Carrock Fell tungsten deposits (e.g. Shepherd et al., 1976; Tindle, 2008) and to the Buckbarrow Beck occurrence (Young et al., 1986 and 1991) in Cumbria. The W-bearing quartz veins at Carrock Fell occur within a greisened biotite granite cupola of the Skiddaw Granite. The fluids which caused the greisen alteration and precipitated the early quartz-wolframite veins were high temperature (235-335°C), low salinity, CO₂-rich aqueous fluids (Shepherd et al., 1976). Formation of scheelite as an alteration product of wolframite, and deposition of As-Fe-Cu-Mo-Bi sulphides, occurred at lower temperatures of 170-235°C. Based on oxygen isotope ratios, the high and lower temperature fluids contain a major non-magmatic component that was considered by Shepherd et al. (1976) to be meteoric waters modified by fluid-rock interaction and driven into circulation by heat from the cooling pluton. They conclude that tungsten in the Carrock Fell orebody was derived from the country rock, and not from a magmatic source. By contrast, tungsten in the Mournes is probably magmatic in origin as the occurrence within greisened granite at Wee Roosley is at least 200 m from the nearest country rock, and no tungsten mineralisation was found in greisen proximal to country rock at Gruggandoo.

In the tungsten occurrences associated with the Leinster Granite in southeast Ireland, scheelite and arsenopyrite are the dominant minerals within greisened tonalite sheets. The absence of wolframite in this setting is attributed by Gallagher (1989) to the low oxygen fugacity of the hydrothermal fluids during the mineralizing event, due to the presence of methane derived from adjacent carbonaceous metasediments. This situation presumably did not arise in the Mournes Granite as the country rocks, predominantly greywacke with lesser shale, have a low organic content.

Low temperature hydrothermal fluids, and/or supergene alteration associated with the ingress of meteoric water and kaolinisation of the greisen at Wee Roosley, have produced a series of secondary tungsten minerals. The occurrence of scheelite intimately banded with an undetermined probably hydrous Ca-W-Mo mineral as oscillatory zoned crystals within cavities inside ferberite prisms, suggests a late paragenetic alteration by molybdenum-bearing fluids. Bismutite crystals found in samples from both greisen localities in the western Mournes suggest that bismuth was also introduced, or perhaps remobilised, by late-stage hydrothermal fluids. This hypothesis is supported by the occurrence at Wee Roosley of Bi-bearing, Fe-rich ferberite pseudomorphs which contain microscopic crystals of the W-Bi oxide russellite.

Although no discrete uranium mineral species were found in the western Mournes greisen veins, microprobe analyses of bismutite show enrichment in uranium (Table 2). This is consistent with previous studies (Moles and Higgins, 1995) which suggested that late magmatic or hydrothermal fluids were responsible for uranium migration to the periphery of the granite intrusions. The recent discovery of fergusonite and gadolinite in alluvial sediments derived from the Mournes Granite (Moles and Tindle, 2011), provides further evidence that late-stage magmatic-hydrothermal processes operated during crystallization of the Mournes intrusive complex.

This study is based on microprobe analysis of samples from only two localities in the western Mournes. It seems reasonable to presume that greisen veins from other localities in the Mournes Granite Complex could also host W-Bi minerals. Further research is planned.

ACKNOWLEDGEMENTS

NRM is greatly indebted to Richard Warner for his hospitality during many visits to the Mournes, and for drafting Figures 1 and 2. Richard Roper and Joe Valentine, graduates of the University of Brighton, are thanked for their enthusiasm during the summer of 2010 when the greisen veins described here were found. AGT thanks the Open University for provision of electron microprobe machine time. We thank Brian Young and David Green for their helpful suggestions that improved the manuscript.

REFERENCES


COPPER MINERALISATION AT RASSAL, KISHORN, HIGHLAND REGION

J. Faithfull
Hunterian Museum, Gilbert Scott Building, University of Glasgow, University Avenue, Glasgow G12 8QQ

B. Young
Department of Earth Sciences, University of Durham, South Road, Durham DH1 3LE

R.E. Starkey
15 Warwick Avenue, Fringe Green, Bromsgrove, Worcestershire B60 2AH

A variety of copper sulphide minerals have been identified from a narrow vein within Cambrian dolostones, formerly worked on a small scale for copper, at Rassal, Kishorn, Highland Region. Copper sulphides within this suite include anilite, chalcopyrite, bornite, roxbyite, spionkopite and yarrowite, the last of these reported here for the first time from a Scottish location. Unusually high levels of germanium (up to 1 wt%) have been detected in samples of the chalcopyrite, and it is suggested that this could form a potentially useful metallurgical “fingerprint” for copper derived from this mine.

INTRODUCTION

The long-disused copper mine at Rassal, near Kishorn, Highland Region [NG 8486 4332], worked one of the very few vein deposits of copper mineralisation known in the Northern Highlands of Scotland (Fig. 1). Although the vein worked is clearly depicted on British Geological Survey 1:50000 Sheet 81(E) (Loch Torridon) (British Geological Survey, 1975), and despite it being mentioned, albeit very briefly, by Williams (1810), Heddle (1901), Wilson and Flett (1921) and Berridge (1969), the occurrence has attracted little other attention and no detailed description of the site’s geology or mineralisation has yet been published.

The mine, which is today designated as a Scheduled Ancient Monument, is a comparatively conspicuous feature on the bare hillside on the left bank of the River Kishorn approximately 200 m east of the northernmost extremity of Rassal Ashwood National Nature Reserve (Fig. 2).

GEOLOGICAL BACKGROUND

At Rassal, copper mineralisation occurs as an isolated vein within the Eilean Dubh Formation, of the Cambrian-Ordovician Durness Group. In the Rassal area, rocks of this group occur within the structurally complex zone of imbrication beneath the Kishorn Thrust, the lowest major thrust within the Moine Thrust zone in this part of the NW Highlands. The Kishorn Thrust plane crops out on the hillside approximately 0.4 km east of the copper mine.

Rocks of the Eilean Dubh Formation at Rassal consist of compact, fine-grained, pale grey argillaceous dolostones. Although Johnstone and Mykura (1989) noted the abundance of stromatolitic algal bands, together with a variety of sedimentary structures, elsewhere within this
formation, none has been observed in the vicinity of the Rassal cooper workings during the present investigation.

The outcrop of the Eilean Dubh Formation dolostones, together with small portions of the underlying dolostones of the Grudaidh Formation, form a narrow elongated outcrop, up to about 1 km wide, that extends for almost 8 km from the head of Loch Kishorn north eastwards to Coille Dhubh at the northern foot of Cnoc Gorm. Over much of its extent this outcrop is conspicuous due to the striking contrast between the brighter green calcareous grassland on the dolostones with the darker acidic moorland on the outcrops of the Torridonian sandstones to the west and north west and the Lewisian gneisses to the east and south east. In common with much of the outcrop of the carbonate rocks of the Durness Group in the NW Highlands, this area is of considerable botanical interest for its characteristic calcareous plant communities. The Rassal Ashwood National Nature Reserve, immediately south and west of the copper mine, is of particular ecological importance as a fine example of ancient native ash woodland.

SITE GEOLOGY AND MINE WORKINGS

The abandoned Rassal copper workings exploited a vein which, according to Wilson and Flett (1921) occupies a crush zone in dolostones of the Eilean Dubh Formation. The workings visible today comprise a prominent E-W orientated trench, approximately 100 m long, the westernmost extremity of which lies approximately 120 m east of the north eastern corner of the Rassal Ashwood National Nature Reserve enclosure fence, together with an adit level driven eastwards into the vein beneath the opencast. Although the trench has obviously been excavated along a mineralised vein, no exposures of copper mineralisation may be seen in-situ at the site today.

The field descriptions presented here are based on examinations undertaken during 2011. No attempts were made to enter or examine the underground workings which, at the time of these investigations, were partially flooded and judged to be potentially unstable and thus unsuitable for entry.

An adit, now partially collapsed and flooded, has been driven eastwards into the presumed vein structure at the westernmost extremity of the trench (Fig. 3). No copper mineralisation is visible here, but the dolostones of the Eilean Dubh Formation adjacent to the adit entrance are shattered, in places with narrow (≤5 mm) calcite veins and locally a little hematite staining, over a width of approximately 2 m. A small spoil heap, apparently derived from this adit, consists entirely of pale grey dolostone: no copper minerals were observed within it. Immediately west of this adit, the vein has no topographical expression and cannot be traced further westwards.
East of the adit the vein outcrop may be traced uphill for approximately 100 m as a conspicuous open cast trench. A few metres east of the adit, the trench is up to 0.75 m wide (Fig. 4). Here, the southern wall is comparatively smooth and well-defined, dipping steeply southwards at around 80° and locally exhibiting faint sub-horizontal slickensides which dip westwards at approximately 20° (Fig. 5). The northern wall of the trench is irregular and generally ill-defined, consisting of rather shattered grey dolostone with no sign of any introduced minerals. In the absence of any other conclusive field evidence this suggests that the vein may occupy a fault with a steep southerly inclination. If so, the hanging wall of the vein forms the southern wall of the trench.

Prominent, though modest sized, spoil heaps adjoining the north side of the trench here too are composed predominantly of pale grey dolostone, though with conspicuous small (mainly ≤40 mm) fragments of malachite some of which exhibit cores of copper sulphides. A few fragments (≤30 mm) of compact reddish grey hematite were observed within the soil on the southern side of the trench, though none was seen to be associated with any copper minerals.

Towards its eastern end, the trench widens to 2 m in width (Fig. 6). Although the vein walls are not clearly defined here, the dolostone on the southern side of the trench locally exhibits anastomosing hair-like veinlets of massive red hematite, unaccompanied by any other obvious introduced mineral.

At the eastern-most extremity of the trench, a fenced-off open excavation, up to 6 m deep, may be a deep surface excavation or a collapsed stope. This excavation is up to 3 m wide at the surface, narrowing to 1 – 0.75 m in width at 5 m depth. Although close examination of the faces exposed here could not be safely undertaken, as in the exposures noted towards the western end of the trench, the vein here also appears to exhibit a clearly defined steeply dipping southern hanging wall with a less clearly defined northern, footwall. The dolostones exposed at surface immediately above the eastern extremity of this deep excavation are shattered over a width of about 2 m, though without any obvious introduced minerals.

Spoil heaps on both sides of the trench immediately downhill from this deep excavation are composed predominantly of pale grey dolostone, but with substantially greater amounts of copper minerals, both malachite and sulphides, than seen on the smaller dumps further west. Blocks of dolostone here commonly exhibit narrow veinlets, up to 2 mm wide, of massive grey copper sulphides. From the comparatively greater size of the excavations, the amount of spoil and the abundance of remnants of copper mineralisation within it, it seems likely that this part of the mine may have been the main focus of working.

Eastwards from this deep excavation, the course of the vein may be traced uphill for at least 40 m as a shallow gully up to 0.75 m wide through exposures of dolostone. No traces of copper mineralisation are visible, though a little hematite staining on joints and bedding planes can be seen locally. There is no evidence of any trial excavations having been made on this part of the structure.

