JOURNAL
OF
The Russell Society

JOURNAL OF THE RUSSELL SOCIETY

The journal of British Isles topographical mineralogy

Aims and Scope: The Journal publishes refereed articles by both amateur and professional mineralogists dealing with all aspects of mineralogy relating to the British Isles. Contributions are welcome from both members and non-members of the Russell Society. Notes for contributors can be found at the back of this issue, or obtained from the editor.

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The Russell Society, named after the eminent amateur mineralogist Sir Arthur Russell (1878—1964), is a society of amateur and professional mineralogists which encourages the study, recording and conservation of mineralogical sites and material. For information about membership, write to the Membership Secretary, Mr F.K. Werner, 12 Martinshaw Lane, Groby, Leicestershire LE6 0BJ, U.K.

FRONT COVER: Cuprite, variety chalcotrichite, from Fowey Consols mine (Lanescot section). Tywardreath. Cornwall. Field of view 13 mm × 9 mm. Roy Starkey specimen (0526-007) and photograph.

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EDITORIAL

I must apologise both to our subscribers and to our authors for the late appearance of this issue, originally intended to come out in March or April. Delayed publication has been a recurring problem in recent years; we are working on this and hope to get it right next time. However, the timely appearance (and certainly the thickness) of the Journal also depends on the Editor receiving enough material, and members are again urged to write up their observations and submit them for publication. Contributions from non-members of the Society are, of course, also welcome.

There have been minor changes in the appearance of the Journal over the years, some simply aimed to reduce production costs, such as the change to a smaller font size in 1995. I hope subscribers will approve the sturdier covers of the current issue, the contents printed on the outside back cover, and the lists of contents of all the past issues on pp. 45–48. It has been decided that, from this issue, we will no longer carry advertisements, and Harry Day and I would like to thank all former advertisers for their support of the Journal in the past.

The Journal's Editorial Board has lost two members through retirement: Dr Brian Atkins from the Oxford University Museum of Natural History, and Dr Alec Livingstone from the Royal Museum of Scotland in Edinburgh. Both have given valuable and unstinting service to our Journal as board members and referees for many years, and I would like to record our thanks and appreciation, and to wish them a happy retirement. Brian, by the way, once wrote what must be the shortest abstract for *Mineralogical Abstracts* (71-1400). The entire abstract reads "About 70 km." and refers to a letter in *Nature* entitled "How thick is the lithosphere?" Now there's a lesson in conciseness!

Although most of our readers are not within easy reach of London, I would like to draw attention to some important developments at The Natural History Museum. Three new long-term exhibitions have just opened in the Earth Galleries (that's the old Geological Museum building for those who remember it) – see page 34. *Earth's treasury* is the one displaying some of the museum's finest mineral specimens, and a stunning collection of gemstones (as well as various instructive exhibits). These three exhibitions deserve a proper review, and we plan to include one in our next number.

Another new addition to the Earth Galleries is *Earth Lab*, not mentioned in the announcement on page 34. It is housed in two rooms, the first containing show-cases of 1100 British fossils, 200 British rocks, and 250 British minerals (mostly from the Ludlam Collection), as well as a couple of computer terminals with open access to an excellent, easy-to-use database of information about these specimens. The room beyond is equipped with high-quality microscopes (each with a monitor screen so that a specimen can be viewed by more than one person), and eventually will have reference books, geological maps, and other tools for the study of British geology and mineralogy – it is not a children's play-room. Staff from the Palaeontology and Mineralogy departments are in attendance to answer visitors' questions and identify specimens. *Earth Lab* is a new concept and thus a bit experimental; it will be interesting to see how it develops and what use the public make of it.

All this is *in addition* to the existing mineral gallery in the main building of the museum, housing the very large and famous systematic collection of minerals. There are no plans to close this gallery, as was once feared. Londoners are indeed lucky to have access to such a wealth of mineralogical material on open public display.

George Ryback

SUPERGENE MINERALS OF THE NORTHERN PENNINE OREFIELD – A REVIEW

Trevor F. BRIDGES

10 Springfield, Ovington, Northumberland NE42 6EH

Brian YOUNG

British Geological Survey, Murchison House, West Mains Road, Edinburgh EH9 3AL

The occurrence and distribution of all supergene minerals known to occur within the Northern Pennine Orefield is reviewed. Brief descriptions are given of the range of characteristics exhibited by each species present, together with references to literature and other sources of information.

INTRODUCTION

The veins and related deposits of the Northern Pennine Orefield have long been well known to mineralogists throughout the world as a source of fine specimens of several minerals, notably fluorite, quartz, galena, sphalerite, baryte, witherite, alstonite and barytocalcite. The orefield includes the type localities for the last two species and there is strong evidence that it was the source of the first known specimens of witherite. These minerals comprise important elements of the field's primary, or hypogene, assemblage. A considerable volume of work carried out on many of these minerals has greatly advanced our understanding of the origins of this and related orefields. Although the field has yielded a number of fine examples of a few secondary, or supergene, species and has in recent years provided a new zinc carbonate–sulphate mineral, brianyoungite, comparatively little attention has been paid in the mineralogical literature to the supergene assemblages.

In this review, the Northern Pennine Orefield, which lies between Stainmore and the Tyne Gap, is considered. The area coincides with the structural unit known as the Alston Block and includes not only the Northern Pennine uplands, but also the adjoining structurally related lowlands of the Durham Coalfield. This is the area described in detail by Dunham (1990).

The regional geology, structural setting, form and origin of the Northern Pennine deposits have been the subject of detailed research by numerous authors. Comprehensive summaries of this work are given in Dunham (1990) and by the British Geological Survey (1992, 1996). A detailed outline of the orefield is not required here. Suffice it is to note the essential features of the field.

Vein deposits in the Alston Block occupy a series of conjugate minor faults within a cyclical sequence of limestones, sandstones and mudstones of Carboniferous age, ranging from Dinantian to Westphalian. These overlie shallow Lower Palaeozoic basement rocks, including the concealed Caledonian Weardale Granite. In places limestone wall-rock has suffered extensive metasomatic replacement by introduced minerals, giving rise to horizontally extensive 'flat' deposits adjacent to

several veins. Throughout the orefield the economic ore mineral assemblage is dominated by abundant argentiferous galena, with locally large amounts of sphalerite and some minor concentrations of chalcopyrite. Iron carbonate minerals, including siderite and ankerite of a variety of compositions, are extremely widespread elements of the gangue assemblage. Other ore minerals include arsenopyrite, bismuthinite, cassiterite, cobaltite, gersdorffite, glaucodot, nickeline, pyrrhotite, pyrite and ullmannite. Whereas several of these are of widespread occurrence, none is known in workable amounts. Gangue minerals include fluorite in the inner, central zone of the field. Surrounding this central zone, deposits are characterised by the abundance of barium minerals, including baryte and witherite, with appreciable concentrations of barytocalcite and some alstonite.

Whereas historically lead and iron were the principal metals sought, with smaller amounts of zinc and copper, the gangue minerals have become the main economic products of the field over the past century. The orefield was an early world leader in the commercial production of fluorite. Large tonnages of baryte and witherite have also been raised. Mining for fluorite and baryte continues today with very small amounts of lead and zinc concentrates produced as by-products.

In reviewing the occurrence of supergene species an extensive search of published literature has been supplemented by reference to unpublished data and collections of Northern England minerals in both museums and private collections. In this review descriptions of minerals or sites for which no literature or other reference is cited are new records. Whereas the majority of the minerals discussed are from deposits clearly forming part of the Northern Pennine Orefield suite of deposits it has, in some instances, proved difficult or impossible to divorce these from other, perhaps unrelated, modes of occurrence. We have therefore found it desirable to extend the scope of the review slightly to encompass occurrences of all minerals found within the district which are of obviously secondary or supergene origin, including those formed by normal weathering processes and by post-mining alteration.

So far as we are aware all supergene mineral species known or reported to occur within the district at the time of writing are included. However, it is clearly impossible to cite all known localities for every species. Included in this review are representative localities, or those at which the mineral is present in noteworthy abundance, in a particular form, or at which it exhibits other features of significant interest or importance for that species.

Grid references are generally given to either six or eight figure accuracy, dependent upon the need or appropriateness for this level of detail. Where large areas of country are referred to without specific locality details, four-figure grid references are used. Abbreviations used below are: BGS = British Geological Survey; NHM = The Natural History Museum, London.

NATIVE ELEMENTS

COPPER, Cu

Dunham (1990, p. 90) noted the occurrence of native copper in a vein in limestones of the Raisby Formation (Permian) in Raisby Quarry, Coxhoe (National Grid Reference NZ 342 352). We have been unable to trace any specimens of native copper from here, though small amounts of chalcopyrite coated with malachite were found several years ago partly filling calcite-lined vugs in the southern part of the quarry. Copper mineralisation, including abundant malachite, azurite and some chalcocite, is present in brecciated Raisby Formation limestones in the old railway cutting (NZ 350 349) immediately south of this quarry. Within this mineralised breccia occur rare concentrations of cuprite in which flakes of native copper <1 mm across have recently been found.

Smith (1973) described the occurrence of native copper as platy, dendritic growths, associated with ferricopiapite, on etched faces and cleavage surfaces of fluorite in Groverake Vein in the New Firestone Level of Groverake Mine, Rookhope (NY 896 442).

Very thin coatings of native copper, <1 mm across, are present on quartz–chalcopyrite veinstone, possibly derived from the Great Sulphur Vein, at Sir John's Mine, Tynehead (NY 7614 3782), and in the outcrop of the Great Sulphur Vein at Cross Gill, Alston Moor (NY 7394 3832). Similar veinstone at Westernhope Old Mine, Westgate, Weardale (NY 9196 3450), also contains small coatings of dendritic native copper.

Quartz–chalcocite veinstone sparingly present on the spoil heaps of an old dressing floor at Cornriggs, Alston Moor (NY 7178 3724), has yielded a few specimens of copper in the form of irregular masses up to 2 mm across.

There is no doubt that in all of these instances the copper is of supergene origin.

SULPHUR, S

Native sulphur can form as the result of the oxidation of marcasite and of most of the common sulphides found in the orefield, under conditions of relatively low pH and oxidation potential (Eh).

Greg and Lettsom (1858) describe the occurrence of small crystals of sulphur on large galena crystals at Dufton Mine, near Appleby (NY 719 281), and also note its association with gypsum at Alston. At Harehope Gill Mine, Weardale (NZ 0330 3600), epimorphs in quartz after marcasite are commonly coated with dull, pale yellow sulphur (Dunham, 1990, p. 90). Similar thin powdery crusts of sulphur, probably formed by the oxidation of pyrite or marcasite, occur at Smittergill Head Mine, Alston Moor (NY 6720 3895), and at Shildon Mine, Blanchland (NY 962 508). Thin crusts of pale yellow sulphur crystals, up to 0.5 mm across, associated with covellite, anglesite and cerussite in a baryte–galena matrix, have been found at Closehouse Mine, Lunedale (NY 850 228). Pale yellow crystals of sulphur up to 1 mm across occur in corroded galena in the flats associated with Middle Vein at Brownley Hill Mine, Nenthead (NY 7762 4465); in the flats associated with the Dryburn Washpool Vein in Tynebottom Mine, Garrigill (NY 7394 4183); and on the spoil heaps from workings on the Burntshieldhaugh Vein, Blanchland (NY 925 541), and the Drypry Vein, Wolsingham (NZ 0676 4327). At the last locality a single specimen with a bright yellow waxy deposit of sulphur, 5 mm across, has been found.

SULPHIDES

CHALCOCITE, Cu$_2$S

Chalcocite occurs as silver-grey masses up to 10 mm across associated with malachite, cuprite and minor native copper in brecciated limestones of the Raisby Formation (Permian) in the old railway cutting near Raisby Quarry, Coxhoe (NZ 350 349). It is also present as a minor component of the copper-rich veinstone at Cornriggs, Alston Moor (NY 7178 3724). Although its supergene origin cannot be conclusively established, its occurence is consistent with such an origin.

CINNABAR, HgS

Extensive earthy coatings of dull red cinnabar, up to 10 cm across, occur at Silvertop Quarry, Brampton (NY 586 606), in association with aurichalcite and 'dry bone' smithsonite (Young et al., 1989). The same authors noted traces of cinnabar encrusting 'dry bone' smithsonite at the Natrass Mines, Alston (NY 735 448). In both instances the cinnabar appears to be a residual phase resulting from the oxidation of sphalerite.

COVELLITE, CuS

Dunham (1932) described covellite replacing galena at the Horse Level horizon at Sedling Mine, Weardale (NY 858 410), in circumstances which suggest supergene enrichment.

Dark blue coatings of covellite have been found on well-oxidised galena at Closehouse Mine, Lunedale (NY 850 228), and Healeyfield Mine, Castleside (NZ 0689 4866). Similar coatings, on anglesite–quartz matrix, occur at workings on Drypry Vein, near Wolsingham (NZ 0676 4327).

GREENOCKITE, CdS

The oxidation of sphalerite may result in the formation of bright yellow earthy coatings of cadmium sulphide in cracks and on cleavage planes. Examination by X-ray diffraction has revealed the presence of greenockite in only a few of these occurences. Young *et al.* (1987) postulate that, as sphalerite oxidises and zinc is removed in solution as zinc sulphate, amorphous cadmium sulphide is liberated from solid solution in the sphalerite. Only rarely does the cadmium dissolve and later crystallise as greenockite.

Greenockite was first recorded in the area by Dunham (1948) from Ashgillhead Mine, Teesdale (NY 8083 3550). The mineral has subsequently been reported from Reddycombe (also known as Willyhole) Mine, Upper Teesdale (NY 8020 3355), and Blagill Mine, Nenthead (NY 742 473). Bright yellow coatings of apparently amorphous cadmium sulphide have been noted from several sites including Rotherhope Fell Mine, Alston (NY 6993 4264); Settlingstones Mine, Newbrough (NY 848 687); Stonecroft Mine, Newbrough (NY 855 687); Hardshins Level, Teesdale (NY 7579 3388); Tynebottom Mine, Garrigill (NY 7394 4183); and Hilton Mine, Scordale, near Appleby (NY 7624 2281).

HALIDES

FLUORITE, CaF₂

The widespread presence of deep etching on the surfaces of fluorite crystals within the oxidation zone indicates that fluorite may pass into solution, particularly in the presence of sulphate-rich groundwater (Dunham, 1990, p. 88). There is, however, no reliable record of the deposition of fluorite as a supergene mineral within the orefield. The fluorite crystals found within a stalagmitic deposit formed on fallen timber in Old Fall Mine, Weardale (NY 8760 3865), reported by Watson (1900), may have been fragments of primary crystals incorporated into the stalagmite.

SAL-AMMONIAC, NH₄Cl

Brief reference is made by Greg and Lettsom (1858) to the presence of this mineral in the vicinity of burnt coal seams near Newcastle upon Tyne, though no precise localities are mentioned.

OXIDES AND HYDROXIDES

BISMITE, Bi₂O₃

X-ray powder photography of samples of quartz veinstone from the Great Sulphur Vein outcrop in Crossgill, near Garrigill (NY 7394 3833), revealed the presence of bismuthinite accompanied by a little bismite (C.J. Stanley, *personal communication*, 1987).

CORONADITE, $Pb(Mn^{1+},Mn^{2+})_8O_{16}$

Young *et al.* (1996) recorded the presence of abundant coronadite from shallow workings on the Sedling Vein,

Cowshill (NY 8698 4076). They note that the apparent rarity of the mineral may reflect the lack of precise identification of otherwise relatively common black manganese oxides.

CUPRITE, Cu₂O

Small crystalline masses of cuprite up to 2 mm across, associated with native copper, occur in brecciated Raisby Formation (Permian) limestones in the old railway cutting south of Raisby Quarry, Coxhoe (NZ 350 349). Bright red octahedral crystals up to 0.1 mm long and partly crystalline crusts up to 10 mm across, associated with native copper and a little malachite, occur on quartz at Westernhope Old Mine, Weardale (NY 9196 3450). Small masses of cuprite up to 1 mm across also occur at Closehouse Mine, Lunedale (NY 850 228), and on old workings on the Cornriggs Vein, Alston Moor (NY 7178 3724).

GOETHITE, FeO(OH)

For the purposes of this review, goethite is taken to include 'limonite' and 'brown hematite' of the older literature. The deposits of the Northern Pennine Orefield typically contain abundant iron carbonate minerals, a feature which serves to distinguish this district from the other Pennine orefields to the south (Dunham, 1990). Siderite and ankerite occur widely both as constituents of veins and the associated wall-rock alteration, and as major components of the numerous flat deposits which replace limestone adjacent to many of the veins.

Substantial tonnages of carbonate ores have been mined from the orefield, though the district's most valuable iron ores have been those found in the supergene zone of the deposits, particularly the flats. The oxidation of otherwise subeconomic or uneconomic carbonate protores has produced numerous valuable orebodies which have sustained an iron mining industry for at least as long as lead mining. Supergene alteration of both siderite and ankerite has typically produced deposits referred to in most older literature as 'limonite' or occasionally as 'brown hematite'. Dunham (1990) notes that hydrated iron oxide is the product of this process in the Northern Pennines. Goethite appears to be the most abundant mineral present though, in the absence of any systematic study of the iron oxide mineralogy of these deposits, the presence and relative abundance of other iron oxides is largely unknown. The iron oxide-rich deposits produced here by supergene processes comprise good examples of those classified as of Bilbao type (Percival, 1955).

Such 'limonitic' ores have been worked at many localities throughout the orefield. Some of the largest orebodies of this type include those at West Rigg (NY 912 393) and other sites adjacent to the Slitt Vein in Weardale, and at Carricks Mine (NY 861 380), also in Weardale. Smaller but very similar deposits have been worked elsewhere in the orefield.

The most completely oxidised ores of the district typically comprise massive, rather earthy, dark brown goethite. A cavernous cellular texture is common. Good examples of this mineral may be seen at any of the

district's numerous old iron ore mines. Soft, ochreous 'limonite' is locally abundant and has been worked as 'umber' in the Alston area, notably at Horse Edge (NY 685 446). 'Yellow ochre' has been noted at several sites including West Rigg, Weardale (NY 912 393); High Sedling Mine, Weardale (NY 870 408); and Dun Fell Hush, Great Dun Fell (NY 714 318). Smythe (1926) refers to several occurrences of 'ochre' derived from the weathering of sandstones and limestones, in the Alston, Slaggyford and Hexham areas, which appear to have provided raw material for pigment making in the past. Crystalline goethite occurs sparingly within the district. Dunham (1990, p. 108) notes that the cavernous 'limonite' ore at Ardale Head Mine, Ousby Fell (NY 671 357) contains an unusually high proportion of crystalline goethite. Small amounts of crystalline goethite, commonly with a glossy black mamillated surface, have been collected from Hard Rigg Edge, Melmerby Fell (NY 6552 3876); Aglionby Beck, Melmerby Fell (NY 657 396); Silverband Mine, Great Dun Fell (NY 705 319); Coldberry Sun Vein, Grasshill Common, Teesdale (NY 827 356); West Rigg, Weardale (NY 912 393); Heights Quarry, Weardale (NY 924 389); Langdon Mines, Teesdale (NY 852 334); and West Binks Edge, Teesdale (NY 865 313). Dull brown goethite pseudomorphs after either siderite or ankerite are extremely common at most of the workings in 'limonite' rich flats: good examples include those from Carricks Mine, Weardale (NY 861 380); Heights Quarry, Weardale (NY 924 389); Queensberry Ironstone Workings, Weardale (NY 856 414); and Leonard's Hush, Teesdale (NY 906 315). Pseudomorphs after pyrite were recorded from Silverband Mine, Great Dun Fell (NY 705 319), by Davidson and Thomson (1951). Dunham (1990, p. 90) notes that goethite pseudomorphs after cubic pyrite are fairly common: good examples have been found in the South Vein workings at Heights Quarry, Weardale (NY 924 389).

Hydrated iron oxide, presumably consisting mainly of goethite, is common as a post-mining stalagmitic or stalactitic deposit currently forming from iron-rich waters in many of the district's abandoned mines. The accumulation of up to 20 cm of soft, earthy 'brown hematite' within a period of thirty years in Mill Level, Rookhope (NY 9244 4301), was outlined by Hill (in discussion of Hill and Dunham, 1968). Ferruginous springs, commonly known in the past as 'red runers', flow from several abandoned mine workings, especially old coal mines. Smythe (1927, p. 23) cites the Twizell Burn at Chester-le-Street (NZ 20 50) as an example of a stream discoloured by such mine water. Brown, earthy goethite is also a characteristic oxidation product of diagenetic pyrite, and of siderite in the clay ironstone nodules found in many of the district's shales.

HEMATITE, Fe$_2$O$_3$

Dunham (1990) notes that hematite is a rare oxidation product of carbonate iron ores in the orefield. He comments on the occurrence of "some greasy hematite" in the limonitic ores at the Nest Mines, near Alston (NY 718

443), and refers to the possible, but unconfirmed, presence of red hematite within similar ore at Ardale Head Mine, Ousby Fell (NY 671 357). Davidson and Thomson (1951) comment that the variety 'turgite' or 'hydrohematite' was recorded from here by previous workers though they cite no reference. The possible presence of hematite at Silverband Mine, Great Dun Fell (NY 705 319), was also noted by Davidson and Thomson (1951). Hematite may well be widely present in small amounts within the district's oxidised iron ores.

MINIUM. Pb^{2+}$_2$Pb^{4+}O$_4$

Phillips (1844, p. 537) records minium from "Grasshill Chapel in Weirdale [sic], Yorkshire" and Greg and Lettsom (1858) note its presence at "Alston, in Cumberland ... Weardale, and at Grasshill Chapel", though without further details.

Fragments of a vivid orange-red crystalline mineral, found amongst lead slag at Nenthead Smelt Mill, Cumbria (NY 7834 4330), have been identified by X-ray diffraction as minium (L.K. Gurney, *personal communication*, 1990). There seems little doubt that the mineral is here a product of smelting. We have been unable to trace any other confirmed specimens of minium from the orefield.

Grasshill Chapel of Phillips (1844) and Greg and Lettsom (1858) is almost certainly Grasshill Mine, Teesdale (NY 819 355). Highly oxidised lead minerals, including pyromorphite and cerussite, are locally abundant in these ancient surface workings, though we have been unable to confirm minium as part of this assemblage. Early lead smelting at this site, reported by Beadle (1969), is evidenced by fragments of lead slag amongst the spoil. It is possible that here, as at Nenthead, minium is a smelting product.

PYROLUSITE, MnO$_2$

A bed of pyrolusite up to 20 cm thick, with the appearance of "soft coke", was described from Silverband Mine, Great Dun Fell (NY 705 319), by Orchard (1921). Traces of pyrolusite are recorded from old workings on Remmington's Vein on the east side of Great Dun Fell (NY 7180 3240) (B. Young, *personal communication* in Dunham, 1990). The mineral here occurs as thin crystalline coatings on romanèchite. Whereas no other records of pyrolusite are known from the orefield, it is likely that a careful search of black manganese-rich oxidised veinstones, present at several localities, may reveal further occurences.

Smythe (1927) makes reference to several occurrences of soft black manganese oxide as dendritic markings within the Magnesian Limestone of east Durham, and as a black coating to sand grains in the Permian Yellow Sands at Downhill Quarry, Boldon, Tyne and Wear (NZ 348 602). He also describes the occurrence of abundant soft black manganese oxide ochre being deposited from a spring at Pit Wood, Riding Mill (NZ 02 60). We have been unable to locate this site. For none of these occurrences does Smythe suggest the identity of the manganese mineral, though pyrolusite may be a possibility.

ROMANÈCHITE, $(Ba,H_2O)_2Mn_5O_{10}$

Dunham (1990) comments briefly on the presence of small amounts of 'psilomelane' on the dumps from the old workings on Remmington's Vein on the east side of Great Dun Fell (NY 7180 3240). Recent examination of this material by X-ray powder photography (BGS X-ray XE879) has confirmed the mineral as romanèchite. No other records of this mineral are known from the orefield, though it is likely that it is widely present amongst the black, manganese-rich oxidised iron ores at several localities. The 'psilomelane' reported from Silverband Mine, Great Dun Fell (NY 705 319), by Davidson and Thomson (1951) and Seager and Davidson (1952) may well be romanèchite.

CARBONATES

ARAGONITE, $CaCO_3$

Aragonite is a relatively common primary mineral in the area. However, it also occurs in a clearly supergene paragenesis where it usually takes the form of hemispheres, 1 to 3 mm in diameter, of compact radiating needles with a pearly lustre and is associated with other supergene species. These hemispheres commonly aggregate to crusts covering several square centimetres. Good examples of supergene aragonite are common at Brownley Hill Mine, Nenthead (NY 7762 4465); Tynebottom Mine, Garrigill (NY 7394 4183); and on the dumps of Blagill Mine, Nenthead (NY 742 473).

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

Turquoise-blue crusts of aurichalcite crystals occur at several localities in the area. Rudler (1905) refers to aurichalcite from Nenthead but gives no precise locality details. Davidson and Thomson (1951) note the mineral's presence on Alston Moor but cite no exact localtions. Sir Arthur Russell (personal communication in Dunham, 1948) first noted the mineral from Hilton Mine, Scordale (NY 763 227). Young et al. (1985a) recorded it as small crusts of pale turquoise-blue pearly crystals from Fosters Hush, Lunedale (NY 8556 2040); Windy Brow Vein, Tynehead (7698 3812); and Greenhurth Mine, Teesdale (NY 7792 3278). Aurichalcite has subsequently been found at at Silvertop Quarry, Brampton (NY 586 606) (Young et al., 1989) and more recently at Closehouse Mine, Lunedale (NY 850 228).

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

Dunham (1990, p.90) noted that azurite and malachite are widespread in the orefield, usually in trace quantities though with rather greater amounts in the Tynehead and Crossgill areas.

The occurrence of azurite on Alston Moor was reported by Phillips (1844) though no localities were given. Azurite occurs as good crystals up to 2 mm long and extensive crystalline crusts on quartz veinstone from old dumps on the Cornriggs Vein, Alston Moor (NY 7178 3724). Crystalline crusts up to 0.5 mm across also occur at Westernhope Old Mine, Weardale (NY 9196 3450). Small crystals have also been found on spoil heaps at Copper Slitts Vein, Tynehead (NY 7698 3832); Allen's Cleugh, Tynehead (NY 765 364); and at Yew Tree Mine, Stanhope (NY 9940 3536). Spherules of azurite up to 3 mm across occur in brecciated limestones of the Raisby Formation (Permian) in the old railway cutting south of Raisby Quarry, Coxhoe [NZ 350 349].

Small nodules of azurite embedded in baryte were described by Phillips (1819) from "... Durham, at Wassinghope lead mine, near Stanhope". We have been unable to identify this locality .

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

Brianyoungite was first described by Livingstone and Champness (1993) on specimens from the Wellgill Cross Vein in Brownley Hill Mine, Nenthead (NY 7762 4465). It was also identified from the Middlecleugh First Sun Vein in Smallcleugh Mine, Nenthead (NY 7877 4298), by the same authors. In both localities it occurs as small white spherules composed of minute, pointed, blade-like crystals with a pearly lustre, typically associated with crusts of gypsum of post-mining origin.

CALCITE, $CaCO_3$

Calcite is a comparatively common primary mineral in the orefield and also occurs as a supergene mineral, commonly of post-mining origin. In this paragenesis it typically occurs as stalactitic and stalagmitic deposits in many old mine workings, where it may encrust mine debris. Smythe (1926, p. 144) comments on fine encrustations of this sort on wood and iron in the baryte–witherite workings at New Brancepeth Colliery (NZ 223 420). Similar 'flowstone' deposits are common at many of the district's limestone quarries. At Tynebottom Mine, Garrigill (NY7394 4183), post-mining calcite, some in the form of hollow 'straw stalactites', is commonly bright pink owing to abundant included erythrite. Some post-mining crusts of stalagmitic calcite at Tynebottom Mine are coloured bright blue by inclusions of unidentified supergene copper minerals.

Tufa or travertine is also common around calcareous springs. Smythe (1926, p. 144) drew attention to notable occurences in Beldon Cleugh in the Devils Water valley (NY 91 50) and elsewhere. Tufa is forming today around a calcareous spring in the west end of Greenfoot Quarry, Stanhope (NY 982 392). Well preserved fossils of Quaternary insects have been described from a tufa deposit in High Hurth Edge Quarry, Langdon Beck, Teesdale (NY 865 314) (Rhodes, 1954).

CERUSSITE, $PbCO_3$

Cerussite is common throughout the orefield as the normal supergene alteration product of galena. Dunham (1990, p. 89) observes that this alteration typically develops along cleavage planes. Within the orefield cerussite occurs in a variety of forms. White to pale grey or buff crystalline coatings on oxidised galena may be seen at almost every lead mine in the orefield. He also

notes "scaly carbonate of lead" from Allenheads and "earthy carbonate of lead" from Grassfield Mine, Nenthead (NY 767 446). Cerussite is also common at very many localities as small white equant crystals, often showing complex twinning. The presence of crystals, of unspecified form, was noted by Davidson and Thomson (1951). Rashleigh (1797, plate 30, figure 2) figured a specimen of "white lead" consisting of "straw-yellow ... prisms standing parallel to each other" from "Burne Mine, Durham". This mine cannot be identified with certainty but it could be a reference to Stanhopeburn Mine. Beautiful acicular crystals, commonly forming confused 'jackstraw' aggregates, have been obtained from several mines, notably in the upper workings of Stanhopeburn Mine, Stanhope (NY 9867 4130); Redburn Mine, Rookhope (NY 928 432) (Dunham 1990, p. 89); Stotsfield Burn Mine, Rookhope (NY 9435 4238); and Burtree Pasture Mine, Cowshill (NY 8603 4133).

Dunham (1990, p. 89) notes that significant quantites of cerussite occur only on the NE slopes of Middle Fell, near Alston, most notably at Hudgill Burn Mine (NY 7506 4547), where it was worked as an ore along with galena. Despite its former abundance here we are not aware of any specimen of the mineral from this mine in a major mineralogical collection. It is thus likely that it was not normally present here as well-formed crystals. Compact crystalline grey, buff or white cerussite may today be found sparingly on the dumps. Phillips' (1819) reference to a black variety of cerussite at "Fairhill and Flow Edge in Durham" almost certainly relates to Middle Fell, Alston.

CARBONATE-CYANOTRICHITE, $Cu_4Al_2(CO_3,SO_4)(OH)_{12}.2H_2O$

A single specimen of carbonate-cyanotrichite, consisting of sky-blue spherules up to 0.5 mm across and associated with malachite on baryte, has been identified (NHM film 7431F) from the spoil heaps of Lunehead Mine, Lunedale (NY 8460 2051). This is the first record of the mineral from the Northern Pennines.

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

Hydrozincite is common throughout the orefield as white crusts of post-mining origin on the walls of old mine workings and on zinc-rich dumps (Dunham, 1990, p. 91).

Particularly good examples, comprising thick stalagmitic crusts, occur in the Middle Vein Flats at Brownley Hill Mine, Nenthead (NY 7762 4465); in flats above Carr's Level, Nenthead (NY784 433); in parts of Smallcleugh Mine, Nenthead (NY 7877 4298); and in Scraithole Mine, West Allendale (NY 8032 4694). Similar coatings may be seen in the workings of many mines throughout the district. Dunham (loc. cit.) refers to massive hydrozincite in the heavily oxidised orebodies at Hudgill Burn Mine, Alston (NY 7506 4547).

Good examples of hydrozincite are common on many of the district's mine dumps, particularly those derived from the zinc-rich deposits of the Nenthead and Alston areas. Parts of the dump immediately adjacent to the entrance to

Breckonsike Mine, Cowshill, Weardale (NY 8604 4184), are cemented into a breccia by crusts of hydrozincite apparently being deposited by zinc-rich water draining from the mine.

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

Dunham (1990, p. 90) notes that malachite, like azurite, is widespread in the orefield though generally in very small amounts. It is, however, rather more abundant in the small copper-rich Cornriggs Vein, Alston Moor (NY 7178 3724), where it occurs as earthy and crystalline crusts, mainly on quartz–chalcopyrite veinstone. It is also locally abundant at old workings on Copperslitts Vein on Windy Brow, Tynehead (NY 7696 3834), and at the nearby workings at Allen's Cleugh (NY 7650 3636). Tiny crystals have been found at Hilton Mine, near Appleby (NY 763 227) (Davidson and Thomson, 1951). In Weardale malachite is relatively common as crusts of minute acicular crystals lining cavities in 'limonitic' veinstone at Westernhope Old Mine, Westgate (NY 9200 3454). In the old railway cutting south of Raisby Quarry, Coxhoe (NZ 350 349), malachite is conspicuous as crystalline and earthy coatings in brecciated limestones of the Raisby Formation (Permian).