**MINING HISTORY**

Little is known of the dates of copper working at Rassal and no records of output have been found. The workings were clearly long-abandoned when described by Wilson and Flett (1921) and it is rather difficult to reconcile the features visible today with their comment that “…a good deal of work appears to have been done, and at least two shafts have been sunk…” The partially collapsed entrance to a level driven on the vein is clearly visible at the western extremity of the workings. The large excavation or open stope at the eastern extremity of the workings may relate to one of the shafts referred to by Wilson and Flett, but no sign of any other shaft could be discerned at the time of this investigation. Moreover, the amounts of spoil seem consistent with the size of the visible surface excavations, perhaps suggesting that comparatively little underground extraction may have taken place. It is also significant that the site appears to exhibit no obvious evidence of significant ore dressing: there are no accumulations of fine tailings.

Claims by Williams (1810) that the mine contained “…the best copper ore he had ever seen…”, and that the vein was very rich (Berridge, 1969) are almost certainly exaggerations.

From the evidence discernible from the surviving features, the mine cannot have yielded more than a few tons of ore at best. The dates of its operation are not known, but
it seems likely to have been a comparatively short-lived and ultimately unsuccessful trial working.

MINERALISATION

Heddle (1901, p. 29) briefly noted the presence of bornite, in association with malachite and brochantite, at Rassal, though he made no reference to the presence of any other copper minerals. In their brief descriptions of the mine, Wilson and Flett (1921, p. 145) reported that the ore occurred here in small pockets and that it consisted of bornite, together with malachite and brochantite. They offer no further descriptions of the minerals and, although they do not cite Heddle, it is likely that they were merely repeating his observations. Berridge (1969) also seems to have been repeating Heddle’s comments.

Sulphide mineralogy

Sulphides typically occur as solid ribs and veinlets mostly ≤2 mm wide, but exceptionally up to 10 mm wide, forming delicate networks within fractured pinkish dolostone. These veinlets are frequently altered to malachite and goethite.

Although many of the sulphide veinlets appear to be a clean, massive granular dark-grey sulphide, polished sections reveal that almost all samples show complex fine-grained intergrowths (Fig. 7). One consequence of this admixture is that XRD patterns, even on apparently clean grains hand-picked under binocular microscope, generally gave complex and hard-to-interpret patterns.

The mineralogy of the Cu-S system is very complex, with many potential phases in a limited compositional space, and coexistence of these phases in nature is very common, often as fine intergrowths. For this reason it is likely that mineralogical complexity is often overlooked, or missed during investigations. To further complicate the identification process, grinding (e.g. to prepare powder diffraction samples), heating during cutting or polishing, and even electron beams can cause phase transformations, especially of anilite (Morimoto et al., 1969; Posfai and Busek, 1994).

Any identification of grey to blue copper sulphides in the compositional range Cu$_2$S to CuS is thus extremely difficult. Intergrowths, peak proximities/overlaps, and sample-preparation-induced phase changes, mean that techniques like powder XRD which require crushing or grinding of material will not give robustly interpretable patterns. Generally, in-situ measurements and observations on a micro-scale on smooth broken or polished surfaces are required to support any identification, although even these techniques require cautious application and interpretation.

Large et al. (1995) provide a good review of the issues in identifying such Cu-S phases within the Permian Kupferschiefer. Given these factors, the reliability of published identifications in the mineralogical literature over this compositional range is probably rather low when based on single techniques, especially XRD.

The identifications presented here are primarily based on reflected light, and SEM/EDAX examination, augmented by insights from XRD data. XRD data were obtained by powder diffractometer from several crushed grey-blue sulphide grains, following minimal grinding under acetone in an agate mortar, and pipetting the suspension onto a silicon substrate. Although grinding was kept to a minimum, no other checks for grinding-induced phase changes were made, as it was immediately apparent that the samples were complex mixtures in any case. Despite this, the XRD data do provide some general constraints on the mineralogy: peaks matching major malachite, bornite, anilite and roxbyite peaks were seen in one or more grey-blue sulphide samples, while major geerite peaks were absent. However, the major XRD peaks for yarrowite, spionkopite and covellite are all subject to overlap with each other, or other phases and could not be unambiguously identified or distinguished in the diffractometer results.

Reflected-light and SEM imaging and analytical work were carried out on four samples, of hand-broken fragments, mounted in epoxy blocks, and polished using minimal wet
grinding and polishing. These samples included material from the same hand-specimens which provided the material for XRD, but due to sample limitations, were not necessarily from the same parts of the hand-specimens.

For SEM/EDAX work, polished blocks were carbon-coated, and examined using backscattered electron imaging on the Carl Zeiss Sigma SEM at the University of Glasgow ISAAC facility using a 20kV beam. Focussed beam EDAX analyses were obtained using Oxford Instruments INCA software on the same instrument, using Cu metal, sphalerite, and hematite as standards for Cu, S and Fe respectively, a beam current of 450 picoamps, and count times of 30 seconds, with ZAF corrections applied. Analyses were inadvertently normalised to 100 wt% Cu+Fe+S (Table 1). This is not rigorously good practice, but a measure of quality is provided by the close match in expected copper contents in analysed grains of the following known minerals:
- bornite: 61.5 to 62 wt% Cu measured (should be 63.3 wt% on basis of Cu₅FeS₄ normalised to 100 wt%)
- malachite: 60 to 61 wt% Cu measured (should be 61.4 wt% on basis of 57.48 wt% Cu, and 36.18 wt% O normalised to 100 wt%)
- chalcopyrite: 34.6 wt% Cu measured (should be 35 wt% on basis of CuFeS₂ normalised to 100 wt%)

All Cu contents in these phases are around or slightly below the theoretical values, exactly as expected where other unanalysed minor-to-trace constituents may be present. This suggests that the presented copper contents are likely to be accurate to within one weight per cent or better.

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Table 1. Chemical data for analysed points on figures. Analytical limitations and procedures are discussed in the main text.

Figure 8. Anilite (A) with bornite (B), spionkopite (S) and yarrowite (Y) in plane polarised reflected light (top) and crossed polars (bottom). Field of view approx. 0.7 mm wide.
Brief descriptions of the copper sulphide minerals present within the Rassal ores, together with the methods employed in their identification, follow.

**ANILITE Cu₇S₄ (XRD, optical and EDAX identification)**

Anilite is a difficult phase to identify, being prone to phase-change during grinding (e.g. for XRD) or polishing. However, the three largest peaks for anilite are present in two of the three grey-blue sulphide XRD patterns, and this would fit with the widespread presence of a weakly anisotropic, blue-grey phase with approximately 75% Cu in the intergrown sulphides (Fig. 8, see p. 53). One polished sample shows distinct clean, prismatic crystals of this phase in a carbonate vein (Fig. 9), the habit resembling that of published pictures of anilite (e.g. Pracejus, 2008, p. 123).

**GEERITE Cu₃FeS₄ (optical and EDAX identification)**

Geerite is another pale bluish grey, very weakly anisotropic mineral, with a very similar copper content around 75% Cu. Given the other minerals present in the assemblage at Rassal, its presence would not be unexpected. Geerite commonly forms lamellar intergrowths with spionkopite (R. Ixer, personal communication, and Large et al., 1995). However, none of the XRD patterns show any evidence of the most intense geerite peak, and its presence in the Rassal ores examined here cannot be confirmed.

**BORNITE Cu₅FeS₄ (optical and EDAX identification)**

Bornite is a conspicuous component of the Rassal ore assemblage. It commonly occurs within most samples of grey copper sulphide samples, often as patches and blebs enclosed within blue-grey sulphides (e.g. Figs. 7 and 8) suggesting that it might at least in part, be an early relict phase.

**CHALCOPYRITE CuFeS₂ (optical and EDAX identification)**

Less common than the grey copper sulphide assemblages, and generally altered to goethite (with minor yarrowite and covellite?) around margins and along cracks (Fig. 10). Unusually, the chalcopyrite is Ge-rich, with approximately 1 wt% levels of germanium. Ge is also enriched (up to

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**Figure 9.** Backscattered electron image of anilite crystals (A), with marginal alteration to malachite (M), and isolated grain of spionkopite (S). Analytical data for marked points are given in Table 1. Using this imaging technique, phases with higher average atomic number appear brighter, and phases with lower average atomic number appear darker.

**Figure 10.** Germanium rich chalcopyrite (Cp), altering to goethite (G), yarrowite (Y) and unidentified sulphides (X). Plane polarised reflected light. Field of view approx. 0.35 mm.

**Figure 11.** Deep blue flaky aggregates of covellite (C), with anilite (A) and bornite (B), in plane polarised reflected light (top) and crossed polars (bottom). Field of view approx. 0.7 mm wide.
3.2%) in small grains of unidentified Cu-Fe sulphides in goethite next to chalcopyrite. Such Ge-enrichment is rare, and might be a potential metallurgical “fingerprint” for copper derived from this mine, although no Ge has been thus far been detected in bornite or grey Cu-sulphides using EDAX (detection limit approximately 0.2-0.3%).

**COVELLITE CuS** (optics and EDAX identification)

Covellite typically occurs as small flakes and rosettes on the edges of, or along cracks in paler blue grey-blue sulphides, or enclosed in goethite (Figs. 11 and 12). The anisotropy tends to be significantly brighter, and more orange than that of the larger, slightly paler blue yarrowite grains. It is also distinguished from yarrowite by its lower Cu content (64% vs 68%), although intermediate compositions also occur (e.g. Figure 12, points 4 and 5; Table 1). Although close to the limits of analytical precision here, if real, these may represent fine-scale intergrowths of the two phases, or as suggested by Putis et al. (1977), a wider variety of Cu-S superstructures may occur, and intermediate compositions may actually be possible.

**DJURLEITE? Cu$_{31}$S$_{16}$ (XRD)**

Peaks similar to the principal peaks of djurleite are present in two of the XRD patterns. However, no phases with Cu contents as high as 79% have been detected by EDAX, and given the complexity of the assemblages, the complex mixed XRD patterns cannot be regarded as proof of occurrence without further supporting analytical data.

**ROXBYITE Cu$_9$S$_5$** (optical, EDAX and XRD identification)

One sample contains an abundant near-isotropic greyish white phase, with around 77% Cu (Fig. 13), matching the Cu content of roxbyite. In addition, all three of the most intense roxbyite XRD lines are also present in one of the XRD samples. It seems likely that roxbyite is present in at least some of the grey sulphide assemblages at Rassal. Even though the difference between anilite (75-76%) and roxbyite (77%) is small, and around the limit of analytical precision in the present work, the occurrence of anilite plus an optically paler phase with small but distinctly higher average atomic number (consistent with roxbyite) is supported by BSE imaging (Fig. 14).

Digenite is another bluish copper sulphide mineral with about 77% Cu, but it almost always contains traces of iron, and it has been suggested that this is necessary to stabilise the structure (Morimoto and Gyobu, 1971). None of the XRD traces show good evidence for the main digenite peaks, so it is suggested that the 77% Cu phase most common at Rassal is more likely to be roxbyite. This would be the first Scottish record of this mineral, and only the second in the UK after its original reporting from Dolyhir Quarry, Powys, Mid Wales (Cotterell et al., 2011).