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

Rosasite has been reported as small turquoise-blue spherules up to 1 mm across on baryte from Closehouse Mine, Lunedale (NY 850 228) (Young et al., 1985a). Similar spherules on quartz have also been reported from West Pasture Mine, Stanhope (NY 9878 4091) (Young and Francis, 1989).

SMITHSONITE, $ZnCO_3$

Smithsonite is the most widespread supergene zinc mineral in the orefield and is common at very many localities. In places, notably on Middle Fell near Alston, smithsonite was particularly abundant and was worked, under the name of 'calamine', at several mines. In the Northern Pennines the cellular, brown 'dry bone' form is most common. Excellent examples of this can be seen at Bayle Hill Mines, Alston (NY 728 456); Hudgill Burn Mine, Alston (NY 7506 4547); old workings on the Cowslitts Veins, Nenthead (NY 786 427); Greenhurth Mine, Teesdale (NY 7792 3278); Reddycombe Mine, also known as Willyhole Mine, Teesdale (NY 8020 3355); and Stonecroft Mine, Haydon Bridge (NY 855 687). Good specimens were formerly obtainable at Silvertop Quarry, Brampton (NY 586 606). Ill-formed, rather rounded crystals, sometimes aggregated into crude mamillated crusts, occur locally at most of these localities. Smithsonite pseudomorphs after sphalerite occur at the workings on Cowslitts Veins, Nenthead (NY 728 456), and at old workings on Lough Vein, Blagill (NY 7420 4760). Pseudomorphs after small 'nail head' calcite crystals have been found at Reddycombe Mine, Teesdale (NY 8020 3355). Under the name of "carbonate of zinc" Phillips (1844, p. 568) described a "compact, fibrous, semi-transparent variety [of smithsonite] of a pale yellow colour

deposited in concentric laminae" from Alston Moor, without further locality details. Dunham (1990, p. 90) reports that massive green and yellow smithsonite was formerly obtained from the Farnberry (NY 7319 4493) and Holyfield (NY 7320 4491) Mines, Alston. Davidson and Thomson (1951) described mamillated smithsonite banded in shades of yellow and green, some with a radiating crystalline structure, from here. Beautiful mamillated masses of crystalline smithsonite from these mines, some colour-banded in shades of yellowish green and brown, are prominent in many major collections of Northern Pennine minerals. We have seen small examples of this material, referred to as 'bonamite', cut and polished as an ornamental stone.

SILICATES

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

Davidson and Thomson (1951) comment on encrustations of chrysocolla at Tynebottom Mine, Garrigill (NY 7394 4183), and Braithwaite (1982) notes its presence here in association with other supergene minerals.

Specimens of pale turquoise-blue earthy and mamillary coatings of chrysocolla on quartz–ankerite matrix occur on the spoil heaps of Westernhope Old Mine, Westgate, Weardale (NY 9196 3450). Veinlets of blue-green chrysocolla up to 5 mm wide have been found at the Murton Mines, Scordale, Appleby (NY 7613 2271) (H. Wilkinson, *personal communication*).

HEMIMORPHITE, $Zn_4Si_2O_7(OH)_2.H_2O$

Dunham (1990, p. 90) observed that throughout the orefield hemimorphite is locally associated with smithsonite. Amounts are, however, small and this mineral is strikingly less abundant in the veins of the Alston Block than in those of the Askrigg Block, where hemimorphite is commonly the principal zinc mineral in the supergene assemblage. In the Alston orefield smithsonite is the dominant zinc supergene mineral. The reasons for this difference seem not to have been explored. It is, however, worth noting that, unlike those of the Alston Block, the veins of the Askrigg area commonly occur within chert wall-rocks which, during supergene alteration, may have provided the necessary silica to form hemimorphite.

Within the district described here hemimorphite has been reported as small colourless to brown radiating crystal aggregates at Swathbeck Mine, Great Dun Fell (NY 7140 3319); Bayle Hill, Alston (NY 7285 4565); Nenthead Field mines, Nenthead (NY 7774 4374); Nentsberry mines, Nenthead (NY 7557 4804); Ashgillhead, Teesdale (NY 8083 3550); and Forster's Hush, Lunedale (NY 8556 2040) (Dunham, 1990, p. 90). The mineral also occurs as colourless to white radiating crystals, commonly encrusting fluorite, at West End Hushes, Pike Law Mines, Teesdale (NY 9000 3138), and pale brown crystalline cellular masses of hemimorphite

are locally abundant in the spoil from old workings on Black Leader Vein at Grasshill Mine, Teesdale (NY 8190 3552). Hemimorphite has also been found in small and generally inconspicuous amounts, usually associated with smithsonite, at several other sites throughout the orefield.

THAUMASITE, $Ca_3(CO_3)(SO_4)[Si(OH)_6].12H_2O$

The discovery of thaumasite as small coatings on fracture surfaces of silicified siltstone from the wall-rocks of Sedling Vein, Weardale (NY 8638 4099), is reported elsewhere in this volume (Young et al., 1998).

PHOSPHATES AND ARSENATES

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

Annabergite occurs as an alteration product of nickeline and gersdorffite in Dow Scar Level at Hilton Mine, Scordale, near Appleby (NY 763 227) (Bridges, 1982). Much of the mineral here occurs as massive or earthy coatings and fillings in cavities in heavily oxidised veinstone. However, it locally forms thin crusts with a radiating structure and more rarely it occurs as euhedral green monoclinic crystals up to 1 mm long. Specimens from here undoubtedly include some of the finest British examples of this mineral.

Young et al. (1985b) recorded thin coatings of pale green annabergite on the outer surface of nickeline–magnetite–calcite ore from the spoil heaps of Lady's Rake Mine, Upper Teesdale (NY 8063 3414). Bridges (1983) reported annabergite as a thin encrustation from the area known today as the Wheel Flats in Smallcleugh Mine, Nenthead (NY 7877 4298).

BEUDANTITE, $PbFe_3(AsO_4)(SO_4)(OH)_6$

A minute pale greenish-yellow mamillary crust from Tynebottom Mine, Garrigill (NY 7394 4183), has been shown by X-ray powder photography (NHM film 10511F) to be beudantite (I. Dossett, *personal communication*). This is the first record of beudantite from the Northern Pennines.

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

Under the name of 'cobalt bloom' erythrite was noted from Tynebottom Mine, Garrigill (NY 7394 4183) by Phillips (1844, p. 449). It was also reported by Dunham (1931). The mineral is common here, both on the dumps and in the abandoned underground workings, as pink earthy coatings and crusts on veinstone and wall-rock. Rarely it forms clear pink monoclinic crystals, which are locally aggregated to form sheaves up to 1 mm long. Dunham (1947) also noted small encrustations of erythrite in the North Side Flats associated with the Rotherhope Vein at Rotherhope Fell Mine, Alston (NY 6993 4264). Davidson and Thomson (1951) recorded rare traces of erythrite on witherite at Nentsberry Haggs Mine, Nenthead (NY 7661 4503). More recently, minute crusts of erythrite have been found in association with annabergite at Hilton Mine, Scordale near Appleby (NY

763 227) (N. Thomson, *personal communication*, 1990), and on quartz veinstone at old workings on the Crossgill Copper Vein, Garrigill (NY 739 389).

MIMETITE, $Pb_5(AsO_4)_3Cl$

Greg and Lettsom (1858) make brief reference to the presence of mimetite at "Allendale, Grasshill and Teesdale", though they give no descriptions, analyses or precise localities. We have been unable to locate any confirmed specimen of mimetite from the district. In view of Young's (1985a) observation that all of the pyromorphite samples examined during his investigaton were close to pyromorphite end-member composition, the presence of mimetite is likely to be, at best, very restricted.

OLIVENITE, $Cu_2AsO_4(OH)$

Phillips (1844) refers to olivenite from "Alston Moor" though without more specific locality details, and without any comment on the appearance of the mineral. Greg and Lettsom (1858, p. 320) refer to the mineral "in small distinct crystals, with malachite, on quartz, at Tyne Head mine, near Alston." It is not clear to which of the many workings in this area these authors are referring. A specimen showing green acicular crystals on quartz, labelled "Alston", is in the NHM collections. We have been unable to locate any more accurately localised specimen of this mineral from the district and, so far as we are aware, no specimen has been collected from the district in recent times.

PYROMORPHITE, $Pb_5(PO_4)_3Cl$

Dunham (1948, p. 113) commented on the presence of pyromorphite at Grasshill Mine, Teesdale (NY 819 355); Aglionby Beck, Alston Moor (NY 6552 3876); Closehouse Mine, Lunedale (NY 850 228); and elsewhere, but gave no descriptions or analyses of the mineral. In a review of the occurrence of pyromorphite in the orefield, Young (1985a) described the mineral from a number of localities and reported that in all cases the composition was close to the pyromorphite end-member of the pyromorphite–mimetite series.

Notable localities for pyromorphite in this district include Hard Rigg Edge, Alston Moor (the Aglionby Beck locality of Dunham, 1948; NY 6552 3876), where the mineral is abundant as green hexagonal prismatic crystals up to 2mm long forming crusts up to 10 cm across. Similar, but less extensive, crusts occur on baryte at Closehouse Mine, Lunedale (NY 850 228). At Grasshill Mine, Teesdale (NY 819 355), crystalline botryoidal and cellular masses up to 10 cm across are locally common. Similar botryoidal crusts are sparingly present at Yorkshire Silverband Mine, Teesdale (NY 8345 2736). Small amounts of pyromorphite have also been found at Silverband Mine, Great Dun Fell (NY 705 319); Gale Sike, Smittergill Head, Alston Moor (NY 672 389); Whitfield Brow Mine, Bollihope, Weardale (NZ 008 341); and Healeyfield Mine, Castleside (NZ 071 488) (Young, 1985a). Greg and Lettsom (1858) refer to the occurrence of pyromorphite in Allendale, though no localities are

mentioned. More recently, pyromorphite has been found at Hilton Mine, Scordale near Appleby (NY 763 227) (M. Wirth, *personal communication*, 1988), and Pikestone Mine, Pikestone Fell, Weardale (NZ 0535 3360).

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

In the only published reference to the presence of vivianite within the district, Birley and Young (1993) describe the mineral's occurrence in association with artifacts of Roman age. Vivianite is said to have been found in superficial deposits excavated as overburden from the ganister quarries at Harthope, Weardale (NY 865 351) (G.A.L. Johnson, *personal communication*, 1997), and traces of the mineral were reported in post-glacial clay in a trial boring at Swalwell, Tyne and Wear (NZ 2045 6246) (T. Neall, *personal communication*, 1995). No occurrence of vivianite associated with the metalliferous deposits of the orefield has been traced.

ANTIMONATES

BINDHEIMITE, $Pb_2Sb_2O_6(O,OH)$

Pale yellow powdery bindheimite, in association with highly oxidised galena and cerussite, has been identified by X-ray powder photography (NHM film 7432F) from Pike Law, Newbiggin, Teesdale (NY 902 314). This is the first record of bindheimite from the Northern Pennines. The mineral is easily overlooked, since it resembles sulphur and jarosite, and may be widespread in small amounts in well-oxidised galena throughout the field.

BOTTINOITE, $Ni[Sb(OH)_6]_2.6H_2O$

Clark and Rust (1993) reported bottinoite as light blue spherulitic aggregates up to 3 mm in diameter on galena from Brownley Hill Mine, Nenthead (NY 7762 4465).

SULPHATES

ALUMINIUM SULPHATES

Clapham and Daglish (1863) comment on the occurrence, in considerable quantities, of a soluble aluminium sulphate, containing "29.6% sulphate of alumina", at Hetton Colliery, Co. Durham (NZ 361 469). We have been unable to trace specimens of this mineral, the precise identity of which is unknown.

Smythe (1933) suggested that white powdery inclusions in a crystalline melanterite stalactite from Ushaw Moor Colliery, Durham (NZ 220 427), contained an aluminous mineral as well as possible copiapite. He refers to this as "allied in composition to alunite", with the formula $Al_2O_3.SO_3.9H_2O$, though ruling out alunite itself because the mineral in the inclusions, unlike alunite, was biaxial with a large optic angle. Alunite, $K_2Al_6(SO_4)_4(OH)_{12}$, is also ruled out by the absence of potassium, on which Smythe comments, and it is clear that "alunite" is a misprint for *aluminite*, $Al_2(SO_4)(OH)_4.7H_2O$ (= $Al_2O_3.SO_3.9H_2O$). The large optic angle and refractive

indices near 1.52 reported by Smythe correspond to those of an apparent dehydration product of aluminite mentioned by Palache *et al.* (1951, p. 600), but the true identity of Smythe's mineral remains uncertain.

ANGLESITE, $PbSO_4$

Anglesite occurs in small amounts in many localities in the area, but was never worked as an ore. Phillips' (1844, p. 551) comment that "the massive and compact varieties |of anglesite| are chiefly from Siberia, Andalusia and Alston Moor" suggests that anglesite was well-known from the district at this time and may, at least locally, have been more common then than it is today. Dunham (1990, p. 89) reports well developed crystals from old workings at Pike Law, Newbiggin, Teesdale (NY 902 314), where bladed crystals reach 15 mm in length. and from Closehouse Mine, Lunedale (NY 850 228), where crusts of bladed crystals up to 5 mm long occur on baryte and occasionally cover areas of several square centimetres. On dumps associated with trial workings on Drypry Vein, Wolsingham (NZ 0676 4327), lustrous rhombic and bladed crystals, which reach 4 mm in length, are common. Small crystals have also been found at Brownley Hill Mine, Nenthead (NY 7762 4465); Tynebottom Mine. Garrigill (NY 7394 4183); and several other localities in the orefield.

BARYTE, $BaSO_4$

Baryte is a widespread supergene mineral in the near-surface portions of deposits containing barium carbonate minerals, and in weathered dumps derived from such deposits. Supergene baryte occurs as fine-grained, sometimes rather chalky, masses, commonly with a crudely banded texture or as an open mesh of tiny crystals, and often more or less stained with iron oxides (Dunham, 1990). Such supergene baryte was present as a near-surface capping on witherite deposits such as that at South Moor (Dunham, 1990). Crusts of this material commonly surround masses of witherite or barytocalcite in spoil heaps, perhaps suggesting that at least some of this alteration may have occured within the spoil. Pseudomorphs of compact, chalky baryte after barytocalcite are common at Blagill Mine, near Alston (NY 742 473). Pseudomorphs of compact baryte after well-crystallised witherite have been observed at a number of sites.

When well-crystallised, supergene baryte is recognisable by its distinctive morphology, with sharply pointed crystals dominated by (110) and (001) faces. These are commonly intergrown in complex, rather coral-like aggregates. Such crystals may be either white and opaque or, more rarely, colourless and transparent. Good examples may be seen at most barium carbonate mineral localities. This form may indeed be a reliable indicator of the presence, or former presence, of barium carbonates, as at the highest workings on Rampgill Vein, Nenthead (NY 7984 4416) (Young, 1985b). Supergene baryte crystals exhibit the same morphology as those recovered in large quantities from cavities within the witherite oreshoots at,

e.g., Settlingstones (NY 848 687) and South Moor (NZ 175 508) mines (Dunham, 1990). In these instances, however, the crystals are commonly much larger and were found well beneath the level of present-day oxidising groundwaters. They were probably produced at a late stage during the primary mineralising process and are therefore not of supergene origin. Whether of primary or supergene origin, this distinctive morphology seems to be closely associated with the presence, or former presence, of barium carbonate minerals.

BROCHANTITE, $Cu_4SO_4(OH)_6$

Davidson and Thomson (1951) described small, lustrous crystals and botryoidal coatings of brochantite from Tynebottom Mine. Garrigill (NY 7394 4183), and Braithwaite (1982) noted its presence with numerous other supergene species. It is comparatively common here as small emerald-green crystals, usually less than 0.5 mm across, but locally aggregated into dark green crusts. Similar but less extensive crusts have been found in the Firestone Level of Groverake Mine, Rookhope (NY 896 442). Crusts of minute crystals, associated with cuprite. also occur at old workings on the Cornriggs Vein, Alston Moor (NY 7178 3724); at Crossgill. Garrigill (NY 7394 3832); and at Cashburn, Alston Moor (NY 7130 3768).

CHALCANTHITE, $CuSO_4.5H_2O$

The presence of crystals of chalcanthite, of post-mining origin, in the Firestone Incline workings of Groverake Mine. Rookhope (NY 896 442) was reported by Smith (1973) though no other details were given.

COPIAPITE, $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2.20H_2O$

On the basis of an analysis of a melanterite stalactite from Ushaw Moor Colliery, Durham (NZ 220 427), supported by an optical examination, Smythe (1933) suggested that the white powdery spots embedded in the stalactite contained copiapite, "$2Fe_2O_3.5SO_3.18H_2O$" (with some aluminium sulphate, q.v.). The precise identity of the mineral remains uncertain.

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

Devilline occurs in Tynebottom Mine, Garrigill (NY 7394 4183), as crusts of blue-green platy crystals, up to 1 mm thick and with a distinctive pearly lustre (Bridges. 1987). Traces of this mineral have also been found associated with serpierite in Smallcleugh Mine, Nenthead (NY 7877 4298).

EPSOMITE, $MgSO_4.7H_2O$

Greg and Lettsom (1858) note the occurrence of this mineral in unspecified coal mines near Newcastle upon Tyne. Clapham and Daglish (1863) comment on the occurrence, in large quantities, of needle-shaped crystals of 'Epsom salts' [epsomite] at Hetton Colliery, Co. Durham (NZ 361 469). Smythe (1933) describes epsomite as an efflorescent crust of long slender white crystals from New Brancepeth Colliery. Durham (NZ 223 420). Dunham (1990. p. 91) comments on the occurence of

epsomite as an efflorescence on the walls of old workings in the flats in Smallcleugh Mine (NY 7877 4298), where it has formed by the reaction of sulphate-rich groundwaters with ankerite. Epsomite is locally very abundant in parts of the Smallcleugh workings, commonly forming colourless acicular crystals up to 4 cm long and <0.25 mm across.

Granular efflorescences of epsomite have been found on outcrops of dolomitic limestone of the Ford Formation (Permian) on the north side of Hesledon Dene, Peterlee, Co. Durham (NZ 443 373).

FERRICOPIAPITE, $Fe^{3+}_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2.20H_2O$

Smith (1973) identified pale yellow botryoidal crusts associated with with native copper from the Firestone Incline at Groverake Mine, Rookhope (NY 896 442) as a copiapite group mineral, probably ferricopiapite.

GOSLARITE, $ZnSO_4.7H_2O$

Smythe (1933) identified nickel-bearing goslarite as an efflorescent crust of slender white crystals from the baryte–witherite workings at Ushaw Moor Colliery, Durham (NZ 220 427). Two analysed samples contained 0.06 and 0.22 wt % NiO, respectively. In describing efflorescent goslarite from here Dunham (1947, p. 48) observed that one sample showed 1.9% $NiSO_4.7H_2O$; another was nickel-free.

GYPSUM, $CaSO_4.2H_2O$

Dunham (1990, p. 91) noted the presence of secondary gypsum in 'limonite' near oxidising pyrite at the Hilton Mines, Scordale, near Appleby (NY 763 227), and as efflorescences at Brownley Hill Mine, Nenthead (NY 7762 4465); Smallcleugh Mine, Nenthead (NY 7877 4298); and Boltsburn Mine, Rookhope (NY 937 428). Good examples are to be seen today in many parts of the Nenthead mines, in Tynebottom Mine, Garrigill (NY 7394 4183), and at many other old mines throughout the district where sulphate-rich groundwaters are actively attacking calcareous wall-rocks or vein minerals. Colourless 'selenite' has been described by Davidson and Thomson (1951) from Long Fell Mine, near Brough (NY 765 196); Tynebottom Mine, Garrigill (NY 7394 4183); and Handsome Mea (Smallcleugh) Mine, Nenthead (NY 7877 4298). A few colourless crystals of 'selenite' up to 15 mm long have been found in cavities in supergene baryte on the dumps from Leadbitter Shaft, Langley Barony Mine, Haydon Bridge (NY 8260 6610). Similar crystals, forming coatings on the bedding surfaces of sandstone, have been found at Nentsberry Haggs Mine, Nenthead (NY 766 450).

White, acicular crystals and elongate twin crystals were described from Felling Colliery, Tyne and Wear (NZ 280 628), by Greg and Lettsom (1858). A fine specimen of this is in the collection of the Hancock Museum, Newcastle upon Tyne.

Thick, coral-like crusts of minute gypsum crystals are today being deposited on the Great Limestone at Crindledykes Quarry, near Bardon Mill (NY 781 671), where sulphate-rich groundwater, percolating through pyrite-rich colliery spoil filling an adjacent part of the quarry, emerges to flow over the quarry face.

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

Although jarosite is generally regarded as a common mineral in oxidised pyrite-rich mudstones and veinstones, we have been unable to trace any published reference to jarosite in the orefield, and have encountered only one positive confirmation of the mineral. X-ray powder photography (NHM film 85527F) of dull yellow earthy crusts, associated with malachite and cerussite, on quartz from the upper workings of the Yew Tree Mine, Bollihope, Weardale (NY 994 354), confirmed the mineral as jarosite. Examination of similar yellow earthy crusts, widely present throughout the area, would, no doubt, add many more occurrences of this frequently overlooked mineral.

KTENASITE, $(Cu,Zn)_5(SO_4)_2(OH)_6.6H_2O$

Livingstone (1991) described an as yet unnamed zinc analogue of ktenasite from Smallcleugh (NY 7877 4298) and Brownley Hill (NY 7762 4465) mines. Rust (1991) reported ktenasite from the Middlecleugh First Sun Vein in Smallcleugh Mine, Nenthead (NY 7877 4298), where it occurs as blue-green tabular crystals up to 0.4 mm long in association with serpierite and schulenbergite. Rust's identification was solely by X-ray diffraction. It is thus not clear whether his description is of ktenasite *sensu stricto* or the zinc-rich variant described by Livingstone.

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

Leadhillite has been found as white to colourless hexagonal prisms up to 1 mm long in small cavities in oxidised galena–baryte matrix from Closehouse Mine, Lunedale (NY 850 228) (Young *et al.*, 1994). Leadhillite also occurs as clusters of hexagonal platy crystals associated with galena and 'limonite' from workings on the Middlegrove Vein, Killhope, Upper Weardale (NY 8218 4325).

LINARITE, $PbCuSO_4(OH)_2$

Linarite is widespread in the orefield in trace quantities. Davidson and Thomson (1951) recorded it from the Top Level dump at Rotherhope Fell Mine, Alston Moor (NY 6996 4100). Braithwaite (1982) noted it from Tynebottom Mine, Garrigill (NY 7394 4183), where crystals up to 0.5 mm long occur. Young (1985a) reported it from Smittergill Head Mine, Melmerby (NY 6720 3895). Crystals up to 1.5 mm long, of post-mining origin, occur on the spoil heaps of Westernhope Old Mine, Weardale (NY 9196 3450). Minute crystals and crystalline crusts occur at Healeyfield Mine, Castleside (NZ 0689 4866), and on the dumps of a trial on the Drypry Vein, near Wolsingham (NZ 0676 4327), while traces of the mineral have been noted at several other localities in the orefield.

MELANTERITE, $FeSO_4.7H_2O$

Clapham and Daglish (1863) note the occurrence of 'copperas' [melanterite], sometimes in large quantities, at

Hetton Colliery, Co. Durham (NZ 361 469). Spencer (1910) described bright green fibrous crystalline melanterite encrusting pyrite-rich shale at New Brancepeth Colliery, Durham (NZ 223 420). Smythe (1933) described a clear green stalactite, composed mainly of melanterite, from the baryte–witherite workings of Ushaw Moor Colliery, Durham (NZ 220 427). Dunham (1990, p. 91) noted the presence of melanterite in the flats of Smallcleugh Mine, Nenthead (NY 7877 4298). It occurs at several places within the mine as masses of green to blue glassy crystals in association with oxidising pyrite.

NAMUWITE, $(Zn,Cu)_4SO_4(OH)_6.4H_2O$

Minute sea-green flat triangular crystals of namuwite up to 0.2 mm across occur in the Middlecleugh First Sun Vein, Smallcleugh Mine, Nenthead (NY 7877 4298) (Livingstone et al., 1990).

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

Livingstone et al. (1990) reported pearly blue-green trigonal crystals of schulenbergite from the Middlecleugh First Sun Vein, Smallcleugh Mine, Nenthead (NY 7877 4298). It has also been reported as a blue-green earthy encrustation from a small stope on the High Raise Vein in Nentsberry Haggs Mine (NY 7661 4503) (Rust, 1997).

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

Bridges (1987) noted the occurence of serpierite from the Middlecleugh First Sun Vein, Smallcleugh Mine, Nenthead (NY 7877 4298), and from Tynebottom Mine, Garrigill (NY 7394 4183). At both localities the serpierite occurs as crystalline crusts and radiating groups of blue lath-like crystals up to 2 mm long.

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

Braithwaite (1982) noted the occurence of wroewolfeite, as small blue needles up to 0.5 mm long in association with devilline and brochantite, from Tynebottom Mine, Garrigill (NY 7394 4183).

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BARBOSALITE, FRONDELITE AND OTHER PHOSPHATES FROM GUNHEATH CHINA CLAY PIT, ST AUSTELL, CORNWALL, ENGLAND

Nicholas J. ELTON

Tregears, Little Treviscoe, St Austell, Cornwall PL26 7QL

Several unusual iron and iron-containing phosphates occur in N or NE trending iron oxide veins in kaolinised granite at Gunheath China Clay Pit, St Austell, Cornwall. Re-examination of specimens collected around 1987 has shown the mixed valence iron phosphates barbosalite, $(Ca_{0.01}Mn_{0.07}Fe_{2.91})_{\Sigma=2.99}(PO_4)_{1.96}(OH)_{2.16}$ and frondelite $(Mn_{0.57}Ca_{0.12}Fe_{4.27})_{\Sigma=4.96}(PO_4)_{3.08}(OH)_{4.68}$ occurring in intimate association. Unit cell dimensions for the frondelite ($a = 13.960(3)$, $b = 16.874(3)$, $c = 5.169(1)$ Å) are significantly different from previously published values. Hydroxyl-chlorapatite, fluorapatite and cassiterite are also present in these specimens. In a second group of specimens, barbosalite occurs in intimate association with dufrenite, hentschelite, chalcosiderite-turquoise, fluorapatite, quartz and grains of altered stannoidite. Vesicles in the matrix contain leucophosphite and, more rarely, libethenite, torbernite and brochantite. These specimens represent the first occurrence of frondelite and chlorapatite in the British Isles, and the second of barbosalite and hentschelite.

INTRODUCTION

The Hensbarrow section of Gunheath China Clay Pit, St Austell, Cornwall (National Grid Reference SX 005571) is noted for the occurrence of uncommon iron or iron-containing phosphates (e.g. Weiss, 1994), most of which are found in iron oxide-rich NE-trending fracture veins in kaolinised granite. The majority of recorded species contain trivalent iron, indicative of oxidising conditions during formation, and include cacoxenite, chalcosiderite, cyrilovite, leucophosphite and mitridatite (Grigg, 1986; Ince, 1986; Hawkes *et al.*, 1987; Weiss, 1994). Two mixed valence iron phosphates have been recorded: dufrenite, $CaFe^{2+}_2Fe^{3+}_{10}(PO_4)_8(OH)_{12}.4H_2O$ (Weiss, 1994) and rockbridgeite, $Fe^{2+}Fe^{3+}_4(PO_4)_3(OH)_5$ (Hawkes *et al.*, 1987). Pegmatite is locally quite common in Gunheath Pit, but ferrous phosphates like triphylite and lithiophylite, which are often precursors of extensive secondary phosphate mineralisation in pegmatite phosphate deposits elsewhere, have not been recorded.

SPECIMENS

A number of specimens originally collected around 1987 from the northern part of Gunheath Pit have been re-examined. The specimens in question are complex and intimate mixtures of phosphates and sulphides. Although the gross mineralogy of the specimens is similar, they may be divided conveniently into two groups, denoted type A (two specimens) and type B (four specimens). These groups are discussed separately below. Specimens were obtained from a rib of rock separating the Gunheath and Hensbarrow china clay pits shortly before the two pits merged around 1988. Hensbarrow Pit now forms the northern extension of Gunheath Pit, and similar mineralogy to that previously found in the rock dividing the two pits can now be traced in the northern face currently exposed. Identification of individual species was carried out by EDX spectroscopy and XRD.

TYPE A SPECIMENS

Type A specimens (maximum size 50×50×20 mm) are composed largely of dull black barbosalite, $Fe^{2+}Fe^{3+}_2(PO_4)_2(OH)_2$. Inclusions and veinlets (≤0.5 mm wide) of silvery chalcocite are scattered throughout the specimen, together with grains of quartz and fluorapatite. Fig. 1 shows a backscattered electron micrograph of a polished section of type A assemblage and gives an impression of the relations between the various phases. The intergrowth of quartz, fluorapatite and barbosalite is very intimate in places. Both type A specimens also have patches of creamy-brownish horn-like hydroxyl-chlorapatite covering part of the outside of the specimen (Elton, 1997).

The barbosalite is slightly manganoan; an analysis is presented in Table I. Recalculation of analytical data on
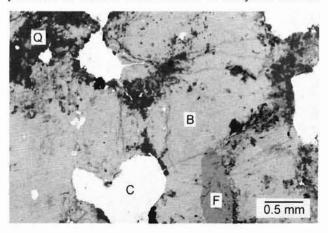

FIGURE 1. Backscattered electron micrograph of a polished section through a type A specimen, showing relations between barbosalite (**B**), fluorapatite (**F**), chalcocite (**C**) and quartz (**Q**).

the basis of 10 oxygens yields the structural formula $(Ca_{0.01}Mn_{0.07}Fe_{2.91})_{\Sigma=2.99}(PO_4)_{1.96}(OH)_{2.16}$. XRD data for Gunheath barbosalite were corrected for systematic errors using NIST SRM 675 fluorophlogopite as internal standard. Refined cell parameters are shown in Table II. The cell is slightly larger than that reported by Lindberg and Christ (1959). The presence of manganese cannot account for the difference because Lindberg and Christ's original sample was also manganoan (their sample actually contained 2.8 wt % MnO, about twice that in the present sample). Substitution of Ca^{2+} for Fe^{2+} would certainly increase unit cell dimensions, but the amount present in the sample seems too small to account for the observed differences.

TABLE I. Analytical data for barbosalite (in wt % element).

	1	2	3
Mn	0.93 (0.63–1.58)		
Fe	41.99 (40.88–42.93)	42.80	39.31
P	15.71 (15.27–16.02)	15.82	16.37
Ca	0.10 (0.00–0.26)		
O	41.27*	40.87	41.49
H	–	0.51	0.54
Total	100.00	100.00	100.00

*Oxygen by difference.
1. Barbosalite from Gunheath China Clay Pit, Cornwall (specimen from type A matrix). EDX analysis, average of 7 analyses. Beam current = 5×10^{-10} A, accelerating voltage = 25 kV.
2. Theoretical composition, $Fe_3(PO_4)_2(OH)_2$.
3. Barbosalite from Minas Gerais, Brazil (Lindberg and Pecora, 1955). Converted from normalised wt % oxides

TABLE II. Unit cell data for barbosalite (setting $P2_1/n$).

	1	2	3
a (Å)	7.306 (1)	7.308 (1)	7.25
b (Å)	7.482 (2)	7.481 (2)	7.46
c (Å)	7.396 (3)	7.398 (2)	7.35
β (°)	118.52 (2)	118.52 (1)	118.25

1. Barbosalite from Gunheath China Clay Pit (specimen from type A matrix). Data corrected for systematic errors using NIST SRM 675 internal standard. Figures of merit: M(16) = 31.4, F(16) = 27.6 (0.009, 65).
2. Barbosalite from Gunheath China Clay Pit (specimen from type B matrix). Data corrected as above. Figures of merit: M(19) = 31.3, F(19) = 30.4 (0.009, 67).
3. Data from Lindberg and Christ (1959). Transformation matrix $P2_1/c$ to $P2_1/n$: 100, 0-10, -10-1).