**SPIONKOPITE Cu$_{39}$S$_{28}$** (optical and EDAX identification)

Spionkopite is always intergrown with other blue-grey sulphides, as blebs, and as lamellar aggregates, and as more regular lamellae in anilite (Figs. 15-17, see p. 56).
It shows a faint blue-grey bireflectance, and strong orange-brown anisotropy, and consistently has around 71% Cu. The first confirmation of spionkopite in Scotland was that of Prichard et al. (1994) from sulphide-bearing dunite pods at Cliff, Unst, Shetland. The material formerly known as “blaubleibender covellite” is now known to be spionkopite and/or yarrowite (Goble, 1981). Hall and Donovan (1978) recorded this from sulphide assemblages in lacustrine Old Red Sandstone sediments in Shetland, and hence spionkopite and/or yarrowite (see below) almost certainly occur there as well.

**YARROWITE Cu₉S₈ (optical and EDAX identification)**

Most samples contain a blue-grey to deep blue bireflectant, strongly anisotropic (orange-brown) phase (Figs. 10 and 15-17). Typically, this forms coarse flakes in goethite, or coarse flakes/broad lamellae with good cleavage, intergrown with other grey-blue sulphides. It shows a strong tendency to be more abundant towards the margins of grey-blue sulphide aggregates. It is clearly distinct in habit and occurrence from the smaller, bluer, more strongly anisotropic flakes and rosettes of covellite, and from the much less blue spionkopite. Yarrowite has not previously been recorded from Scotland, although, as noted above,”blaubleibender covellite” has been recorded by Hall and Donovan (1978).

**Gangue mineralogy**

A notable feature of the Rassal mineralisation is the scarcity of gangue minerals. White or colourless, sparry calcite (dilute HCl effervescence), and some sparry dolomite? (no dilute HCl effervescence) have been seen in a very few of the wider copper sulphide veinlets, both as incomplete selvages to the sulphide veins and as small ≤4 mm inclusions within them.

Veinlets of white to cream sparry calcite, ≤5 mm wide, unaccompanied by copper minerals, occur in shattered dolostone above the adit entrance at the western end of the vein (see above) and similar calcite, in veins up to 10 mm

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![Figure 15](image15.png)

**Figure 15.** Spionkopite (S) with yarrowite (Y), anilite (A), and minor covellite (C), bornite (B), and malachite (M), in plane polarised reflected light (top) and crossed polars (bottom). Field of view approx. 0.7 mm wide.

![Figure 16](image16.png)

**Figure 16.** Backscattered electron image including the area covered by Figure 15. Analytical data for marked points are given in Table 1.

![Figure 17](image17.png)

**Figure 17.** Backscattered electron image part of Figure 16, showing pale anilite (points 2, 4 and 12) with respectively darker grey spionkopite (points 1 and 3), yarrowite (points 10 and 11), and covellite (or admixed yarrowite/covellite?; points 5-9). Analytical data for marked points are given in Table 1.
wide in pale grey dolostone, is present in the spoil heaps adjoining the fenced-off excavation at the eastern end of the workings.

The only other introduced mineral observed during this investigation is hematite. This occurs very locally as stains on the hanging wall of the vein and in places massive hematite occurs as hair-like veinlets within the dolostones within a few centimetres of the hanging wall. A few fragments of pure massive hematite, ≤30 mm across, have been observed in parts of the spoil heaps. No copper minerals have been seen in association with this hematite.

Hematite veins within the Eilean Dubh dolostones have been worked on a small scale during the 19th century at Tornapress and Sanachan, 1 and 3 km respectively south of the Rassal Copper Mine (Macgregor et al., 1920), though neither copper, nor any other metalliferous minerals, are recorded from these deposits.

**Supergene mineralogy**

Malachite (confirmed by XRD) is the most abundant supergene copper mineral present within the spoil heaps. It is most abundant as small fragments, typically ≤40 mm across, composed of cellular fine-grained crystalline or earthy masses, in some instances exhibiting crude minutely botryoidal surfaces. Earthy brown ‘limonite’ is commonly present within many of these fragments. In a small number of such specimens cellular or earthy malachite cements angular fragments of dolostone up to 15 mm across. Thin (1-2 mm thick) coatings of similar malachite on dolostone are also locally common, and thin malachite films are abundant on the exposed surfaces of sulphide veins, and on grain boundaries within sulphide aggregates.

Heddle (1901, p 176) reported brochantite from this locality as an associate of bornite and malachite, but made no mention of the occurrence under the entry for brochantite in his Mineralogy of Scotland (1901, p. 176). As noted above, other reports of brochantite from Rassal seem to simply repeat Heddle’s original report. No specimens of brochantite were found at Rassal during the present investigation.

Massive blush green to brownish chrysocolla, with a distinctive waxy texture, in masses up to 5 mm across, have been found associated with copper sulphide veinlets in a handful of specimens.

**ORIGINS OF MINERALISATION**

The rich suite of Cu-S minerals present at Rassal represents a low temperature assemblage, with covellite (all copper as Cu2+) representing the end-point of oxidation of chalcocite-like (Cu+) precursors. The samples available do not support a robust paragenetic model for the Rassal assemblages, and it is currently unclear what the “primary” assemblage might have been.

The relationships between the chalcopyrite-rich veinlets and the more abundant grey Cu-S sulphide veinlets are also obscure, although yarrowite seems to be a common oxidation product of both.

The available field relationships offer no evidence of the age or likely affinities of the Rassal mineralisation, other than that it post-dates the host Cambrian dolomitic limestones. The vein appears to represent a single isolated occurrence of epigenetic copper mineralisation in this part of the NW Highlands. The temperature of any primary mineralisation is likely to have been very low, as there is very little evidence for associated recrystallisation of the host dolostones.

No similar Cu mineralisation is known in the NW Highlands. Other Cu concentrations include the amphibolite facies Besshi-type stratiform massive sulphide deposit within the Loch Maree Group (Lewesian) gneisses at Gairloch, west Sutherland, which carries copper, zinc, gold and silver (Jones et al., 1987) and a syngenetic (i.e. Proterozoic) occurrence of chalcocite- and hematite-bearing nodules within sandy shales of the Torridonian Stoer Group on the Stoer peninsula, Sutherland (Fernmor, 1951). However, neither of these has any spatial, temporal or genetic link with the style of mineralisation at Rassal.


HYDROZINCITE FROM SWAREDALE, NORTHERN PENNINES

Brian YOUNG
Department of Earth Sciences, University of Durham, South Road, Durham DH1 3LE
Trevor F. BRIDGES
1 Mill Court, Waddingham, Lincolnshire DN21 4SD
David I. GREEN
School of Earth, Atmospheric and Environmental Sciences (SEAES), Manchester University, Manchester M13 9PL

Hydrozincite, with a distinctive radiating fibrous crystalline texture, has been found as part of the supergene mineral assemblages on the spoil heaps of three mines within the Askriigg portion of the Northern Pennine orefield. At White-side mines the hydrozincite is interbanded with crystalline smithsonite, a relationship not previously described for either of these minerals within the Pennine orefields. This paragenesis is interpreted as indicating unusual fluctuating geochemical conditions during formation of these supergene species.

INTRODUCTION AND GEOLOGICAL BACKGROUND

Whereas hydrozincite is well known as a common supergene mineral at many locations in the near-surface zones of sphalerite-rich veins and associated deposits in the northernmost, or Alston Block, portion of the Northern Pennine Orefield (Dunham, 1990; Bridges and Young, 1998; Tindle, 2008), rather surprisingly the mineral has hitherto been reported from only one location within the southern, or Askriigg Block, portion of this orefield. Dunham and Wilson (1985, p. 107) commented that the species had not then been specifically identified within that region, but suggested that white coatings of post-mine origin, commonly seen in old workings in the area, may include hydrozincite. Subsequently, Wood (1993) referred to its presence within the supergene assemblage at Gunnerside Gill mines in Swaledale, though gave no description of the mineral at this location.

Hydrozincite is reported here from three locations in Swaledale, within the Askriigg Block portion of the Northern Pennine orefield, where its form and paragenesis differs from that seen elsewhere in the Northern Pennines. Hydrozincite has been identified within the supergene assemblage on spoil heaps at the White-side, Grinton and Grovebeck mines. At these three mines a small number of veins and associated replacement flats, or ‘flots’ as they are known locally, within limestone wall-rocks, were worked for galena both from surface opencasts or hushes, and from comparatively shallow underground workings. In common with many of the nearby deposits in Swaledale, these deposits proved most productive within the Main Limestone (Namurian) with some ore locally won from...
veins within the overlying chert beds. Gangue minerals associated with the galena at these mines include baryte, calcite, minor amounts of witherite and some aragonite (Dunham and Wilson, 1985). Sphalerite has only been identified at Grovebeck Mine in this investigation. It occurs rarely as inconspicuous anhedral yellow-brown to dark brown masses within hemimorphite. The abundance of hemimorphite and smithsonite, of supergene origin at these sites strongly suggests that sphalerite was formerly abundant within the hypogene assemblage.

HYDROZINCITE AT WHITASIDE MINES

Spoil heaps from these workings [SD 9876 9580] have yielded a small number of blocks composed of cellular crystalline smithsonite and hemimorphite in which these minerals locally exhibit a crudely inter-banded relationship.

The smithsonite typically occurs as pale buff to pale yellowish green crystalline, botryoidal bands and crusts up to around 3 mm wide. Freely grown botryoidal surfaces of bright yellowish green smithsonite occur in cavities up to around 10 mm across. No unaltered sphalerite has been seen, though a few small masses of apparently fresh galena, up to a few millimetres across, occur embedded within the smithsonite.

Hemimorphite is common in this material, typically forming discontinuous crystalline bands up to 2 mm across composed of colourless radiating platy crystals which, in some small cavities, exhibit lustrous euhedral terminations.

Conspicuous within this material are discontinuous bands of a white mineral, identified by X-ray diffraction as hydrozincite (Manchester University X-ray number XRD1422) (Fig. 1). The mineral here typically exhibits a distinctive internal radiating fibrous crystalline texture and characteristic faint silky lustre. On fracture surfaces of the smithsonite/hemimorphite veinstone, layers of hydrozincite, up to about 0.5 mm thick, are composed of rather scaly crystalline aggregates in which a crude spherulitic texture can locally be seen. Very locally, the hydrozincite occurs as discontinuous bands up to 1 mm thick in which faint concentric layering may be detected. A small number of cavities, up to a few millimetres across, are lined with hydrozincite which displays smooth crudely botryoidal surfaces (Fig. 2). Elsewhere, botryoidal layers of hydrozincite are overgrown either by millimetre-scale layers of colourless bladed euhedral hemimorphite crystals or pale yellowish green crystalline botryoidal smithsonite.

HYDROZINCITE AT GRINTON MINES

Parts of the dumps at the mouth of the How Level [SE 0430 9268] contain abundant blocks of brown cellular crystalline hemimorphite up to 30 cm across. Within these blocks, hemimorphite occurs as pale greyish brown bands composed of radiating crystals which commonly form spherulitic aggregates up to 3 mm across. Open cavities, up to 20 mm across, are common and are typically lined either with crudely botryoidal aggregates of radiating crystalline hemimorphite or, less commonly, with colourless terminated euhedral bladed hemimorphite crystals up to about 1 mm long. As at Whitaside mines, no fresh sphalerite has been found in any of this material though, here too, a few small masses of fresh galena have been noted embedded within some blocks of hemimorphite.