It proved impossible to isolate pure barbosalite for the XRD analyses and patterns frequently contained lines due to fluorapatite. In some analyses lines due to chalcosiderite, $CuFe_6(PO_4)_4(OH)_8.4H_2O$, and a phase intermediate between frondelite $Mn^{2+}Fe^{3+}_4(PO_4)_3(OH)_5$ and rockbridgeite $Fe^{2+}Fe^{3+}_4(PO_4)_3(OH)_5$ were observed. The latter mineral could not be distinguished reliably from other phases in the hand specimen or in thin section, but fortunately was sufficiently concentrated in the XRD powder mount to allow quantitative EDX analyses to be made on individual grains in a pressed pellet of this sample. The analytical results are given in Table III.

TABLE III. Analytical data for frondelite and rockbridgeite (wt % element).

	1	2	3
Mn	4.86 (3.20–6.31)	8.47	
Ca	0.77 (0.24–1.63)		
P	14.87 (13.89–15.50)	14.33	14.31
Fe	37.13 (35.69–39.04)	34.46	43.02
O	42.37*	41.96	41.90
H	–	0.72	0.71
Total	100.00	100.00	100.00

* Oxygen by difference.
1. Frondelite from Gunheath China Clay Pit. Cornwall. EDX conditions as in Table I.
2. Frondelite, theoretical composition, $MnFe_4(PO_4)_3(OH)_5$.
3. Rockbridgeite theoretical composition, $Fe_5(PO_4)_3(OH)_5$.

Recalculation on the basis of 17 oxygens yields the formula $(Mn_{0.57}Ca_{0.12}Fe_{4.27})_{\Sigma=4.96}(PO_4)_{3.08}(OH)_{4.68}$. Although it was not possible to determine the Fe^{2+}/Fe^{3+} ratio, the formula nonetheless places this mineral in the frondelite half of the frondelite–rockbridgeite series (boundary defined by $Mn^{2+} = 0.5$, $Fe^{2+} = 0.5$, $Fe^{3+} = 4.0$ atoms per formula unit).

Results of a unit cell refinement for the frondelite are given in Table IV. NIST SRM 675 was once again used as an internal standard to correct for systematic errors. The a and c cell dimensions do not lie neatly between those quoted in the literature for end-member frondelite and rockbridgeite (Table IV). In particular, a is significantly larger than previously reported for either mineral. Figures of merit give good confidence in the cell refinement. Van Wambeke (1971) notes that oxidative alteration of frondelite leads to a small increase in cell volume. The process may result in loss of Mn and conversion to rockbridgeite. The intermediate chemical composition and mode of occurrence of the Gunheath specimens is consistent with oxidative alteration, but other indicators of severe alteration such as replacement of phosphate by hydroxyl, or structural disorder, are absent. Nor can the large cell be explained by chemical substitution.

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	1	2	3	4
a (Å)	13.960(3)	13.810	13.89	13.783(12)
b (Å)	16.874(3)	16.968	17.01	16.805(9)
c (Å)	5.169(1)	5.182	5.21	5.172(4)

1. Frondelite from Gunheath China Clay Pit. NIST SRM 675 was used as internal standard to correct systematic errors. Figures of merit: M(19) = 24.6, F(19) = 26.9 (0.0118, 60).
2. Frondelite, quoted in Roberts *et al.* (1990).
3. Frondelite, data from Lindberg (1949).
4. Rockbridgeite, data from Moore (1970).

In addition to the minerals mentioned above, the barbosalite matrix also contains small grains of brown cassiterite. Minor amounts of leucophosphite are associated with the fluorapatite.

TYPE B SPECIMENS

Whereas type A specimens are composed of a solid mass of intergrown minerals, type B specimens (maximum size 35×40×20 mm) contain numerous vesicles, up to a few mm in diameter, allowing the development of minute crystals. The bulk of the specimens is composed of black barbosalite, as in type A specimens. However, grains of greenish to bluish chalcosiderite–turquoise intermediates and spherulitic masses of dull-green fibrous dufrenite contribute a significant part of the bulk composition. XRD analysis of barbosalite from type B specimens revealed also the presence of hentschelite, $CuFe^{3+}(PO_4)_2(OH)_2$, in association with chalcosiderite–turquoise and dufrenite. Examination of polished sections shows that hentschelite is a minor phase intimately associated with other phosphates (see Fig. 2). Cell parameters for barbosalite from type B specimens are virtually identical to those in type A matrix (Table II).

A characteristic of type B matrix is the presence of numerous irregular grains of bronzy-brown stannoidite (see Fig. 2). The grains typically show two concentric alteration haloes. The outermost layer is composed largely of greenish-yellow varlamoffite. The intermediate layer is grey in colour and composed of Cu, Fe, Sn and S with Cu and S dominant. This layer is typically rather granular and takes a very poor polish. Specific minerals have not been identified in this alteration halo. XRD analysis of the whole grains shows the presence of stannoidite, varlamoffite and stannite (or near). The stannoidite grains are sometimes loosely linked together in vaguely linear structures and often seem to be associated with regions of complex intergrowth of barbosalite, fluorapatite, quartz with chalcosiderite-turquoise, dufrenite and, more rarely, leucophosphite.

Dufrenite and leucophosphite commonly occur in open cavities; the dufrenite often lining the cavities with dull green spherulites. Leucophosphite appears to be the later of the two minerals and forms colourless to yellowish transparent bladed crystals, often almost filling the centres of the cavities. Leucophosphite also occurs rarely as orangy-yellow grains embedded in the matrix. The free surfaces of dufrenite spherules are sometimes covered with minute laths of chalcosiderite, which in turn may be coated with spheres of amorphous silica. Green tabular torbernite and dark green lustrous tabular crystals of libethenite are late and uncommon minerals in the cavities. The paragenetic sequence for the type B specimens seems to be: [early] barbosalite → dufrenite → leucophosphite → chalcosiderite → torbernite, silica → libethenite [late]. Where altered stannoidite borders an open cavity, tufts of bladed greenish brochantite crystals are sometimes found.

DISCUSSION

In Cornwall, rockbridgite has been recorded from Stowe's section of Wheal Phoenix, Linkinghorne (Kingsbury, 1957), Gravel Hill mine, Perranzabuloe (Weiss, 1989) and from Gunheath Pit itself (Hawkes *et al.*, 1987), but there appears to be no previous British Isles record of frondelite. Additionally, end-member rockbridgeite was shown to be a component of the discredited mineral andrewsite, also from Wheal Phoenix (Dunn, 1990). 'Andrewsite' occurred as spherulitic aggregates having cores composed of goethite and fibrous radial barbosalite with shells of fibrous to platy green hentschelite, acicular radial rockbridgeite, and minor chalcosiderite. Gunheath Pit represents the second British Isles locality for barbosalite and hentschelite. There are intriguing similarities between the secondary Cu and Fe mineralisation at Gunheath Pit and at Stowe's section of Wheal Phoenix, but little appears to have been documented about the paragenesis at the latter locality.
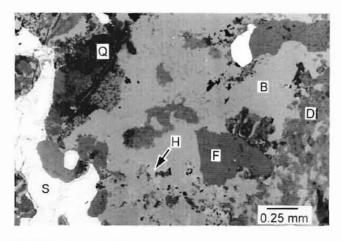

FIGURE 2. Backscattered electron micrograph showing a section through a type B specimen. The matrix is predominantly barbosalite (**B**), but with significant fluorapatite (**F**). Dufrenite (**D**) appears slightly paler than fluorapatite, but is hardly distinguishable from it. Grains of hentschelite (**H**) are paler that the barbosalite, while quartz (**Q**) appears almost black. A grain of stannoidite (**S**) is surrounded by alteration haloes of unidentified (stannite-like?) phases (appearing darker) and varlamoffite.

For the iron-containing phosphates at Gunheath Pit, the paragenetic sequence from early to late also represents a sequence of increasing Fe^{3+}/Fe^{2+} ratio. Oxidative alteration of barbosalite and of stannoidite–stannite phases has produced a sequence of alteration products in which ferrous iron is converted to ferric iron. Moreover, there is also a generally increasing degree of hydration and variety of chemistry along the paragenetic sequence. Such schemes of increasing oxidation and hydration are commonplace in phosphate deposits, especially those ocurring in pegmatites. Hydroxyl-chlorapatite is an unusual mineral for the geological environment at Gunheath, but unfortunately it cannot be placed in the paragenetic sequence with any degree of certainty (Elton, 1997).

Although the Gunheath Fe and Cu phosphates described in this paper occur in granite, they are certainly not pegmatite phosphates. According to Bristow (1993), significant iron was liberated from biotite during the first stages of argillic alteration within the St Austell granite. N–S or NE–SW trending non-tourmaline veins containing free iron oxides were formed around this time (240 Ma). Much of the iron was carried from the granite and formed significant iron lodes in the St Austell district. Sn–Cu metalliferous mineralisation occured earlier (275–270 Ma). Minor amounts of iron were also liberated during the later stages of kaolinisation (180 Ma to present) and contributed to staining of the kaolinised granite. Mesozoic deep supergene alteration and Mesozoic/Early Tertiary chemical weathering were the principal processes in the main stages of kaolinisation, and the granite underwent significant chemical changes. It is not clear how the paragenesis of the phosphate minerals relates to that of the granite or its alteration history. However, it seems likely that the action of phosphatic solutions produced during the later stages of kaolinisation on the earlier-formed N–S iron veins produced the range of Fe and Cu phosphates found today. Barbosalite and frondelite–rockbridgeite probably represent the earliest generation of these phosphates.

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SECTOR PHOSPHORESCENT GYPSUM (SELENITE) CRYSTALS FROM MEPAL BRIDGE, CAMBRIDGESHIRE, ENGLAND

Benjamin A. GRGURIC

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ.

Well-formed crystals of gypsum (var. selenite) from the Jurassic Ampthill Clay near the Mepal bridge, Cambridgeshire, show well-defined sector and zonal fluorescence in long-wavelength UV light. The fluorescence is of a pale- to lemon-yellow colour and the crystals phosphoresce bright green for 0.5 to 5 seconds following removal of the UV source. The phenomenon of sector fluorescence in gypsum is examined and the mode of occurrence and morphology of Mepal selenite is compared with occurrences from other depositional environments.

INTRODUCTION

The occurrence of well-formed crystals of the selenite variety of gypsum in clay units of southern England has long been known, and the fine specimens from the Shotover Hill, Oxfordshire, and Telsford, Wiltshire, localities are well documented in early British mineralogical literature (Phillips, 1823; Greg and Lettsom, 1858). Less well known, however, is the occurrence of similar crystals in clays in the Ely area, Cambridgeshire. In particular, the Jurassic Ampthill Clay, which is exposed at several places on the surface and in clay pits around Ely, has yielded water-clear crystals of selenite (Chatwin, 1948; Worssam and Taylor, 1969). Sharply developed individuals and twins of this mineral up to 8 cm across are included in the Whewell Gallery and the teaching collection of the Cambridge University Earth Sciences Department, all of which are labelled "Mepal Bridge, Cambridgeshire". When these specimens were collected is not documented but it has been suggested that they were exposed during the construction of the bridge across the Old Bedford River at Mepal in 1906 (G. Chinner, *personal communication*). The style of label accompanying these specimens is that used in the Sedgwick Museum during the early part of the 20th century (S. Laurie, *personal communication*), and some crystals are part of the Walker Collection acquired by the museum in 1908; both pieces of evidence being chronologically consistent with Chinner's hypothesis. A recent examination of the locality yielded no crystals in the immediate vicinity of the bridge, but specimens up to 5 cm long were recovered from exposures of the Ampthill Clay along the Old Bedford River north-east of the bridge, at National Grid Reference TL 437 815 (Fig. 1).

DESCRIPTION

The near perfection of form of the Mepal Bridge selenites in the University collection has led to their employment as teaching specimens in undergraduate crystallography practicals; their morphology corresponds to the ideal 'textbook' gypsum crystal (Figs 2a and 3). The recently
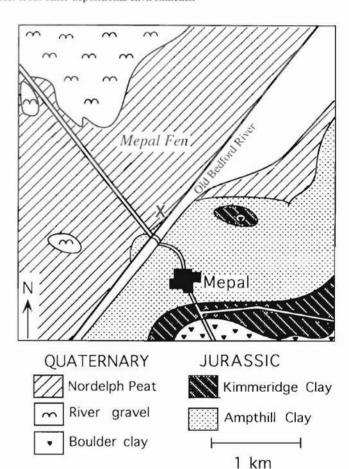

FIGURE 1. Geological sketch map of the area around Mepal (based on British Geological Survey 1:50000 map, sheet 173). Recently collected selenite crystals described here were collected in Ampthill Clay exposed near the spot marked X (at TL 437 815).

recovered crystals are essentially identical to those in the University collection, but have frosted faces on {120}, and show clearer development of fine concentric growth steps on {010} and striations on {$\bar{1}11$} (Fig. 4). These morphological differences may be the result of partial dissolution following extended exposure to rain water, rather than primary features. The form {$\bar{1}03$} is typically very poorly developed or absent. Some of the crystals collected earlier this century show this form but it is usually small and convex curved. Individuals are of more
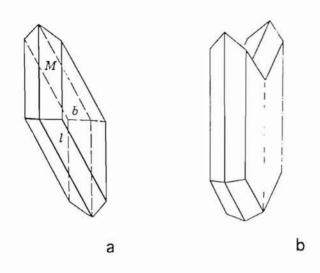
FIGURE 2. General habit of Mepal selenite. (a) Individual crystal. Forms shown are M{Ī11}, b{010}, l{120}. Rarely developed {Ī03} is not shown. (b) Idealised 'swallow-tail' contact twin on {100}.

frequent occurrence in both sets of crystals and show far better development of form than twins (Fig. 3). The twins are of the common 'swallow-tail' {100} composition plane type (Fig. 2b), prismatic, and are lacking in developed terminations. The interior of both individuals and twinned crystals is colourless and flawless, except for occasional plate-like inclusions of organic matter.

LUMINESCENCE

The most striking feature of Mepal selenite crystals is their fluorescence behaviour. In long-wave UV light the individuals exhibit two pyramidal fluorescent sectors, the basal sections of which correspond to (100) and (Ī00) (Fig. 5). This 'hour-glass' sector fluorescence is well documented in gypsum (Palache *et al.*, 1951; Kostov, 1968) and excellent examples of it are also observed in selenite crystals from Chain Lakes, Alberta, Canada (Rakovan and Waychunas, 1996). In contrast to individuals, the twinned crystals from the Mepal location show fluorescence behaviour which is either weak or not detectable. Hour-glass fluorescence in gypsum results from preferential deposition of activators on {100} surfaces (Kostov, 1968) and hence the pyramidal morphology of the sector reflects the growth history of this form. The preference for {100} may be related to the surface chemistry of these faces and/or the surface architecture which may favour the incorporation of inclusions of activators during growth. The frequent occurrence of sand and mud inclusions in these identical sectors of gypsum crystals from numerous other localities suggests that the second ('entrapment') mechanism is probably the dominant one; it is identical to that involved in the formation of zones of fluid inclusions in other minerals. In the case of Mepal selenite the nature of the activators is not known and the fluorescence colour, which varies from pale-yellow to bright lemon-yellow, is alone not diagnostic. However, the crystals also exhibit distinct green phosphorescence, and the combination suggests a hydrocarbon or other organic activator, consistent with the organic-rich appearance of the host clay. The duration of phosphorescence is typically 0.5 to 2 seconds, but some specimens exhibit spectacularly bright phosphorescence lasting up to 5 seconds. In addition to sector luminescence, the crystals also exhibit well defined zonal fluorescence/phosphorescence within the sectors, the zones being perpendicular to the growth direction. This
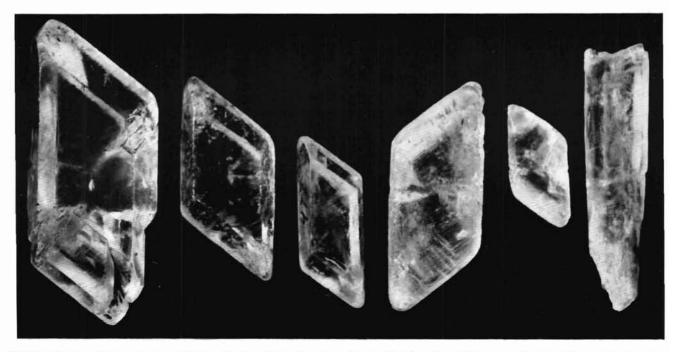

FIGURE 3. Mepal Bridge selenite crystals from the Cambridge University collection (first three from left) and recently collected crystals (last three) including swallow-tail twin (far right). Largest crystal is 6 cm in length.

FIGURE 4. Detail of a recently collected Mepal selenite crystal showing growth (or dissolution) steps on {010} and striations on {111}. Crystal is 5 cm in length.

suggests variations in the supply of activator and/or the growth rate of {100} during their formation. Interestingly, both the recently collected and the older crystals show similar zonal variation, possibly indicating coeval growth.

MODE OF FORMATION AND INFLUENCES ON MORPHOLOGY

The Mepal selenite crystals occurred loose in the dark, organic-rich Ampthill clay together with coarse shell fragments and flint pebbles, and their freedom from abrasion is consistent with growth *in situ*. The formation of gypsum in the Ampthill Clay and in similar argillaceous units such as the Oxford Clay is ascribed to the decomposition of pyrite, which liberates sulphate ions. These combine with calcium, the source of which in this case was probably the abundant shelly material, and gypsum crystals are nucleated. Free space is not required, the surrounding clay is simply displaced by the growing crystal. Growth of gypsum in clay in this manner seems to result in a higher propensity to form individuals relative to evaporitic and playa occurrences where swallow-tail twins and more random intergrowths are typically the rule. This is well illustrated in the salt-lakes of South Australia, where large selenite twins occur in abundance (England, 1982) but individuals are almost unknown. A considerable literature on the growth morphology of gypsum exists, as the subject is of interest to both sedimentologists and chemical engineers (Raju, 1983; Cody and Cody, 1988; Cody, 1991). The two parameters which are the most instrumental in the determination of gypsum crystal morphology during growth are the degree of chemical supersaturation and the presence and type of growth inhibitors (Cody and Cody, 1988; Cody, 1991).

The often high degree of supersaturation in evaporitic conditions and the rapid uptake of ions into the gypsum lattice means that crystal faces which are advantageously located with respect to nutrient supply tend to grow at the expense of less 'well located' forms, the result being distorted morphologies and a greater tendency for twins to develop. Such behaviour was observed by Donnelly (1967) in simple experiments involving the evaporation of seawater on microscope slides.

Growth inhibitors are chemical species (commonly organic) which bind to the surfaces of crystals or nuclei and inhibit the incorporation of nutrient ions into the crystal lattice (Cody, 1991). They are often face-specific by virtue of an affinity for a particular surface chemistry. This can lead to the suppression of growth on some faces, while others are less affected, and the resultant morphological changes are well documented in the case of gypsum (Cody and Cody, 1988). One extreme result of this process is the formation of the familiar 'desert-rose' clusters of lenticular crystals, also observed in baryte (Putnis *et al.*, 1995). Various types of tannic acids derived from the breakdown of plant material are believed to be instrumental as inhibitors in the case of gypsum, and the experiments of Cody and Cody (1988) illustrate the marked effect variations in the polytannate ion concentration has on the morphology of gypsum crystals grown in bentonite clay gels. On the basis of these experiments, the simple prismatic morphology of the Mepal selenites suggests a growth environment with very low concentrations of organic acid inhibitors, and temperatures of less than 15°C. The probable lower concentrations of nutrient ions compared to those in typical evaporitic environments combined with the large surface area of the host clay, would result in a lower degree of supersaturation, consistent with the crystal habits observed.
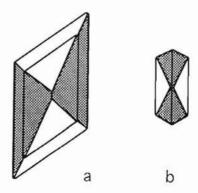
FIGURE 5. Orientation of the fluorescent sectors (stippled) in Mepal selenite, resulting in the characteristic hour-glass pattern. (a) View on (010), (b) View along c-axis.

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THE SILVER AND COBALT MINERALISATION
NEAR ALVA, CENTRAL REGION, SCOTLAND

Stephen MORETON

33 Marina Avenue, Great Sankey, Warrington, Cheshire WA5 1HY

Peder ASPEN

Department of Geology and Geophysics. University of Edinburgh, West Mains Road. Edinburgh EH9 3JF

David I. GREEN

Manchester Museum. The University, Manchester M13 9PL

Simon M. INGRAM

Pitnacree, Pitnacree Street, Alyth, Perthshire PH11 8DY

The Alva silver mine exploited a bonanza-type silver deposit, hosted by Devonian andesitic volcanics, on the southern scarp slope of the Ochil Hills, central Scotland. Examination of contemporary documentary sources has enabled details of the deposit's precise location, dimensions, tonnage and ore grade to be given for the first time. The silver ore consisted almost entirely of crystalline dendrites of the native metal, with a high (12 to 16 wt %) mercury content, which were deposited rapidly from sulphur-deficient hydrothermal solutions. Silver was the first major primary phase to be deposited, followed by Co–Ni arsenides (mostly the rare mineral clinosafflorite) and Cu–Fe sulphides. Dolomite is the principal gangue mineral associated with the metallic mineralisation, baryte is later, while calcite post-dates the major metallic and dolomite–baryte mineralisation. Alva differs mineralogically from Scotland's only other native silver mine, Hilderston, but the two are considered to be related, being associated with late-Carboniferous rifting and with nearby dolerite dykes. Alva has many mineralogical similarities with the Canadian Cobalt–Gowganda deposits.

INTRODUCTION

The silver and cobalt deposits of the Silver Glen, near Alva (Figs 1 and 2), have been the subject of a number of recent studies but as yet these have not included work on the principal ores mined (native silver and cobalt ores), or the primary paragenesis. Lack of specimens, particularly of the Ag–Co–As assemblage, has hampered previous researchers.

The silver mine was first worked in 1715 and was reopened in 1758 when a new vein carrying cobalt ores was discovered (Moreton, 1996). Some £40,000 to £50,000 worth of silver was produced (not including that stolen by the miners which was said to have been considerable) (Duncan. 1796). This represents 5 to 6 tonnes of silver metal (Moreton, 1996).

The first systematic description of the minerals present was by Heddle (1901) who listed silver, bismuth, argentite, smaltite, cobaltite, chalcopyrite, erythrite, malachite, annabergite, arsenopyrite, "black cobalt", baryte and calcite from the mines. Most of these were also listed by Wilson (1921) who gave an analysis of the cobalt ore which also contained galena. The suggestion that the silver was mined from what was later to be called the "Silver Chamber", on the east side of the stream, was first made by Francis *et al.* (1970) and repeated in subsequent publications. In 1978 the British Geological Survey

drilled a borehole to intersect the mineralised structures of the "Silver Chamber" at depth and it was suggested that the deposit was a localised swelling at the intersection of two veins (Hall *et al.*, 1982).

SITE DESCRIPTION

The principal workings visible in the Silver Glen are shown in Fig. 2. They are described by Francis *et al.* (1970), Dickie and Forster (1974), and Hall *et al.* (1982) but in each case "B", the "Silver Chamber", is said to be the main silver mine and the cobalt mine is not located. Two contemporary sources (Hamilton, 1716; Anon., undated) place the silver mine on the west bank of the stream and these, together with recent on-site excavations, show that mine "A" (National Grid Reference NS 8916 9769) is the silver mine. Its position on the west bank of the Silver Burn, the NE–SW trend of the vein, and the dimensions of the working all agree well with contemporary descriptions. Furthermore, its waste heap, the largest in the glen, has yielded hundreds of fragments of native silver together with cobalt and nickel arsenides and erythrite. Although no silver mineralisation is visible *in situ* anywhere in the glen, cobalt ores are present *in situ* in this working.
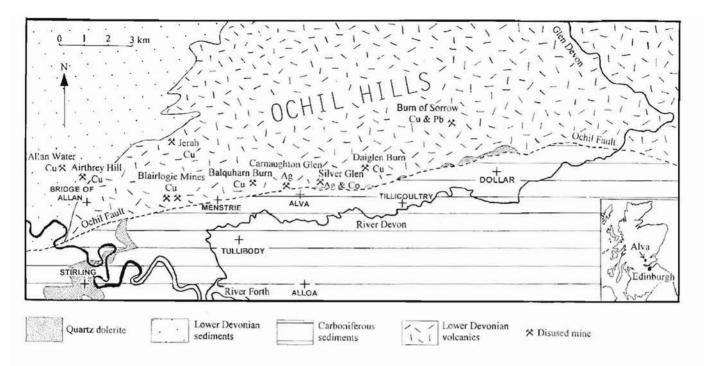
FIGURE 1. Simplified regional geology of the Ochil Hills (derived from the British Geological Survey 1:50,000 geological maps, sheets 58 and 59).

The silver was concentrated at the vein margins, particularly on the west side where, according to Brandshagen (1717), ore assaying up to 5.8 wt % silver attained a thickness of as much as 15 inches (43 cm) in a vein up to 2 feet 8 inches (82 cm) wide. The dimensions of the orebody were later given as four fathoms (7.3 m) vertically, eleven feet (3.4 m) horizontally, in a vein up to three feet (1 m) wide (Anon. miner, 1753). The top of the orebody was just 29 feet (8.8 m) below the surface (Brandshagen, 1717). Material from this orebody was unoxidised and acquired a coating of erythrite only after exposure to the weather for some time (Wright, 1760). In contrast, ore from the cobalt vein was already partially oxidised, its "peach blossom" colour being known, even in 1761, to be a result of exposure to the atmosphere (Crisp, 1761).

The cobalt mine is tentatively identified as adit "C". The earliest 1:2500 Ordnance Survey map (1862) marks this as "Cobalt Mine" while mines "A" and "B" are each marked "Silver and Cobalt Mine". The cobalt mine is known to have been located below the silver mine (Duncan, 1796), while Williamson (1764a; 1764b) relates how the cobalt vein was encountered when driving westward along another vein called "Spar vein". Adit "C" points almost due west along a small vein but is blocked after about 12 m.

MINERALOGY

METHODS

Mineral identification was based primarily on X-ray diffraction (XRD) analyses of representative specimens. Reflected light microscopy of cut and polished specimens was used as a secondary method of mineral identification, particularly for the paragenetic studies.

Polished sections were also prepared to determine species chemistry using a wavelength-dispersive analyser on a Cambridge Mk 5 electronprobe microanalyser. A range of elemental, natural and synthetic materials was used as reference standards and the analyses were performed with a probe current of 30 nA at an accelerating voltage of 20 kV. The data were processed online using a standardised ZAF correction program (Reed, 1993) and the results are expressed as elemental weight percent.

The quantitative chemistry of the mercurian silver was determined using induction-coupled plasma mass spectroscopy (ICPMS). Silver dendrites, freed as far as possible from other phases, were weighed and digested in analytical grade nitric acid. This was diluted to produce a 2 % solution which was analysed using a VG elemental ICPMS with indium as an internal standard. Standard silver and mercury solutions were used for calibration. The isotopes analysed were ^{107}Ag, ^{109}Ag, and ^{202}Hg, from which total silver and mercury were calculated from known natural abundances.

PRIMARY MINERALOGY

Silver occurs almost entirely as crystalline dendrites of the native metal. Individual dendrites up to 30 mm in length have been found, although most range from 5 to 10 mm. The individual dendrites are composed of numerous small (<1 mm) crystallites forming a three-dimensional lattice, with the axes of the lattice propagating along the (100) directions of the individual crystallites. Dendrites may be composed either of cubic crystals, bounded by {100}, or roughly octahedral crystals, some with hopper faces, bounded by {111}.

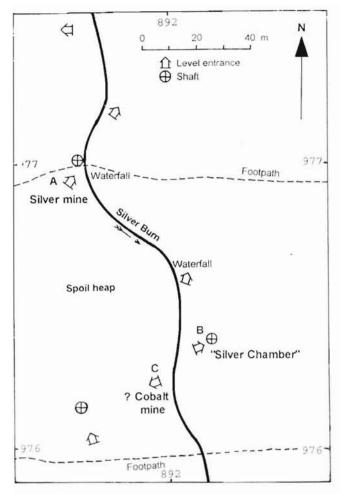Almost all the silver recovered so far consists of crystalline dendrites as described above. One tiny

FIGURE 2. The Silver Glen mine workings near Alva.

specimen of filiform silver, intimately associated with acanthite, and two specimens consisting of thin (<1 mm) films of silver intergrown with acanthite, and interstitial between plates of baryte, have also been found.

The crystalline silver is mercurian, containing between 12.6 and 16.0 wt % Hg (7.2–9.3 mol. %) (Table I). Mercury is often present in native silver and the composition of the Alva silver is comparable with early crystalline dendrites observed at Cobalt–Gowganda, for example, which contain up to about 8 wt % Hg (Petruk et al. in Berry, 1971).

Native silver is very much more abundant than any other silver-bearing phase at Alva. The only other silver minerals discovered so far are acanthite (identified by XRD), described above, and an unnamed silver–bismuth selenide included in hydrocarbon, noted by Parnell (1988).

The silver dendrites are frequently overgrown by cobalt arsenide. One specimen of this has been described as safflorite, $CoAs_2$ (Livingstone, 1993), but all the specimens examined by the authors have been identified by XRD as the rare monoclinic polymorph, clinosafflorite. In addition to forming overgrowths on the silver dendrites, clinosafflorite occurs in intimate association with chalcedonic quartz in narrow (up to 8 mm wide) grey strings, and as steel-grey to dark grey masses up to 4 cm across in dolomite or, rarely, baryte. Exposed surfaces weather quickly to erythrite.

Nickel is much less common than cobalt at Alva. The principal nickel-bearing phase is rammelsbergite which forms small (rarely >1 cm) solid masses of a bright metallic grey colour, occasionally accompanied by nickeline. Three quantitative electronprobe analyses of one sample showed it to be almost end-member $NiAs_2$ with up to 2% cobalt but with only very minor copper (<0.1%) and sulphur (<0.2%) and a trace of iron. The only other primary nickel mineral identified is maucherite, as two fragments (~1 cm size) with galena and minor silver. All the nickel minerals were identified by XRD.

The sulphide phases present at Alva are mostly of iron and copper. They are discussed in detail by Jassim (1979), who describes intergrowths of pyrrhotite, pyrite–marcasite, chalcopyrite, bornite, covellite, digenite and chalcocite. To Jassim's list we add djurleite, which occurs in a similar manner to digenite and chalcocite, and also very rare galena (XRD identifications). Reports of arsenopyrite (e.g. Heddle, 1901; Wilson, 1921; Francis et al., 1970) have not been substantiated, and no specimens are known to exist.

The gangue at Alva is predominantly dolomite, baryte and calcite, with lesser amounts of chalcedony, quartz and kaolinite. Most of the metallic ores are hosted by dolomite which is massive, crystalline and cream-coloured. The pale colour, absence of brown oxidation on weathering, and XRD pattern, which closely matches end-member dolomite, indicate that it is low in iron. The baryte is coarsely tabular, pinkish and occasionally 'cockscomb' in habit while the calcite is white to grey and, when crystallised in vugs, usually adopts the 'nailhead' habit.

Chalcedonic quartz (XRD identification) is common as cream, milky and grey strings, sometimes containing finely-divided clinosafflorite. Euhedral quartz crystals are rare, occurring as discrete, often doubly terminated, colourless individuals up to 3 mm long in cavities in dolomite and baryte, or embedded in hydrocarbon. Those in the hydrocarbon are sometimes smoky, probably because of long exposure to radiation – the hydrocarbon is uraniferous (Parnell, 1988). Quartz, sometimes amethystine, is more common in amygdales in the surrounding lavas and, although they are not thought to be directly related to the vein mineralisation, a few of these amygdales have baryte cores. Kaolinite (XRD

TABLE I. ICPMS analyses of native silver from Alva.

Sample No.	Wt % Ag	Wt % Hg	Total
1	83.6	14.7	98.3
2	81.4	16.0	97.4
3	81.2	15.5	96.7
4	86.4	13.8	100.2
5	86.7	12.6	99.3

Sb and Bi are ca 0.3 and 0.7%, respectively (semiquantitative estimates). Low totals may be due to these and to minor, adhering carbonate.

identification) occurs as a white, powdery material filling irregular cavities up to 1 cm across in vein breccia, and appears to have been formed at a relatively late stage. Blobs of hard (rarely soft) black hydrocarbon up to 2 cm long and 1 cm diameter, are common and are present in dolomite, baryte and calcite gangue. Analyses by Robinson *et al.* (1989) show they contain C_{20} to C_{42} n-alkanes.

PARAGENESIS

Our account of the primary paragenesis is based almost entirely on specimens recovered from the mine waste. The absence of good *in situ* exposures and the oxidation of the more unstable arsenides leaves some doubts as to the detailed interpretation of the paragenetic sequence, but the overall sequence of primary mineralisation is clear (Fig. 3).