Within a few blocks of this hemimorphite, conspicuous small pure white cavity fillings have been identified by X-ray diffraction to be hydrozincite (Natural History Museum

Figure 1. Hydrozincite forming discontinuous layers up to 5 mm thick interbanded with buff crystalline smithsonite and hemimorphite. Whitaside mines. Specimen is 40 mm across. B. Young specimen No. 8363/C. Photo D.I. Green.

Figure 2. Detail of hydrozincite crust, showing crudely botryoidal surface and internal radiating fibrous crystalline texture. Whitaside mines. Field of view is 4 mm across. B. Young specimen No. 8363/C. Photo D.I. Green.
X-ray number G4234) (Fig. 3). Most cavities are up to 5 mm across and are completely filled with hydrozincite, though exceptionally, cavities up to 10 mm across are incompletely filled, and in these the mineral typically exhibits a crudely botryoidal or wart-like surface morphology (Fig. 4). Whereas some of the hydrozincite displays a rather compact chalk-like appearance, most exhibits a faint silky lustre and an internal spherulitic texture, composed of radiating crystals mainly up to approximately 0.5 mm long. In all specimens examined the hydrozincite appears to be the last mineral to have formed within the cavities: no examples from this location have been found in which hydrozincite has been overgrown by any other mineral.

HYDROZINCITE AT GROVEBECK MINES

The extensive dumps north of the entrance to Grovebeck Level [SE 0275 9671] contain numerous blocks of cellular hemimorphite. Similar material is present on smaller dumps in and around Kay Hush, which extends for about half a kilometre southwest up the flank of Gibbon Hill. Cavities within the blocks are commonly lined with drusy crusts of brown prismatic to tabular hemimorphite; crystals are typically 1–2 mm in length and rarely up to 5 mm. Hemimorphite and powdery brown limonite are the only minerals present in the cavities in most of the specimens investigated in this study. White crudely pseudo-octahedral supergene calcite overgrows hemimorphite on a few specimens and translucent plates of supergene baryte are present on others. Smithsonite as curved composite pale buff rhombohedra up to 2 mm across overgrows hemimorphite in a few specimens, but hemimorphite is the dominant zinc-bearing mineral in all of the specimens examined. Rare centimetre-size oxidised masses of relic yellow-brown to dark brown sphalerite, embedded in hemimorphite, strongly suggest that the hemimorphite and associated zinc-bearing supergene minerals were formed by the local oxidation of primary sphalerite.

Copper-bearing supergene minerals include earthy green malachite, a minutely botryoidal blue-green phase which is probably rosasite, and a few dark blue crudely prismatic linarite crystals. Cerussite occurs on a single specimen in a cavity in hemimorphite, but lead-bearing supergene minerals are extremely rare in the zinc-rich supergene assemblage.

Hydrozincite is widespread but uncommon as powdery white masses which partly fill cavities up to about 10 mm across in drusy hemimorphite. A few cavities contain crustose aggregates of pearly white lath-like hydrozincite crystals up to 0.8 mm long and a few micrometres in thickness (Fig. 5). These were identified by X-ray diffraction (Manchester University X-ray number XRD 1489). Hydrozincite was the last mineral to form on all of the studied specimens.

DISCUSSION

Smithsonite, ZnCO₃, and hydrozincite, Zn₅(CO₃)₂(OH)₆, the common carbonates of zinc, both usually form at pH between 5 and 8.5. Given an appropriate pH, the factor that controls which of the two carbonates forms is the availability of CO₂ in the system. For convenience in geochemical calculations, this ‘availability’ is normally expressed as the partial pressure (pCO₂). To illustrate this, the pCO₂ usually used for the preindustrial atmosphere is 0.0003, which is 0.03 %v/v CO₂, but geochemists find it easier to use the logarithm of this which is 10⁻¹.⁵₂.
If the pCO₂ in an environment changes, then the two carbonates can change from one to the other. The equation showing this relationship is:

\[
\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 + 3\text{CO}_2 \leftrightarrow 5\text{ZnCO}_3 + 3\text{H}_2\text{O}
\]

hydrozincite          smithsonite

Note that this reaction is reversible and can go either way, but it clearly shows that high availability of CO₂ drives the reaction towards the formation of smithsonite.

In an oxidising mineral vein, several factors can increase the pCO₂ above atmospheric, but usually the most important is the reaction between sulphuric acid, released by the oxidation of iron-bearing sulphides such as pyrite, with carbonates such as calcite or limestone. In such situations, elevated pCO₂ is the norm and, as can be seen from the above equation, these conditions favour the formation of smithsonite if sphalerite is present. In contrast, hydrozincite only seems to form in well-ventilated situations such as mine walls and spoil heap waste, conditions close to atmospheric where smithsonite does not normally form.

There is a unique pCO₂ at which the two minerals can coexist and this can be calculated from thermochemical data for the two minerals. Using the best data available, Williams (1990) calculated the transitional pCO₂ to be 10^{-1.41} (3.9% v/v), which seems significantly higher than would be expected from the mineralogical evidence. For example, leadhillite can only form below pCO₂ of 10^{-1.95} (1.12 %v/v), so hydrozincite would be expected to be at least as common as leadhillite in oxidising mineral deposits and as this study shows, it most certainly is not. It seems likely that the true value of pCO₂ at the transition is only a little above that of the atmosphere. Further investigation is thus needed to understand the details of the geochemical relationships between the formation conditions of smithsonite and hydrozincite.

Notwithstanding these difficulties, the following observations may be made on the wider occurrence of these minerals throughout the Northern Pennine orefields and their much more unusual coexistence at Whitaside, Grinton and Grovebeck mines.

Within the oxidising upper zones of veins with the mineral compositions most commonly encountered in the Northern Pennines, high pCO₂ conditions are usual. In consequence, in such environments the normal supergene zinc carbonate mineral formed is smithsonite. Where abundant oxygen is available, for example on vein exposures, within old mine workings, or in blocks within spoil heaps, low pCO₂ conditions typically prevail, resulting in the formation of hydrozincite as the normal zinc supergene species. In most British zinc-bearing ore deposits, for example those of the Alston Block portion of the Northern Pennine orefield, the almost universal mutually exclusive occurrence of smithsonite and hydrozincite clearly reflect these conditions during supergene alteration. Smithsonite is the normal zinc carbonate supergene species in the near-surface portions of zinc-rich deposits: hydrozincite is normally encountered only within vein outcrops, blocks within spoil heaps, or as stalactitic or stalagmitic crusts, sometimes up to several centimetres thick, on the walls of underground workings where a recent, post-mining, origin seems obvious.

The occurrences of the mineral at Whitaside, Grinton and Grovebeck mines are unlike those normally encountered elsewhere in the Pennine orefields. At Whitaside hydrozincite is clearly interbanded with both hemimorphite and smithsonite, the normal and most abundant zinc supergene species found within the deposits formerly worked at these mines. This relationship suggests that during the main episode of supergene alteration here, the prevailing chemical and associated physical conditions locally fluctuated around the pCO₂ that controls which of the carbonates, smithsonite or hydrozincite, will form. In consequence, rare brief episodes of low pCO₂ allowed the deposition of layers of finely crystalline hydrozincite, followed by further episodes of more normal high pCO₂ conditions which allowed the resumption of deposition of smithsonite. No comparable interbanding of any of these species has been seen elsewhere within the orefield. No evidence has been seen at Whitaside of any hydrozincite being of post-mining origin.

At Grovebeck and Grinton mines, where hydrozincite fills cavities within cellular hemimorphite, it is clearly a late-stage phase within the supergene paragenesis. However, so far as it has been possible to determine, its presence here is limited to these cavity fillings: it is not interbanded with hemimorphite and no obviously post-mining coatings of the mineral have been observed. Its comparatively well-developed crystalline texture and presence suggests

![Figure 5. Botryoidal crust of finely crystalline hydrozincite lining cavity in crystalline hemimorphite. Grovebeck mines. Field of view is 8 mm across. D.I. Green specimen and photo.](image-url)
that, as at Whitaside, hydrozincite may have been a minor, though significant, phase formed during the main episode of supergene alteration in these deposits.

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REFERENCES


COPPER AND BARIUM MINERALISATION AT FORCETT QUARRY, EAST LAYTON, NORTH YORKSHIRE

Brian Young
Department of Earth Sciences, University of Durham, South Road, Durham DH1 3LE

Trevor F. Bridges
1 Mill Court, Waddingham, Lincolnshire DN21 4SD

Peter Tandy
Department of Earth Sciences, The Natural History Museum, Cromwell Road, London SW7 5BD

Over at least 50 years the workings of Forcett Quarry have, from time to time, exposed copper- and barium-rich mineralisation within the Carboniferous (Namurian) Main Limestone. This mineralisation has been found both within fault-hosted veins and as vug fillings within extensive areas of dolomitisation within the host limestone and as veins and nodules in underlying beds. The mineralisation, together with its stratigraphical and structural setting, invites comparison with the nearby copper mineralisation of the Middleton Tyas area and the adjoining Askrigg and Alston portions of the Northern Pennine orefields. Aspects of the mineralisation are consistent with emplacement from saline fluids during Upper Permian times.

INTRODUCTION

Forcett Quarry comprises a long-established extensive group of workings situated between the villages of Forcett and East Layton, in North Yorkshire, approximately 13 km ESE of Barnard Castle (Fig. 1). The quarry, which works the Main Limestone (Upper Carboniferous – Namurian) for roadstone and crushed rock aggregate, lies within the northern limb of the WNW – ESE trending Middleton Tyas – Sleightholm Anticline. Vein mineralisation, in which copper is the most abundant introduced metal, is present in many places within the Main and underlying Undersett limestones in the northern limb of this structure. A cluster of extremely rich copper-bearing veins and related deposits towards the eastern extremity of the structure, centred around the village of Middleton Tyas, approximately 8 km SE of Forcett Quarry, supported an important, though

Figure 1. Location map.
short-lived, copper mining industry during the second half of the 18th century. Comparatively little is known of the geology of these remarkable deposits as the former mines have long been inaccessible, few good representative samples of the ores worked survive, and exposures of mineralised ground are limited. Over the past half century, the workings of Forcett Quarry have, from time to time, revealed local concentrations of rich copper mineralisation which appear to resemble those of Middleton Tyas. The abundance of associated barium, together with minor amounts of lead and zinc mineralisation invite comparison with, and perhaps a genetic link between, these deposits and those of the adjacent main Northern Pennine orefields.

GEOLOGICAL BACKGROUND

Forcett Quarry lies in the Main Limestone on the northern limb of the Middleton Tyas – Sleightholm Anticline, a broad WNW – ESE trending anticlinal structure, which extends from the Sleightholm area, west of Bowes, to Middleton Tyas, near Scotch Corner. At outcrop the fold affects strata extending downwards from beds above the Main Limestone (Namurian) through the cyclothem of Dinantian strata to a little below the Simonstone Limestone. A few kilometres east of Middleton Tyas, these Carboniferous rocks dip beneath the unconformable onlapping cover of Permo-Triassic limestones and marls.

The Carboniferous rocks of this area occur within the Stainmore Trough, between the Alston Block to the north and the Askrigg Block to the south (Trotter and Hollingworth, 1928; Hudson, 1938; Dunham and Wilson, 1985). During Carboniferous times an appreciably greater thickness of sediments accumulated in the Stainmore Trough than in the adjacent ‘blocks’ (Johnson et al., 2011).

Since the earliest days of mining and quarrying, the succession of Carboniferous rocks in each of these areas has acquired its own nomenclature for individual rock units. These names were subsequently adopted by the Geological Survey and have become standardised in the geological literature. Whereas many of these units, especially the limestones, may be readily correlated from one block to another, the naming of these units within the intervening Stainmore Trough is commonly a matter of some confusion.

Mills and Hull (1976), presented cogent arguments for adopting Alston Block nomenclature for their detailed description of the Carboniferous rocks of the Barnard Castle district, which includes representatives of the Alston and Askrigg blocks, and the Stainmore Trough, successions. Whereas this approach is entirely feasible for the rocks of that district, more difficult issues of correlation and nomenclature become apparent when tracing the geology southwards into lower stratigraphical horizons within the core of the Middleton Tyas – Sleightholm Anticline. Accordingly, in this paper we follow the practice of Dunham and Wilson (1985) and employ Askrigg, rather than Alston Block, nomenclature for the area around Forcett Quarry. Thus the Great and Four Fathom limestones of the Barnard Castle sheet are here referred to as the Main and Undersett limestones respectively.

Known mineralisation within the Middleton Tyas – Sleightholm Anticline is concentrated within beds from immediately beneath the Undersett Limestone up to beds above the Main Limestone, with the greatest concentrations of mineralisation within the limestones themselves. Details of this succession have been given by Wells (1957), Mills and Hull (1976) and Dunham and Wilson (1985) and only a brief summary is given here.

In the area considered in this paper, a sandstone, correlated with the Nattrass Gill Hazle of the Alston Block, is overlain by the Undersett Limestone. This is typically a grey, fine-grained argillaceous biosparite in which crinoid and bryozoan debris is common. Chert nodules are locally present. Over much of the area, the limestone is around 9 m thick, but around Middleton Tyas it expands to a little over 24 m in an exceptionally crinoid-rich grainstone facies. Wells (1955; 1957) drew attention to the common occurrence of brown dolomitisation within the lowest beds of this limestone.

A succession, up to about 45 m thick, composed predominantly of argillaceous beds, but with beds of sandstone and siliceous limestones, may be the local representatives of the Undersett Chert, separate the Undersett Limestone from the Main Limestone. Sandy beds predominate in the uppermost part of the succession beneath the Main limestone, where a sandstone that is locally up to 3 m thick, may be the equivalent of the Tuft of the Alston Block succession. This sandstone forms the floor to large areas of the present Forcett Quarry.

The Main Limestone is also an argillaceous biosparite. According to Wells (1955) it ranges in thickness from 10 to 26 m within the Middleton Tyas – Sleightholm Anticline, though he noted that over much of the area it was around 20 m, a thickness comparable to that of the Great Limestone throughout much of the Alston Block. Mills and Hull (1976) described the presence in this area of two of the three bioherms described by Johnson (1958) from the Great Limestone Block. These are the Chaetetes band, characterised by the presence of silicified laminae of the sponge Chaetetes depressus, typically around 1 to 2 m above the base of the limestone, and the Frosterley Band, characterised by the abundance of the solitary coral Dibunophyllum sp., typically found at between 5 and 10 m below its top. Wells (1955) and Mills and Hull (1976) commented on the common occurrence of conspicuous brown dolomitisation within the lowest beds of this limestone and, in a detailed study of the geotechnical properties of the Great Limestone of the East Layton area, Attewell (1971) discussed the likely origins of this dolomitisation.

Within the Middleton Tyas – Sleightholm structure, the Main Limestone is overlain by a succession of shales and sandstone, in part equivalent to the Coal Sills of the Alston Block (Mills and Hull, 1976).

The Middleton Tyas – Sleightholm Anticline was first mapped by Dakyns and Gunn during the primary geological survey in the 1870s, with early descriptions published by Marr (1910) and Kendall (1911). However, the first detailed
study of this structure was by Wells (1957), whose work was summarised and incorporated into their description of the Askripp Block portion of the Northern Pennine Orefield by Dunham and Wilson (1985). In agreeing a Hercynian age for the structure these authors also comment on speculation that it, and the Cleveland Hills Dome, that affects Jurassic rocks further east, may overlie a common belt of crustal instability. Johnson (personal communication in Dunham and Wilson, 1985) has suggested that the structure may be due to halokinesis in Carboniferous halite or other evaporites at depth.

MINERALISATION IN THE MIDDLETON TYAS - SLEIGHTHOLM ANTICLINE

Mineralisation within this structure has been the subject of studies by Wells (1955), Small (1977) and Dunham and Wilson (1985).

Dunham and Wilson (1985) commented on the remarkable absence of fracturing and mineralisation within the Middleton Tyas – Sleightholm Anticline, except at its southern and eastern margins. In these latter areas occur some remarkable centres of mineralisation dominated by very high concentrations of copper minerals with subordinate amounts of lead and zinc ores, most notably those of the Middleton Tyas area. Dunham and Wilson (op. cit) interpreted veins within the Middleton Tyas – Sleightholm Anticline at Feldom, Merrybent and Forcett Quarry as being transitional in type between these and the calcite-baryte-galena veins of the North Swaledale Mineral Belt, concluding that it was appropriate to include all of these deposits as part of the Askripp Block portion of the Northern Pennine orefield under the descriptive heading of the ‘Richmond Copper Mines’. These authors did, however, recognise the copper mineralisation at Middleton Tyas as being a type unique to that area.

The small, but dense, concentration of deposits in and around the village of Middleton Tyas comprises the most significant occurrence of workable mineralisation within the Middleton Tyas – Sleightholm Anticline. In a comprehensive study of the mining history, Hornshaw (1975) noted that the deposits were first discovered in 1733. Early descriptions of the workings were published by Angerstein (1755) and Jars (1765). The most significant features of these accounts, together with others by Raistrick (1936; 1975) have been summarised by Dunham and Wilson (1985).

From these it seems that profitable mining had begun by 1742, but that by 1763 the deposits were nearing exhaustion, with mining ending in about 1779. In 1856 a small mine was established at Merrybent, approximately 2 km NW of Middleton Tyas. This yielded small amounts of both lead and copper ores but was closed by 1879. Some exploration undertaken here prior to World War I proved unsuccessful. A more recent investigation of the Middleton Tyas area, employing geochemical and geophysical techniques, backed by drilling, identified anomalously high concentrations of copper, lead and zinc at several locations, but failed to identify exploration targets worthy of further investigation (Wadge et al., 1981).

Historical records suggest that the ores from Middleton Tyas were extremely rich, perhaps yielding as much as 66% Cu (Hornshaw, 1975; Dunham and Wilson, 1985). However, it is clear that, whereas such remarkable ores proved extraordinarily profitable for the 30 or so years of the main period of mining, the gross tonnage of ore raised was almost certainly modest. Whereas reliable contemporary production figures are not known, Dunham and Wilson (1985) have suggested that the total tonnage mined probably did not exceed 3500 tonnes, from which they suggest a total yield of only about 1575 tonnes of copper metal.

In the absence of reliable mine plans, together with the long inaccessibility of the workings, the precise form and nature of these deposits is uncertain. However, based upon Angerstein’s (1755) observations, Dunham and Wilson (1985) conclude that the deposits comprised a number of ‘flat’ deposits, each perhaps up to 0.38 m thick, on two horizons up to 3.6 m apart, within the Undersett Limestone, extending laterally for several tens of metres from two or more vertical veins, or pipes. The upper flat appears to have rested upon clay: the lower flat on sandstone. Jars (1765) refers to ‘kidneys’ (presumably nodules) of ore found in cavities filled with iron-stained sand. Dunham and Wilson (op. cit) interpret Jars’ description of the ore minerals as covellite, chalcocite, chalcopyrite, cuprite, bornite, malachite and azurite. In addition, from scarce small fragments of ore minerals recovered from the spoil heaps, Small (1977) identified small amounts of digenite. The few remaining spoil heaps from the shafts, which according to Dunham and Wilson (op. cit) were up to 15.5 m deep, are today mostly overgrown and appear to comprise mainly limestone, much of it dolomitised, with only rare traces of copper minerals.

Deans (1951) demonstrated minerals including nodules composed of chalcocite, bornite and covellite, locally accompanied by baryte and coatings of malachite and azurite, found in the decomposed base of the Undersett Limestone exposed in Black Scar Quarry, Middleton Tyas [NZ 231 052] at a meeting of the Mineralogical Society in 1951. He also reported chalcocite, covellite, malachite, baryte and tiny crystals of native copper and ‘limonite’ in sand pockets within the limestone at this locality. In the light of Dunham and Wilson’s (1985) conclusion that the mineralisation exposed at Black Scar Quarry may comprise a low grade example of the deposits formerly worked at Middleton Tyas, the site is today protected as a Site of Special Scientific Interest (Bevins et al., 2010). Specimens of minerals from this locality are preserved in the Russell Collection at the Natural History Museum, London, and in the mineral collection of the Department of Earth Sciences, University of Durham.

Elsewhere within the Middleton Tyas – Sleightholm Anticline, copper ores have been raised in small quantities from vein deposits at Merrybent, Gingerfield, Feldom and at Billy Bank, near Richmond. The local presence of galena, baryte and calcite may serve to link these veins with those of the North Swaledale Mineral Belt, where copper minerals are typically found only in very minor amounts (Dunham and Wilson, 1985).
In addition, traces of copper minerals, mainly azurite and malachite stains on joints in limestone, were reported by Wells (1955) from a number of locations near the eastern end of the Middleton Tyas – Sleightholm Anticline.

GEOLOGY OF FORCETT QUARRY

Descriptions of several substantial quarries in the outcrop of the Main Limestone, north of East Layton, by Wells (1955), Mills and Hull (1976) and Dunham and Wilson (1985), refer variously, and somewhat confusingly, to East Layton Quarry and to Forcett Quarry. Modern Ordnance Survey maps of this area employ the name Forcett Quarry collectively for all of these large quarries that lie immediately north of East Layton. The present workings of Forcett Quarry lie south of these older workings, and post-date these descriptions. The Forcett Quarry workings, including individual locations described in this paper, are shown on Figure 2.

Within the East Layton area, the Carboniferous rocks from below the Five Yard Limestone up to the beds above the Main Limestone are cut by two sub-parallel WSW-ENE trending normal faults which form a horst structure up to about 450 m wide. For the purposes of description in this paper on Figure 2 these are named the North and South faults respectively. According to Mills and Hull (1976, Figure 16) the North Fault exhibits a throw of around 6 m to the north west: the South Fault exhibits a throw to the south east of up to 26 m. The current workings of Forcett Quarry lie south of these older workings, and post-date these descriptions. The Forcett Quarry workings, including individual locations described in this paper, are shown on Figure 2.