Silver was the first major primary phase to be deposited. The long three-dimensional dendrites have clearly grown unrestricted in open spaces. They commonly abut wallrock and are enclosed by later phases. The observation that silver is early is corroborated by a contemporary diagram and description of Brandshagen (1717), which shows silver concentrated at the vein margins with "spar" in the centre.

The next major primary phase to be deposited was clinosafflorite, which commonly occurs in direct contact with the silver, although a thin layer of dolomite is sometimes present between the two indicating minor carbonate mineralisation at this stage. Veinlets of bornite, chalcopyrite, dolomite and the grey copper sulphides commonly cut the clinosafflorite and indicate later Cu–Fe sulphide mineralisation accompanied by hydrothermal brecciation. These, in turn, are sometimes overgrown by a later generation of clinosafflorite.
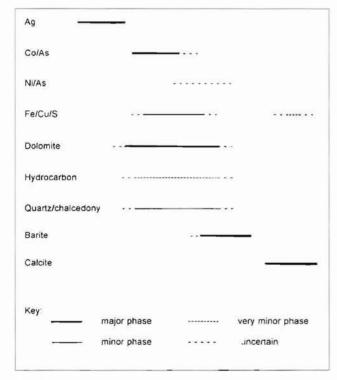
Dolomite was the first gangue mineral to crystallise. Baryte post-dates most of the dolomite and metallic mineralisation. Euhedral dolomite overgrowing baryte indicates some minor dolomite deposition after the baryte. The chalcedony and rare euhedral quartz appear to be largely contemporaneous with the early dolomite phase, extending slightly into the baryte phase.

The final primary phase was calcite. This was preceded by hydrothermal brecciation since the calcite commonly cements shattered vein material and wallrock clasts. Chalcopyrite is present in the calcite, although rarely, indicating minor late-stage copper mineralisation or remobilisation.

The absence of good matrix specimens has made the nickel arsenides difficult to place with certainty in the sequence. The presence of baryte on a few specimens suggests they are relatively late-stage phases, probably accompanying the final period of clinosafflorite deposition.

The hydrocarbon is largely contemporaneous with the early dolomite mineralisation and accompanies both copper and cobalt ores. Baryte blades sometimes cut through earlier hydrocarbon botryoids, while at other times the hydrocarbon is interstitial between the blades, showing that some hydrocarbon deposition continued into the baryte phase or was remobilised by it. The globular shape of the botryoids shows that the mineralising fluids at this stage of the mineralisation were hot enough to melt the hydrocarbon. Angular fragments of shattered hydrocarbon are frequently enclosed in late-stage calcite and show that by this time the brine temperature had dropped below the melting temperature of the hydrocarbon.

Dendritic patterns, identical in morphology to the silver, occur within the dolomite and sometimes contain corroded relict silver (Figs 4 and 5). These indicate that some of the silver subsequently dissolved. The isolated specimens of filiform and filmy silver with acanthite, the latter interstitial in baryte and therefore clearly late in the paragenesis, may represent redeposition of this silver.

The paragenesis at Alva is very similar to that at the Cobalt–Gowganda deposits in Canada. In both deposits,
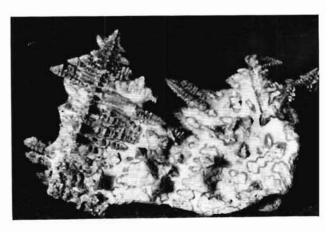
Ag	▬▬▬
Co/As	▬▬▬ ...
Ni/As	··········
Fe/Cu/S	·· ▬▬▬ ·· ·· ···· ·
Dolomite	·· ▬▬▬▬ ··
Hydrocarbon	·· ···················· ··
Quartz/chalcedony	·· ▬▬▬▬ ··
Barite	·· ▬▬▬
Calcite	▬▬▬

Key:

| ▬▬▬ | major phase | ·········· | very minor phase |
| ▬▬ | minor phase | · · · · · | uncertain |

FIGURE 3. Simplified paragenesis of the Alva silver deposit.

FIGURE 4. Silver dendrites up to 12 mm long in dolomite (which has been partly removed by acid), showing relict dendritic patterns in the matrix.
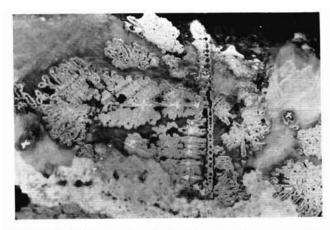
FIGURE 5. Polished section showing silver dendrites overgrown by clinosafflorite in dolomite–baryte matrix. The main silver dendrite has been largely redissolved and replaced by carbonate, but silver in the side branches remains intact. Field of view 20 mm × 30 mm

arsenides and most of the silver were deposited early, dolomite is early, and a later sulphide assemblage is present. At Cobalt–Gowganda, minor late-stage silver mineralisation is present in the sulphide assemblage as native filiform silver and as silver sulphides or sulphosalts, and this is thought to be a result of the remobilisation of the early silver (Petruk et al. in Berry, 1971). Many specimens from Cobalt–Gowganda show dendritic silver overgrown by safflorite, the silver then being partly or completely dissolved and replaced by carbonate in a manner strikingly similar to that observed at Alva.

DISCUSSION

The dendritic habit of the silver suggests rapid crystallisation in a non-equilibrium environment (Ben-Jacob and Garik, 1990), possibly from a supersaturated solution low in particulate matter. The absence of sulphides and sulphosalts in association with the silver (the Fe and Cu sulphides are later in the paragenesis) indicates that very little reduced sulphur was present in the early silver-bearing solution. Furthermore, since pyrrhotite and sulphur-poor copper minerals are present in the later sulphide assemblage, even during this later period of mineralisation, the solutions remained relatively sulphur-deficient (Jassim, 1979).

The virtual absence of filiform (and filmy) silver at Alva is significant. It has long been suspected that filiform silver is produced by the thermal or chemical alteration of earlier silver sulphide minerals. Much of the wire-silver in the Norwegian deposits, for example, appears to have formed in this way (Johnsen, 1986). Primary crystalline dendritic silver, on the other hand, is commonplace in the more sulphide-poor silver deposits such as Great Bear Lake, Cobalt–Gowganda, Wittichen and Batopilas.

Clinosafflorite, $(Co,Fe,Ni)As_2$, is known only from its type locality at Cobalt, Ontario (Radcliffe and Berry, 1971); Nord mine, Sweden (Burke and Zakrzewski, 1983); and the Bou Azzer region, Morocco (Vinogradova et al., 1980). Electronprobe microanalyses of three Alva specimens (the first two data sets being different analyses of the same sample) and published data for XRD-confirmed clinosafflorite from elsewhere are shown in Table II. In the Alva clinosafflorite, as in the Ontario type material, iron is dominant over nickel. Sulphur is typically present at a few tenths of a percent at Alva and in the Swedish and Moroccan examples. Copper has not been previously reported in clinosafflorite but is present in specimens from Alva at around 2–3 wt %. Sub-microscopic inclusions of copper sulphide seem an unlikely explanation of the high levels of copper observed. The average Cu and S contents are 2.48 and 0.22 wt %, respectively, which correspond to a molar Cu:S ratio of 5.7:1, far higher than in any natural copper sulphide. Copper, therefore, is almost certainly substituting for cobalt in the clinosafflorite lattice.

Clinosafflorite may be more common than the few records outlined above suggest. It is easily mistaken for safflorite and tends to occur intimately mixed with other cobalt arsenides, as in the Canadian and Moroccan deposits. The occurrence of large pure masses of

TABLE II. Electronprobe analyses of XRD-identified clinosafflorites from published sources compared with those of Alva specimens (wt %).

Locality & reference	Co	Ni	Fe	As	S	Cu	Total
Nord mine, Sweden (1)	27.4	0.7	0.4	70.1	0.6	n.d.	99.2
Nord mine, Sweden (1)	27.4	0.7	0.3	70.7	0.2	n.d.	99.3
Agbar, Morocco (2)	28.2	n.d.	1.7	69.7	0.1	n.d.	99.7
Ambed, Morocco (2)	28.8	n.d.	1.1	70.7	n.d.	n.d.	100.6
Cobalt, Ontario (3)	21.5	2.8	3.8	71.9	n.d.	n.d.	100.0
Cobalt, Ontario, (3)	20.7	0.3	7.0	72.0	n.d.	n.d.	100.0
Cobalt, Ontario (3)	19.8	2.5	5.6	72.0	n.d.	n.d.	99.9
Alva	23.56	0.04	3.42	71.55	0.24	1.94	100.75
Alva	23.04	0.02	3.35	71.78	0.24	2.76	101.19
Alva	23.07	0.04	2.97	71.72	0.27	2.57	100.64
Alva	21.46	0.02	3.88	72.29	0.14	2.65	100.44

n.d. = not determined.

References: (1) Burke & Zakrzewski, 1983; (2) Vinogradova et al., 1980; (3) Radcliffe & Berry, 1971, converted to wt %.

TABLE III. Comparison of Alva and Hilderston mineralogies.

Minerals	Alva	Hilderston
Silver	Crystalline Primary	Filiform Secondary(?)
Silver sulphides	Extremely rare	Common
Copper sulphides	Common	Rare
Iron sulphides	Minor	Common (pyrite)
Galena	Extremely rare	Major ore mineral
Sphalerite	Absent (1)	Minor
Mercury	Up to 16 wt % in silver; rare tiemannite	Traces of native Hg, amalgam & cinnabar (2)
Co/Ni ores	Co > Ni	Ni > Co
Barium carbonates	Absent	Common (3)

(1) Absent from the silver deposit but has been found in drill core nearby (Hall *et al.*, 1982).
(2) Meikle (1994), no data available for the Hg content of the silver.
(3) Meikle (1994), witherite and barytocalcite.

clinosafflorite, as seen at Alva, is unusual.

The relatively close proximity of Alva to Scotland's only other (native) silver mine at Hilderston, 25 km to the SSE (Meikle, 1994; Stephenson *et al.*, 1983), begs a comparison of the two deposits. At Hilderston, barium carbonate minerals (witherite and barytocalcite) are common, acanthite is one of the principal silver minerals. and traces of mercury occur both as the native metal and as cinnabar. Table III summarises similarities and differences in the mineralogy of the two deposits. Hilderston is much richer in sulphides; indeed, the silver itself may have been originally deposited as sulphide and subsequently converted to the native metal, as suggested by its filiform habit. The wallrock lithologies also differ. The Hilderston deposit is developed in Carboniferous sediments while the Alva deposit is a vein cutting Devonian andesitic lava in a sequence of lavas, tuffs and agglomerates (Hall *et al.*, 1982).

Nevertheless, the deposits are almost certainly related. both being of similar age, close to quartz-dolerite dykes, and developed in a rifting environment as discussed below. Detailed mineralogical differences may be attributable to compositional differences in the host rocks which are sulphide- and carbonate-rich at Hilderston, but sulphide- and carbonate-poor at Alva.

The Hilderston silver vein is adjacent to a Late Carboniferous (Stephanian) quartz-dolerite dyke which has been extensively hydrothermally altered (Stephenson *et al.*, 1983). There is a quartz-dolerite dyke 130 m south of the silver mine at Alva, which also exhibits evidence of hydrothermal alteration (Jassim, 1979). The age of this dyke (295 Ma) is similar to K/Ar ages of wallrock clays in the silver mine (264–299 Ma) (Ineson and Mitchell, 1974). The association of Stephanian dykes with mineral deposits in central Scotland has been discussed by Russell (1985). Jassim *et al.* (1983), and Parnell and Swainbank (1984). The baryte veins at Muirshiel, Gasswater and Kaim, and minor galena occurrences in Fife and Lothian, are in proximity to quartz-dolerite dykes. A geochemical copper

and silver anomaly at Glanderston, Aberdeenshire, is also close to such a dyke (Chung, 1991). However, the dykes certainly cannot be invoked to explain the genesis of all known deposits as many mineral deposits in the Ochils, particularly the copper–baryte veins, are well removed from known quartz–dolerite intrusions (e.g. Francis *et al.*, 1970; Dickie and Forster, 1974). Minor silver occurrences at Airthrey (NS 81 97), Carnaughton Glen (NS 878 975), and the Burn of Care above Dollar (NS 962 997), also do not appear to be related to intrusions. More importantly, an occurrence of silver with cobalt ores at Daiglen Burn mine (Heddle, 1901) is removed from any known mafic intrusion.

Most of the known mineral veins in the Ochils lie within a few kilometers of the Ochil fault, on its north side, in a belt stretching for some 17 km from west to east. This suggests a relationship with the fault but it could also be argued that it is simply a result of better exposure on the steep scarp slope compared with the drift-covered areas to the north and south. The discovery of fragments of dendritic mercurian silver in streams (Thorter and Chapel Burns) to the east of Glen Devon (Brian Jackson, Royal Museum of Scotland, *personal communication*) supports the latter argument and provides direct evidence that silver veins await discovery further north in the Ochils.

The Alva and Hilderston silver deposits belong to a world-wide class of deposits which are described as five-element (Ag–Co–Ni–As–Bi) type. Traditionally, attempts have been made to associate five-element assemblages with nearby intrusions. Thus the Canadian Cobalt–Gowganda deposits have been linked to the Nipissing diabase (Berry, 1971), the Great Bear Lake veins with felsic intrusions (Andrews, 1986), and the Thunder Bay deposits with diabase and gabbro (Franklin *et al.*, 1986). Others, however, are related to granitic intrusions or have no obvious igneous association at all (Andrews *et al.*, 1986).

The ores at Cobalt–Gowganda were deposited after the diabase had cooled and the sulphur and lead isotope signatures of this and other five-element deposits, such as Great Bear Lake, Thunder Bay and Black Hawk (New Mexico), are not consistent with a magmatic origin (Kissin, 1988). Sulphur isotope studies at Alva also suggest a groundwater source for the sulphate in the baryte (and rule out Carboniferous seawater or magmatic fluids) (Jassim *et al.*, 1983). Robinson *et al.* (1989) showed the Alva hydrocarbons to be similar in composition to those in the Carboniferous rocks to the south suggesting that some, at least, of the mineralising fluids originated in or passed through these rocks. It may also be argued that the hydrothermal alteration of the dykes associated with the Alva and Hilderston deposits indicates that they were already solidified and cool enough for water to hydrate their constituent minerals by the time the hydrothermal activity occurred. This would make them seem poor candidates as either heat or fluid sources.

What role intrusions play in the mineralisation is, therefore, unclear and their proximity to ore deposits may be misleading. At Cobalt–Gowganda they appear to have

had a structural rather than a genetic role, the shrinkage stresses caused by the cooling of the intrusions generating a fracture system which was exploited by later mineralising fluids (Jambor in Berry, 1971). In view of the discussion above, this may also be the case at Alva and Hilderston.

A more significant genetic relationship is with rifting and basinal subsidence. This has been described by various authors, including Andrews (1986) in relation to Cobalt–Gowganda and Great Bear Lake, and Kissin (1988) who, in addition to discussing these two areas, also pointed out the association of the Thunder Bay district with the Keweenawan rift; Black Hawk with the Rio Grande rift; Kongsberg with the Oslo Graben; Wittichen, Nieder-Ramstadt and Ramsbeck with the Rhine Graben; and the Erzgebirge with late Triassic rifting. According to this theory, it is the increased heat flow associated with rifting, rather than the cooling of intrusions, which mobilises the connate brines and meteoric waters that in turn give rise to five element veins.

Late Carboniferous (Stephanian) rifting in northern Britain is evidenced by the extensive quartz-dolerite dyke swarm of that period (Smythe et al., 1995). The dykes follow an arcuate trend from the Western Isles through central Scotland and northern England. Alva and Hilderston are located in areas where the dyke swarm is particularly dense. The Oslo Graben, which is similar in age, is located along the eastward extension of the swarm and shares its overall trend (Smythe et al., 1995). This suggests that the Scottish and Norwegian silver deposits, which are also of a similar age, might owe their origin to the same geotectonic event. Furthermore, we suggest the whole of the Scottish mineral subprovince (Russell, 1985) ought to be regarded as favourable to similar five-element type deposits, which do not generally occur in isolation.

It may be of use for others researching the Alva and Hilderston deposits to know that, in addition to specimens in the Royal Museum of Scotland, a large suite of ore specimens from both Alva and Hilderston mines are preserved in Manchester Museum (accession numbers N12791 to N12810 and N13074 to N13099), and in the Cockburn Museum, Edinburgh University.