Apart from the uppermost few metres, the full thickness of the Main Limestone, here up to approximately 16 m, was exposed within the current quarry during this investigation (Fig. 2, A). It is typically a medium grey, fine- to medium-grained argillaceous biosparite in which fossils, other than crinoid fragments and indeterminate shell fragments, are generally inconspicuous in hand specimen. Bedding is prominent with individual beds, or ‘posts’, typically up to around 1.5 m thick, in places separated by very thin mudstone partings up to about 4 cm thick. The latter are most abundant within the uppermost 4 m, coinciding with the ‘Tumbler Beds’ of the Great Limestone of the Alston Block (Dunham, 1990). In common with the Main Limestone elsewhere in the district, bedding planes are commonly markedly undulating. Mills and Hull (1976) record the presence of the Frosterley Band, 0.76 m thick, within the topmost 6 m of the limestone then exposed in the face at NZ 1556 1066. These authors also record the occurrence here of the Chaetetes band, 0.5 m thick, close to the base of the limestone. Neither of these stratigraphically significant units have been recognised in the current workings during the present investigation.

In the southern and eastern faces of the quarry, pale buff-coloured dolomitisation is conspicuous as rather irregular roughly vertical patches, up to several metres across, extending upwards from the base of the limestone and apparently terminating against a persistent and comparatively prominent 4 cm thick mudstone parting. Exactly similar dolomitisation is also conspicuous, though much less widespread, towards the middle of the limestone. This alteration too appears to terminate upwards against a widespread 2 cm mudstone parting (Fig. 3, see p. 66). The nature and potential significance of these dolomitised zones in hosting the mineralisation are discussed below.

Throughout the present quarry, and almost everywhere forming the floor of the workings, the limestone is underlain by a pale buff medium-grained sandstone, in which
fossilised rootlet traces are locally conspicuous. No sections have been seen through the full thickness of this sandstone in the present workings, though elsewhere in the district this sandstone, which may be the correlative of the Tuft Sandstone of the Alston Block, is up to 3 m thick.

The topmost beds of the Main Limestone are seen only in the southernmost faces of the quarry, where they are overlain conformably by several metres of laminated grey mudstone.

Stony till, or boulder clay, lies above this mudstone and mantles the limestones elsewhere throughout the workings.

MINERALISATION AT FORCETT QUARRY

The mineralisation described by Wells (1955; 1957), Mills and Hull (1976) and Dunham and Wilson (1985), was formerly exposed in the abandoned section of workings identified as area B on Figure 2. Although no mineralisation was visible here during the present investigation, specimens collected by these authors are preserved in the mineral collection in the Department of Earth Sciences, University of Durham. In the following section a review of these descriptions, augmented by a re-examination of these specimens, is followed by a description of mineralisation examined by the authors in the modern workings (Fig. 2, A) within the last few years.

Mineralisation formerly exposed within Forcett Quarry

Wells (1955) recorded mineralisation within two NE-SW trending faults exposed within the then southern part of the workings. This portion of the quarry (Locality B1, Fig. 2) has since been backfilled and landscaped.

The northernmost of these fractures, the North Fault of Figure 2, was recorded as comprising a roughly 7 m wide fault zone, with an aggregate throw to the NW of around 7 m. Nodules of bornite, up to about 2 cm across, were common in this fault zone within the thin shaly sandstone immediately beneath the Main Limestone. Wells (1955; 1957) also recorded chalcanthite as a pale sky-blue coating, accompanied by malachite and azurite, on soft carbonaceous sandstone in a cavity within this fracture.

A smaller fault, parallel to and a few metres south of the North Fault, was also described by Small (1977) as having a throw to the NW of about 3 m. It was reported to have been mineralised with small specks of chalcopyrite enclosed in a baryte-cemented fault breccia, presumably composed of limestone fragments. Malachite was commonly associated with the chalcopyrite. Although no longer visible, the position of this fault, parallel to and within a few metres south of, the North Fault is depicted on the British Geological Survey 1:10 560 Sheet NZ11SE.

It is likely that Dunham and Wilson’s (1985) description of the larger of Small’s faults, exposed in the quarry in 1951-52, refers to the North Fault of Figure 2. These authors described it as containing pockets of mineralisation up to 22 cm across which included plates of chalcopyrite, together with small quantities of bornite, covellite and chalcocite within a matrix of wetherite, calcite and baryte. They also recorded flattened nodules up to 5 cm in diameter, composed of bornite, chalcocite, chalcopyrite and covellite, from the shale at the base of the Main Limestone for a strike length of up to 137 m along the fault and for a distance of up to 18 m away from it. Specimens in the University of Durham collections (6680*, 6698*), collected at this time, include rather flattened, crudely ovoid, bornite nodules up to 2 cm across collected from this same shaly sandstone parting which lies between the base of the Main Limestone and the underlying sandstone which formed the floor of the workings (Fig. 4). Other specimens of grey copper sulphides in the University of Durham collections, recovered from this fault zone at that time, were identified in polished
sections as djurleite (2199*) and as complex intergrowths of djurleite, chalcocite and chalcopyrite (2193*). The Durham collections also include several specimens of massive chalcopyrite up to several centimetres across, collected here (e.g. 2200*, 2191*, 2196*). Surfaces of some of these specimens, which appear to have been the lining of cavities within the veins, exhibit very crude tabular crystals of chalcopyrite up to 10 mm long, which closely resemble the morphology of the tabular chalcopyrite crystals described below from the cavities recently exposed in the southern face of the present quarry. Like the chalcopyrite crystals found in the recently exposed faces, some of those obtained from the older workings exhibit a pronounced dark brown tarnish, though more commonly they are coated with a film of minutely crystalline dark green malachite. Fine, deep blue azurite crystals up to 2 mm across, within small cavities in chalcopyrite are present in University of Durham specimen No. 6704*, collected from this fault zone.

Dunham and Wilson (1985) suggest that this mineralised fault zone may be an on strike extension of the vein that had previously been unsuccessfully explored for copper ores at the nearby farm of Sorrowful Hill [NY 151 105]. Two shafts, of unknown depth, depicted on either side of the North Fault on BGS Sheet NZ11SE almost certainly relate to this trial working. In 1985, one of the present authors (BY) collected small specimens of massive cuprite, accompanied by malachite and azurite, from the meagre amounts of spoil then remaining from this trial.

Mills and Hull (1976) recorded that exposures of this same fault then visible in the floor of the quarry revealed that mineralisation, comprising nodules of bornite and covelline, coated with malachite, was almost wholly confined to the beds beneath the Main Limestone. A note on BGS Sheet NZ11SE refers to a “shatter belt rich in copper ore in basal [4.5 metres]” of the Main Limestone then exposed in the easternmost portion of these workings (Locality B2, Fig. 2), though no details of its orientation or mineral content is recorded.

Mineralisation exposed in abandoned sections of Forcett Quarry

The rather extensive, and locally overgrown, long-abandoned group of workings, identified as area D on Figure 2, expose extensive sections through the Main Limestone. Whereas much of the limestone exhibits little alteration, brown dolomitisation is locally prominent in parts of the southern faces which lie a few metres north of the North Fault.

In these workings, a substantial unworked block of limestone that extends for several tens of metres northwards from the main southern face (Locality D1, Fig. 2) locally exhibits abundant baryte mineralisation. Whereas exposure today is limited, this mineralisation appears to comprise white crystalline baryte in cavities scattered through pale brown dolomitised, limestone. No obvious veins were seen. The baryte is apparently unaccompanied by any visible traces of copper, or other metalliferous, minerals. One block of rather compact crystalline baryte was found to exhibit a distinctive radial crystalline pattern, almost certainly pseudomorphous after original witherite. A very few specimens of unaltered witherite have also been found here within the spoil: none has been seen in situ. This mineralisation is confined to the southern faces, within a few metres of the North Fault. It seems that this mineralisation rendered this block of limestone unworkable.

Mineralisation in the most recent workings

Copper- and barium-rich mineralisation has been encountered in several parts of the most recent workings of the quarry (Area A, Fig. 2), both within the Main Limestone and locally within the uppermost parts of the underlying sandstone which forms the floor to most of the workings.

As noted above, a conspicuous feature of the limestone exposed in the southern and eastern faces is the patchy buff-coloured zones of dolomitisation (Localities A1 and A2, Fig. 2). Irregular cavities, up to around 1 m across, which are common within this dolomitised rock, almost invariably contain fillings or partial fillings of witherite, baryte, calcite and small, though conspicuous, amounts of chalcopyrite, locally with supergene coatings of malachite and goethite (Figs. 5 and 6).
Barytocalcite has been found as a rare associate of witherite and baryte in a handful of cavities. It typically occurs as colourless or white monoclinic crystals up to 5 mm long in cavities in witherite and baryte, and as small pale brown crystalline masses up to approximately 15 mm across which appear to have replaced primary baryte (Fig. 8). In a few specimens, where these crystalline masses extend into cavities, they exhibit complex euhedral terminations reminiscent of the morphology common at Nentsberry Hagg Mine, near Alston (Young, 1985; Symes and Young, 2008).

Calcite occurs as an almost ubiquitous lining to the mineralised cavities and joints in the dolomitised limestone where it appears to occupy an early position in the paragenetic sequence. Rhombic, ‘nail head’ crystals, commonly in complex twinned groups, up to 20 mm across, are by far the commonest form of the mineral, though some examples of scalenohedral crystals up to 30 mm long have been seen in a few cavities. Many examples of calcite enclosed plate-like crystals of chalcopyrite.

Very rarely, aragonite also occurs as radiating hemispheres, up to 1 mm across, composed of minute acicular crystals, encrusting witherite and baryte in cavities.

Chalcopyrite is common in the cavities within the dolomitised Main Limestone exposed in the southern faces of the quarry (Localities A1 and A2, Fig. 2). Here, it occurs both as massive patches and veinlets up to around 10 mm across and, much more commonly, as thin tabular crystals up to about 2 mm across. These are present both as closely scattered crystals embedded within calcite, witherite and baryte, and more rarely as small crusts of freely-grown crystals attached directly to the dolomitised limestone walls of the cavities. Within the larger masses of crystalline witherite such chalcopyrite crystals are commonly concentrated within a 10 to 15 mm wide zone in the outer portions of the masses, nearest the dolomitised wall-rock (Fig. 7). These tabular chalcopyrite crystals, both those enclosed within gangue minerals and freely-grown crystals, almost invariably exhibit a dark brown surface tarnish, accompanied in places by small coatings of malachite. The presence of chalcopyrite with an identical morphology,
found in the older workings during the 1950s, and preserved in the University of Durham mineral collections, has been mentioned above.

In a few places adjacent to the southern faces of the quarry (Localities A1 and A2, Fig. 2), narrow veins composed predominantly of copper sulphides, locally with minor baryte, have been traced for strike lengths of several metres in the sandstone beneath the Main Limestone which forms the floor of the workings (Fig. 9). Little, if any evidence of fault displacement has been detected along these veins, though their roughly NE-SW trend approximately parallels the North and South faults of the horst structure which crosses the workings. These veins are typically around

10 mm wide, but locally swell to around 20 mm and in places split into sub-parallel en echelon discontinuous veins (Fig. 10). They are mainly composed of a dense massive intergrowth of copper sulphides, dominated by bornite, but with chalcopyrite and, in places, smaller amounts of dark grey copper sulphides that, on freshly broken surfaces, contrast strikingly with the purplish iridescently tarnished bornite and yellow chalcopyrite (Fig. 11). Within the present study it has not been possible to examine polished sections of these sulphide assemblages. Although not wholly conclusive, X-ray examination of sulphide samples suggests that within these veins, bornite and chalcopyrite are accompanied by a mixture of chalcocite and djurleite. As previously noted, similar grey copper sulphides, collected in the 1950s are preserved within the Durham University mineral collections. Within these veins, malachite occurs in small amount, both as massive coatings and locally as very small clusters of tiny acicular crystals lining cavities <2 mm across. Traces of cuprite are also present as thin dull-red stains and as coatings, <1 mm thick, within these bornite-rich veins. A single specimen comprising a tiny arborescent crystalline mass of cuprite, up to 1.5 mm long, and encrusted with malachite, has also been found. Gangue minerals are generally scarce in these veins, though small amounts of calcite and baryte have been observed locally.

Malachite occurs as conspicuous small earthy coatings and as clusters of crystals, up to a few millimetres across, commonly encrusting massive chalcopyrite in many of the cavities within the dolomitised limestone and associated with copper sulphides in the veins in the underlying sandstone (Fig. 12). In places, conspicuous though extremely thin, coatings of earthy malachite stain the limestone and shale partings adjacent to concentrations of chalcopyrite within the cavities.

A single example of pale yellow radiating crystalline hemimorphite, up to 7 mm across, found in a highly corroded mass of wetherite within a cavity in the dolomitised limestone, indicates the local presence of zinc mineralisation. Sphalerite has not been observed in any of the numerous mineralised cavities in this dolomitised limestone examined during this study, though traces of this

Figure 10. *En echelon* veins of bornite in sandstone from beneath Main Limestone (Locality A1). Scale bar is 5 cm. Photo T.F. Bridges.

Figure 11. Vein of bornite with patches of chalcopyrite, in sandstone from beneath Main Limestone (Locality A1). Scale bar is 5 cm. Photo T.F. Bridges.

Figure 12. Malachite crystals encrusting bornite and baryte in vein in sandstone from beneath Main Limestone (Locality A1). Scale bar is 5 cm. Photo T.F. Bridges.
mineral were found in a galena-bearing vein in the northern faces of the working (Locality A4, Fig. 2), described below.

The topmost 3 m of Main Limestone, exposed in the southern faces of the quarry (Locality A3, Fig. 2), locally exhibits concentrations of anastomosing veinlets of grey copper sulphide, apparently unconnected with any obvious vein or fracture. X-ray examination of samples of this material suggests that here too the grey sulphide comprises a mixture of chalcocite and djurleite, perhaps with some bornite, though the latter mineral is not obvious in hand specimen. Thin crusts of earthy and minutely crystalline malachite, and locally well-developed crystals of azurite, occur coating several square metres of limestone and interbedded shale partings within a few metres of these concentrations of copper sulphide veins (Fig. 13).

A narrow calcite vein, up to 20 mm across and roughly parallel with the South Fault, in the uppermost limestone bed exposed in the northern face of the quarry (Locality A4, Fig. 2), contained small cleavages of galena, up to 10 mm across. A single cubo-octahedral crystal of galena, 1 mm across, was also found here. Associated minerals in this vein included small masses of pyrite and brown sphalerite up to 3 mm across. Thin encrustations of cerussite on some of the galena, and white hydrozincite on sphalerite were also seen. Vivid yellow coatings of cadmium sulphide, up to 20 mm across, have been found on a small number of samples of sphalerite (Fig. 14). It has not been possible to determine which cadmium sulphide species is present though, as has been demonstrated by Young et al. (1987), this may be amorphous.

ORIGINS OF MINERALISATION

As has been outlined above, dolomitisation is widespread within the Carboniferous limestones of this area (Wells, 1955; Attewell, 1971; Mills and Hull, 1976). Much of the mineralisation described here from Forcett Quarry is closely associated with such dolomitisation, with introduced minerals such as witherite, baryte, copper and other ore minerals present mainly as cavity fillings within the intensely dolomitised limestone. These same minerals also occur here as vein fillings, in places within un-dolomitised limestone or the sandstone beneath the Great Limestone, but this style of mineralisation is much less widespread than that found within cavities in the dolomitised limestone.

In order to explore the possible origins of this mineralisation, the nature and possible mechanism of dolomitisation will first be considered.

Mills and Hull (1976) concluded that dolomitisation within the Great Limestone of this area must have occurred either during deposition of the limestone or as a result of subsequent diagenesis.

From considerations of the area’s likely palaeogeography during Permian times, Attewell (1971) suggested that Carboniferous limestones or faults within them, may have cropped out into the Zechstein Sea during deposition of the Magnesian Limestone, enabling magnesium-rich groundwaters to penetrate the Carboniferous limestones, thereby bringing about dolomitisation. The distribution of intense, but very localised, dolomitisation, observed during this investigation, may have resulted from the lateral spread of these fluids through the limestone and underlying sandstone, with fluid flow between beds being constrained by impermeable beds such as thin mudstone partings. Such a genetic model would readily account for the two principal concentrations of dolomitisation within the limestone exposed in the southern and eastern faces of the most recent workings, described above.

It is therefore reasonable to suppose that dolomitisation occurred in advance of, and not necessarily as part of, the mineralising event that deposited the abundance of barium and copper minerals.

A common feature of such dolomitisation is the creation of numerous voids within the altered limestone, the resultant porosity typically providing a receptive environment for the deposition of the later cavity-filling minerals.

Attention now turns to the origins of the main cavity and vein-filling minerals.

The abundance of copper minerals, in association with dolomitised limestone, at Forcett Quarry, and other

Figure 13. Azurite crystals encrusting limestone (Locality A3). Field of view is 3 cm. Photo T.F. Bridges.

Figure 14. Bright yellow stains of cadmium sulphide and brown ‘limonite’ coating limestone which occur scattered grey crystalline patches of galena (Locality A4). Field of view is 2 cm. Photo T.F. Bridges.
mineralised sites within the Middleton Tyas – Sleightholm Anticline, invites comparison with the small concentration of formerly workable copper mineralisation at Middleton Tyas. The abundance of baryte and witherite, together with minor amounts of lead and zinc mineralisation, suggests a close, perhaps genetic, link with the deposits of the nearby main Northern Pennine orefields.

The Middleton Tyas mineralisation, characterised as it is by a dominance of copper minerals, has been regarded as being an expression of a style of mineralisation distinct from the main Northern Pennine orefields (Deans, 1950; 1951). In these studies, Deans suggested that this mineralisation could have originated by downward percolation of mineralising fluids from syngenetic copper deposits in the adjacent overlying Permian Marl Slate at the base of the Magnesian Limestone succession. Whereas the Marl Slate, the correlative of the Kupferschiefer of eastern and central Europe, locally exhibits high concentrations of lead and zinc in North East England, it is not known to contain significant concentrations of copper in this area (Young, 2001). Dunham (1959) pointed out that the known field relations of these deposits did not support epigenetic mineralisation by leaching from overlying Permian sediments. Subsequently, Dunham and Wilson (1985) rejected a syngenetic origin for the Middleton Tyas mineralisation, favouring instead the hypothesis of Small (1977) whereby the deposits originated by the mixing of low Na:K ratio metal-rich brines with high Na:K ratio formation waters. This is broadly consistent with Dunham’s earlier suggestion (1934) that small concentrations of copper mineralisation on the margins of the Northern Pennine orefields may reflect a recrudescence or reactivation of copper mineralisation on the periphery of these orefields. Dunham and Wilson (1985) also advocated supergene enrichment of the deposits so formed, under arid weathering conditions during Permian times, with the formation of digenite, bornite and covellite, followed by later alteration in the oxidation zone to yield widespread malachite, azurite and goethite, with rare traces of cuprite and native copper.

At Forcett Quarry, the widespread small concentrations of chalcopyrite found within cavities in the dolomitised Great Limestone, and in narrow veins within it and the underlying sandstone, are here suggested to be products of the same mineralising processes responsible for the emplacement of the primary sulphides at Middleton Tyas. Bornite, chalcoite and djurleite, found here in veins within the Great Limestone and underlying sandstone, are likely to have formed by secondary enrichment processes during early Permian times.

The witherite and baryte mineralisation, abundantly present within cavities in the dolomitised Great Limestone, closely resembles the barium mineralisation that typifies the outer zones of Northern Pennine mineralisation both within the Askrigg and Alston blocks. Whereas there is evidence that early carbonatisation of primary baryte may have been important in creating significant amounts of witherite, especially in the Alston portion of the Northern Pennines (Hancox, 1934; Dunham, 1990) no evidence of this alteration has been found in any of the witherite examined during the present study. However, as is common in the barium-rich zones of these orefields, witherite at Forcett Quarry locally exhibits significant alteration to coarsely crystallised baryte with, as noted above, the baryte crystal morphology characteristic of this paragenesis. A few examples of baryte pseudomorphing original witherite have also been noted above. The occurrence of very small amounts of galena and sphalerite, locally found associated with these barium minerals, might also serve to link this mineralisation with that of the main Pennine orefields.

If the origin of the dolomitisation of the Great Limestone, proposed by Attewell (1971) is correct, it offers important insights into the timing of mineralisation both here at Forcett Quarry and, more widely, through the Northern Pennine orefields.

Attewell’s (1971) hypothesis for the origins of dolomitisation of the Great Limestone requires that dolomitisation must have taken place in Permian times, during the deposition of the Magnesian Limestone. Emplacement of copper, barium and other introduced minerals must have followed very soon afterwards, if secondary enrichment of the copper minerals was to be accomplished during weathering within Permian times, as advocated by Dunham and Wilson (1985). Such a model is consistent with Cann and Bank’s (2001) suggestion that mineralisation within the Northern Pennine orefields formed during the Upper Permian when an episode of extensional tectonics allowed saline fluids, probably from the Zechstein Sea, to penetrate deep into the basement. Here the fluids reacted with these rocks, where they acquired both the chemical elements necessary for the mineralisation and the heat required to drive the convective flow of mineralising fluids.

**ACKNOWLEDGEMENTS**

We wish to thank Hanson Aggregates Ltd, and particularly Dominic Doyle, Manager of Forcett Quarry, for allowing access to the quarry workings during the course of this investigation. Forcett Quarry is a working quarry and access is not permitted without permission from the owners. Peter Young is thanked for preparing the maps.

**REFERENCES**


Chalcoalumite, CuAl₄(SO₄)(OH)₁₂·3H₂O, is a rare monoclinic mineral, first reported from Bisbee, Arizona, U.S.A. by Larsen and Vassar (1925) and more comprehensively described by Williams and Khin (1971) using better quality material.

The first report of chalcoalumite from the British Isles was of material from South Wheal Crebor, Devon (Braithwaite and Cooper, 1982). Chalcoalumite was subsequently reported from the Britannia Mine, Snowdon, Gwynedd (Bevins et al., 1985) and from Vigra Mine, Bontddu, Gwynedd in (Saich and Rust, 1987). It was recorded from Penberthy Croft Mine in Cornwall by (Camm and Merry, 1991a,b). Recently, one of us (MGHM) has collected good chalcoalumite from Wheal Charlotte, St. Agnes, Cornwall. These finds are described below.

PREVIOUSLY DESCRIBED OCCURRENCES IN SOUTH WEST ENGLAND

South Wheal Crebor

South Wheal Crebor, also known as New East Russell Mine, is an old copper mine, closed before 1870, in Tavistock Hamlets parish. It was re-prospected by tributers in the 1920’s, but was considered to be unfavourable (Dines, 1956a; p. 676). In 1975 an adit level which had been recently dug open at NGR 465 714, was explored, in which childrenite crystals to about 1 mm were found on a grey killas with decomposing chalcopyrite and pyrite. Some of the childrenite was found as matted layers of crystals overgrown with supergene copper minerals, including branching crystals of native copper altering to cuprite, brochantite and chalcoalumite (Fig. 1), some chalcoalumite was also found directly on killas. This chalcoalumite, identified by infrared spectroscopy and confirmed by X-ray powder diffraction, forms pale blue to white to almost colourless compact fibrous radiating crusts (Braithwaite and Cooper, 1982). The late George Ryback (personal communication) identified cyanotrichite by infrared spectroscopy in the sky-blue outer edges of some chalcoalumite spherules passed to him by Richard Tayler, and noted that other material collected by M.A. Vincent in 1987 and X-rayed at the Natural History Museum, London (NHM) was identified as “ajoite + near-carbonate-cyanotrichite”.

A number of other species have been found at this locality, including aragonite (A. Jeal. New East Russell, Devon. Russell Society Newsletter, 1994, 24, 7), arsenopyrite, siderite, a little sphalerite and traces of cassiterite (Dines, 1956a; p. 676).

Penberthy Croft Mine

Chalcoalumite was collected by David Clough from Penberthy Croft Mine, St. Hilary, Cornwall, (Camm and Merry, 1991a,b; Ryback and Tandy, 1992; Betterton et al., 2000). This material consists of white spherules to about 0.5 mm on quartz, with malachite, mimetite, brochantite and “chrysocolla”, and was identified by X-ray diffraction at the NHM (pattern 4729F). Penberthy Croft Mine is famous for the wide range of mineral species which have been found there, as described in detail by Betterton et al. (2000).

NEW OCCURRENCE OF CHALCOALUMITE

Wheal Charlotte, St. Agnes

Wheal Charlotte, also known as Great Wheal Charlotte, is situated just west of Chapel Porth, and centred on NGR SW 697 492, worked for copper from a lode in metamorphosed killas. This lode outcrops in the cliffs, produced 2,800 tons of ore from 1834 – 1836 and was worked again in 1840. An associated smaller lode does not seem to have been economical to work. The workings reached a depth of 82 fathoms and extended under the sea (Dines, 1956b, pp. 478-479). Curiously, much less information has been published about this mine than its mostly smaller neighbours. This Wheal Charlotte should not to be confused with the mine of the same name at Perranuthnoe or with New Wheal Charlotte, which is also known as Charlotte United or North Towan mine, to the
south, or with East Wheal Charlotte, 0.4 km to the north east. Dewey (1923, p. 19) merely lists “Wheal Charlotte” St. Agnes, reporting an output of 23,010 tons of copper ore between 1820 and 1856, but he must have been referring to New Wheal Charlotte, from which this output is recorded. In addition to “copper ore" Collins (1871, p. 57) noted the presence of cassiterite (not recorded as an output), while Henwood (1843) and Greg and Lettsom (1858, p. 307) both reported cuprite. Although a considerable part of the spoil heaps have been removed, mainly for road stone, they are still quite extensive and have produced good specimens of native copper as well as sphalerite, chalcopyrite, cuprite and a few specimens of crystalline cassiterite in recent years.

One of us (MGHM) has recently collected a number of specimens of chalcoalumite, mostly from the largest spoil heap, which is approximately 200 metres from the cliff edge. The specimens are fairly rich but were sparsely scattered in a layer less than a metre thick near the top of the dump. The chalcoalumite forms compact radiating crusts of pale to mid blue acicular micro-crystals lining cavities in gossany quartz matrix containing chalcocite and chalcopyrite. A few striking specimens had plush pale blue chalcoalumite coating cavities which are up to 15 mm across (Figs. 2, 3 and 4). Poor quality specimens, which were commonly weathered were found in other nearby parts of the dumps. The chalcoalumite is sometimes associated with brochantite in unusual pale to deep green lath-like crystals (Fig. 5).

The identifications of the chalcoalumite and brochantite were confirmed by infrared spectroscopy. Infrared spectra were measured in nujol mulls between KBr plates over the range 400 – 4000 cm⁻¹, using a Perkin Elmer Spectrum BX Fourier Transform infrared spectrometer. The spectrum of the chalcoalumite shows a broad strong complex of hydrogen-bonded O–H stretching vibrations with a maximum around 3400 cm⁻¹ and a distinct shoulder at about 3600 cm⁻¹ with hints of further shoulders. An H–O–H “scissor” deformation gives a fairly broad, medium strength absorption at 1630 cm⁻¹. Vibrations of the SO₄ tetrahedron give a strong υ₁ absorption at 1100 cm⁻¹, a medium strength υ₄ absorption at 971 cm⁻¹, medium strength υ₂ absorptions
at 600 and 558 cm⁻¹, and two weak ν₂ absorptions, which could also be due to metal–O stretch vibrations, at 475 and 450 cm⁻¹.

REFERENCES


The first record of native mercury from the British Isles is that of Kingsbury (1969, see Embrey, 1978), who reported it from Chatsworth Mine, Grassington Moor and Greenhow Hill in Yorkshire, but as doubt has been cast on the reliability of Kingsbury’s claims (Ryback et al., 1998, 2001; Ryback, 1999; Bridges, 2009) these records need to be confirmed. The only other record is that of Meikle (1994) who described micrometer-sized particles closely associated with acanthite, which were detected and analysed during SEM examination of acanthite from Hilderston Silver Mine, Bathgate, West Lothian, Scotland. These reports have also been noted in Tindle (2008).

The first confirmed record of any mercury mineral from the British Isles is that of material from Rutland Cavern, Matlock Bath, Derbyshire (Braithwaite et al., 1963). Close examination of a specimen containing cinnabar from this original investigation has now revealed the presence of native mercury.

LOCATION

Rutland Cavern is a show cave in the Carboniferous Dinantian Limestone, based on an ancient lead mine on the Great Rake complex in the Heights of Abraham at Matlock Bath, at NGR SK 293 585 (e.g. Adam, 1843; Bryan, 1903; Braithwaite and Ryback, 1963).

DESCRIPTION

The specimen on which native mercury has now been observed was collected in December 1962 by the authors, and is currently in the T. Greenland collection, No. 2186.

NATIVE MERCURY FROM DERBYSHIRE

Tim B. GREENLAND

39, Rue St. Jean, 69005 Lyon, France

Richard S.W. BRAITHWAITE

School of Chemistry, University of Manchester, Manchester M13 9PL

The first record of native mercury from the British Isles is that of Kingsbury (1969, see Embrey, 1978), who reported it from Chatsworth Mine, Grassington Moor and Greenhow Hill in Yorkshire, but as doubt has been cast on the reliability of Kingsbury’s claims (Ryback et al., 1998, 2001; Ryback, 1999; Bridges, 2009) these records need to be confirmed. The only other record is that of Meikle (1994) who described micrometer-sized particles closely associated with acanthite, which were detected and analysed during SEM examination of acanthite from Hilderston Silver Mine, Bathgate, West Lothian, Scotland. These reports have also been noted in Tindle (2008).

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The specimen on which native mercury has now been observed was collected in December 1962 by the authors, and is currently in the T. Greenland collection, No. 2186.
It consists of a 5 x 3 x 1.5 cm piece of calcite matrix with included galena. A cavity adjacent to the galena shows earthy orange-red cinnabar coatings with micro-botryoidal smithsonite as previously described (Braithwaite et al., 1963). On re-examination of the specimen another cavity in the calcite, and containing similar smithsonite was observed to carry a silvery globular material, which is liquid, as shown by its mobility when touched with a needle point. The globules, which measure about 0.05 to 0.1 mm in diameter, are dispersed over an area approximately 1.5 x 1.5 mm (Fig. 1).

**DISCUSSION**

Limestone is stable at pH values above about 7.8, up to 10 or higher; the acidity associated with the presence of oxidising sulphides suggests that local pH values in an oxidising mineralised limestone environment should be towards the lower end of this range. At these pH values, native mercury is thermodynamically stable with respect to cinnabar at Eh conditions above around -0.2 at pH 7.8 and -0.4 at pH 10, up to at least +0.3 (Brookins, 1988), so relatively mild oxidising conditions should suffice to release native mercury *via* the oxidation of the sulphide in the cinnabar. At normal temperatures, however, cinnabar is not easily oxidised, though native mercury is not uncommon in cinnabar deposits. Any discussion of this conversion at any particular site is also complicated by the high volatility and hence mobility of metallic mercury. The cinnabar at Rutland Cavern is closely associated with smithsonite (Braithwaite et al., 1963) formed from the alteration of sphalerite, and was probably a component of the sphalerite either in solid solution or as inclusions. Being kinetically more resistant to oxidation than the sphalerite, the cinnabar remained intact during sphalerite oxidation. The sulphur in sphalerite is oxidised at pH conditions near 8 at Eh values above about -0.2 (Brookins, 1988), leading to the release of zinc ions, which in the carbonate rich environment forms smithsonite at around those conditions thermodynamically required for forming native mercury.

**ACKNOWLEDGEMENTS**

The authors are grateful to Frank Ince for helpful comments and suggestions.

**REFERENCES**

NOTES FOR CONTRIBUTORS

TYPESCRIPTS
Authors are encouraged to prepare papers in electronic format using Microsoft Word and to send the file(s) as e-mail attachment(s) to the Editor. Templates for the format of articles and notes are available from the Editor and the Journal Manager. Do not embed figures and tables within the text, but indicate where they should be inserted. At the end of the manuscript provide figure captions and any tables with their captions. All pages should be numbered in the footer. 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 welcomed.

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. National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST 40 71 and enclosed in square brackets where necessary, e.g.: [ST 4015 7185], [ST 401 718], [ST 40 71]). Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, microchemical 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.

FIGURES
All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Figure 1, etc. Figures must have descriptive captions, and the scale must be indicated either on the photograph or by specifying, e.g., width of view or crystal size in the caption.
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) should be submitted initially as low-resolution electronic files (.jpeg format is preferred) or draft quality prints, 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.

TABLES
Tables should be numbered consecutively and referred to in the text as Table 1, etc. Each table should have a descriptive title placed beneath. Horizontal lines should mark the top and base of tabulated data; any footnotes should be placed below this.

TERMUNOLOGY
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 10th edition, by Mandarino and Back, 2008) 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, 1967), 22, 45.

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:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>XRD</td>
<td>X-ray diffraction analysis</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence analysis</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron probe microanalysis (electron microscopy analysis)</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive analysis (same as EDA, EDAX, EDS)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope or microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscope or microscopy</td>
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<td>IR</td>
<td>Infrared</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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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.
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