CONCLUSIONS

The true location of the silver mine is "A" on Fig. 2 and not the "Silver Chamber" as was previously thought. Almost all the silver was deposited at an early stage from supersaturated sulphur-deficient solutions as crystalline dendrites of the native metal. Subsequent primary mineralisation includes Cu–Fe sulphides and Co–Ni arsenides, the deposition of which was accompanied by hydrothermal brecciation. Dolomite is the principal gangue mineral associated with these assemblages, baryte comes later, and a final mineralising event is associated with calcite deposition and further hydrothermal brecciation.

Alva differs mineralogically from Hilderston, Scotland's

only other (native) silver mine, having instead strong mineralogical affinities with the Canadian Cobalt–Gowganda veins. Nevertheless, it is almost certainly genetically related to Hilderston, and possibly to Kongsberg, as all these deposits formed at about the same time in a similar rifting environment. The apparent association of both Scottish deposits with hydrothermally altered basic intrusions is intriguing. On balance, the evidence suggests that shrinkage stresses as the intrusions cooled formed conduits for mineralising solutions generated in the surrounding rocks at a time characterised by rifting and high heat flow. However, a magmatic contribution to the mineralisation cannot yet be entirely ruled out.

Alva is the most significant deposit of its kind known in the British Isles and is notable for the particularly well crystallised dendritic nature of the silver and the relative abundance of the rare mineral clinosafflorite. The likelihood of further bonanza-type five-element deposits occurring in central Scotland, particularly in the Ochils, must be regarded as high.

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Abbreviations: f. = folio; MSS = Manuscripts; NLS = National Library of Scotland; PRO = Public Records Office, Kew.

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HARMOTOME FROM BROWNLEY HILL MINE, NENTHEAD, CUMBRIA, ENGLAND

David I. GREEN and John R. NUDDS

Manchester Museum, The University, Manchester M13 9PL.

Harmotome occurs as small prismatic Marburg twin crystals in a large quartz-lined cavity in metasomatised Great Limestone (Namurian) adjacent to the Brownley Hill vein, Brownley Hill mine, Nenthead, Cumbria. In common with other occurrences in the Pennines, it is a late-stage primary vein mineral. Its cationic composition is variable, and many of the crystals are partly altered to baryte. Evidence is presented which suggests that the baryte pseudomorphs were formed by post-mining oxidation processes involving reaction with an acid, sulphate-rich, barium-poor solution.

INTRODUCTION

Harmotome, $(Ba,K)_{1-2}(Si,Al)_8O_{16}.6H_2O$, is the only zeolite group mineral which has been recorded in the vein assemblages of the Northern Pennine Orefield. It was first discovered in the 1930s by Sir Arthur Russell at the Settlingstones and Stonecroft mines near Hexham, Northumberland (Dunham, 1948). Two further Northumbrian localities, Wellhope Shaft at Nentsberry Haggs mine and Maughan's Shaft at Greyside mine, have since been reported (Young and Bridges, 1984). To these we add a fifth locality, Brownley Hill mine, Nenthead, Cumbria.

EXPERIMENTAL TECHNIQUES

The species described were identified by X-ray diffractometry (XRD). However, since harmotome and phillipsite have the same aluminosilicate framework and only differ in the exchangeable cations present in their structure, identifications based solely on XRD data are open to question (Tschernich, 1992). The quantitative chemistry of a number of crystal fragments was therefore determined by energy-dispersive X-ray spectroscopy (EDS) as a check on the XRD results.

Fragments of material for XRD were ground, mixed with an organic solvent, and applied in suspension to a glass slide. Evaporation of the solvent left a thin uniform layer on the slide. This was mounted in a Philips diffractometer, exposed to X-rays (CuKα radiation, 40kV, 20mA), and the diffraction pattern recorded from 5° to 60° in 2θ. The patterns were digitised and analysed using Phillips PAXRD software.

For EDS analysis, crystal fragments were embedded in resin, polished to produced a suitable flat surface, and carbon-coated. They were placed on a cold stage in a JEOL JSM-6400 scanning electron microscope and cooled to −190°C to reduce surface degradation under the electron beam. Analyses were made using a 1.5 nA beam current for 30s. The weight percent of oxides present in the crystals was calculated following a standard ZAF correction and converted to a formula based on 32 (structural) oxygen atoms.

GEOLOGY

Brownley Hill mine is located on the northern edge of Alston Moor, about 1 km west of the village of Nenthead (National Grid Reference NY 7762 4465). It produced lead and zinc ore from veins hosted by Viséan and Namurian limestones and sandstones, and from metasomatic replacement flats which are locally present within the Great Limestone (Namurian). Most of the workings lie within a zinc-rich intermediate zone, with an ankerite–calcite–quartz gangue, which lies between the barium and fluorite zones of the Northern Pennine Orefield (Dunham, 1934). However, barium minerals (primarily baryte) dominate on parts of High Cross vein and West High Cross vein, and fluorite is abundant on Jug vein.

Harmotome occurs with other minerals in a large quartz-lined cavity, 5.5 m above the base of the Great Limestone, adjacent to the Brownley Hill vein. The surrounding limestone is black, fine grained, and siliceous; although it appears micritic, dissolution in dilute hydrochloric acid shows that it contains very little clay. The fourth minor cycle of the Four Fathom Cyclothem (Johnson and Nudds, 1996) underlies the Great Limestone. It comprises a light grey, micaceous siltstone, with a minimum thickness of 2 m, which is overlain by 0.25 m of a dark grey, medium-grained, silicified sandstone containing crinoid columnals.

The harmotome cavity is a prolate ellipsoid, with its major axis elongated NE–SW, parallel to the strike of the Brownley Hill vein. It extends approximately 1.8 m into the limestone wallrock. The cavity is lined with several generations of coarsely crystalline to drusy quartz, which is typically 10 to 20 cm in overall thickness. The first generation of quartz comprises large (up to 4 cm) simple pyramidal crystals. These are overgrown by at least two further generations comprising smaller drusy crystals and minor chalcedony. The different generations of quartz are separated by interconnected gaps a few millimetres wide in which harmotome and other minerals occur. The presence of occasional tabular epimorphs within the quartz suggests that baryte crystals were present in the cavity at an early stage and it may be that baryte originally occupied the spaces between the different generations of quartz. However, no primary baryte was collected from either the

cavity or nearby exposures of the vein.

Harmotome occurs as elongated Marburg twins, up to 1.5 mm long, associated with sugary quartz and occasionally surrounded by a dark grey clay mineral. The surfaces of many of the crystals have been partly altered to baryte (Fig. 1), and in some cases the original harmotome has completely dissolved leaving a thin-walled baryte epimorph. Acute etched calcite rhombs are occasionally present on the unaltered harmotome crystals, whereas jarosite, rarely serpierite, and thin-walled epimorphs of an as yet unidentified mineral after calcite are associated with the more highly altered specimens.

DISCUSSION

The chemistry of six relatively unaltered crystal fragments of harmotome was determined by EDS analysis with the results summarised in Table I. The chemical compositions were determined at positions well removed from the outer edges of the crystals, and no sulphur (which would indicate partial replacement by baryte) was detected in any of the quoted analyses. A complete cationic series extends between harmotome and phillipsite, with crystals containing more than 50 mol. % barium being defined as harmotome. Since barium is the dominant cation in all but one of the analyses in Table I, most specimens can be described as harmotome. Specimen H2 contains less than 50 mol. % barium, and is a barium-rich phillipsite (Gottardi and Galli, 1985; Tschernich, 1992).

The variability in the cationic composition of the harmotome (Table I) might reflect an inherent variability

FIGURE 1. Elongated prismatic harmotome crystals up to 1.2mm long with their surfaces altered to baryte, Brownley Hill Mine.
Manchester Museum specimen (MANCH:N11932)

TABLE I. Chemical formulae of fragments of harmotome from Brownley Hill mine calculated on the basis of 32 (structural) oxygen atoms.

Specimen No.	Chemical formula
H1	$Ba_{1.99}Na_{0.71}Ca_{0.00}K_{0.04}[Si_{11.24}Al_{4.64}O_{32}].xH_2O$
H2	$Ba_{1.21}Na_{1.19}Ca_{0.16}K_{0.55}[Si_{11.34}Al_{4.44}O_{32}].xH_2O$
H3	$Ba_{2.07}Na_{0.44}Ca_{0.06}K_{0.10}[Si_{11.47}Al_{4.41}O_{32}].xH_2O$
H4	$Ba_{1.94}Na_{0.54}Ca_{0.43}K_{0.00}[Si_{11.45}Al_{4.45}O_{32}].xH_2O$
H5	$Ba_{1.93}Na_{0.66}Ca_{0.00}K_{0.10}[Si_{11.35}Al_{4.53}O_{32}].xH_2O$
H6	$Ba_{2.01}Na_{0.67}Ca_{0.00}K_{0.04}[Si_{11.25}Al_{4.70}O_{32}].xH_2O$

in the composition of the solution from which it crystallised, although this seems unlikely in a single cavity where all of the harmotome crystallised at the same stage late in the primary paragenesis. Bearing in mind the ease with which ion exchange occurs in zeolites it seems more likely that the cationic composition of the crystals changed as a result of interactions with the solutions which altered the harmotome to baryte.

Although the cationic composition of the harmotome is variable, the composition of its aluminosilicate framework is fairly uniform. The value of $T_{Si} = Si/(Si + Al)$, which is a measure of the Si:Al ratio in the zeolite framework, varies between 0.705 and 0.722. This is similar to values determined for harmotome from localities worldwide (Tschernich, 1992). Analyses of the surface layers of the relatively unaltered fragments H1–H6 show the presence of sulphur at up to 5 wt %. Furthermore, whereas chemical analyses of the cores of the harmotome crystals are in good quantitative agreement with accepted data (e.g. Gottardi and Galli, 1985), analyses of the altered surface layers give low totals of the wt% oxides, suggesting the presence of voids in their structure.

In common with its other occurrences in the northern Pennines, the harmotome from Brownley Hill mine is a minor late-stage primary mineral. At most other Pennine localities however, harmotome occurs in veins in dolerite and is associated with major primary barium mineralisation (Young and Bridges, 1984). Its occurrence is consistent with formation by the interaction of remnant barium-rich hydrothermal fluids with silicate minerals in the dolerite.

The harmotome-bearing cavity at Brownley Hill mine is unusual since it occurs in limestone, and primary barium minerals are absent from the local area. However, the locality is very near the inner edge of the barium zone of the orefield, and according to Dunham (1990) the continuation of the Brownley Hill vein in Scraithole mine has a barium gangue. It seems likely that the barium-rich fluids from which the Brownley Hill mine harmotome crystallised were produced by dissolution of primary baryte, which was originally present, as evidenced by characteristic tabular epimorphs in the quartz. Quartz and clay minerals were deposited at the same time as the harmotome, indicating that the mineralising solutions were also rich in silica and aluminium, which may have been leached from the underlying siliciclastic rocks.

Much of the harmotome is partly altered to baryte, which in turn is occasionally overgrown by jarosite, or rarely by serpierite, minerals which commonly crystallise from acid sulphate-rich solutions during the post-mining oxidation of sulphide orebodies. The presence of jarosite on the surface some of the more altered harmotome crystals is an indicator of acid (pH <2.5) and highly oxidising conditions (Bauer and Velde, 1997). It shows that acid, oxidising solutions affected some parts of the cavity prior to the collection of the specimens.

Baryte often forms late-stage pseudomorphs after other barium minerals such as alstonite, barytocalcite and witherite in the veins northwest of Nenthead. It is also occasionally found in post-mining assemblages, most obviously as a white powdery coating on witherite in mine dumps (Trevor Bridges, *personal communication*). We propose that the baryte pseudomorphs after harmotome were formed by post-mining oxidation. The low totals obtained during chemical analyses show that they contain voids, suggesting that the supply of barium was local and limited. Furthermore, the pseudomorphs are structurally very different to the late-stage secondary baryte pseudomorphs from the Nenthead area, which are typically composed of interlocking masses of small distinct *euhedral* crystals. Even when examined at high magnification under the scanning electron microscope, the Brownley Hill pseudomorphs show no crystal structure, and the baryte is clearly very finely divided. Finely divided barium sulphate forms when barium- and sulphate-rich solutions come into contact at low temperatures, and might be expected during post-mining oxidation (the reaction is the basis of the standard chemical test for sulphate anions).

In an attempt to mimic the alteration process experimentally, unaltered harmotome crystal fragments were placed in sulphuric acid. If the acid was concentrated (pH <1) the harmotome dissolved rapidly; dilute acid (pH >4) had no discernible effect; but at intermediate concentrations the acid attacked the harmotome along cleavage planes over a period of several weeks. Although there was no immediate alteration to baryte. partly altered crystals coated with opaque white powdery $BaSO_4$ (identified by EDAX analysis), similar to those described above, were present when the acid evaporated.

The presence of jarosite as a coating on the harmotome pseudomorphs shows that they have been exposed to acid (pH <2.5), oxidising, sulphate-rich solutions. Such solutions are commonly generated by the post-mining oxidation of sulphide minerals. The absence of large amounts of carbonate in the quartz cavity would allow the local pH to drop to an abnormally low value for a limestone host. Our experimental work shows that harmotome alters to baryte when exposed to acid sulphate-rich solutions at a pH near to 2.5. Reaction with a post-mining, acid, sulphate-rich but barium-poor solution would account for the presence of voids in the pseudomorphs, due to the differing densities of harmotome and baryte. and also for their structure, as finely divided $BaSO_4$ is precipitated in these conditions. It would also account for the absence of baryte in the cavity, except as a *pseudomorph* after harmotome, since harmotome would be the sole source of barium. It seems likely, therefore, that post-mining oxidation processes produced the baryte pseudomorphs after harmotome.

SUMMARY

Harmotome occurs as prismatic crystals up to 1.5 mm long in a large quartz-lined cavity in metasomatised Great Limestone (Namurian) at Brownley Hill mine. In common with other Pennine occurrences it is a late-stage primary mineral. The Brownley Hill locality differs from other Pennine occurrences in that harmotome is not associated with major primary barium mineralisation, although there is evidence to suggest that primary baryte was present within the cavity prior to the formation of harmotome. Much of the harmotome is pseudomorphed by barite. A simple mechanism for the formation of the pseudomorphs involving the reaction of harmotome with acid, sulphate-rich, barium-poor solutions in the post-mining environment is proposed. Post-mining oxidation processes also account for the presence of jarosite, serpierite and gypsum.

A suite of specimens from the cavity is preserved in the Manchester Museum, (accession numbers MANCH: N11930 to N11939).

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NOTES

VALENTINITE FROM THE ISLE OF MAN

Roy E. STARKEY

15 Warwick Avenue, Bromsgrove, Worcestershire B60 2AH

There are relatively few antimony deposits in Britain. Russell (1949) lists some 40 occurrences of antimony minerals, most of them small. The best known are several mines around St Endellion, on the north coast of Cornwall; Wheal Emily near Wembury in Devon; Bwlch mine near Conway in north Wales; Robin Hood mine, Bassenthwaite, Cumbria; and, in Scotland, Glendinning Mine near Langholm, Dumfriesshire, and Knipes mine near New Cumnock, Ayrshire. More recently, Fortey *et al.* (1984) have described antimony mineralisation at Wet Swine Gill, Caldbeck Fells, Cumbria. In the Isle of Man, Russell (1949) lists two localities for antimony minerals.

Smyth (1880) described in considerable detail an occurrence of "plumosite" (plumose boulangerite) from Foxdale mine, Isle of Man. The mineral was associated with fine-grained galena, and a vughy or cellular quartz with many transparent crystals. The "plumosite" occupied vughs, seldom filling them entirely, and resembled a multitude of metallic-lustred hairs. confusedly flung together. Specimens of this material are preserved in the Natural History Museum, London. The only other antimony mineral recorded from Foxdale mine is argentian tetrahedrite ("polytelite") (Forbes, 1867, p. 350).

Less well known is the small occurrence of stibnite at Niarbyl mine, near Dalby. Greg and Lettsom (1858) record the occurrence of stibnite "sparingly, about ten years ago, at Dalby", and this locality is also mentioned by Lamplugh (1903). A trial made on the westward extension of the Foxdale lode encountered a small body of antimony ore in the mid-19th century. As it was subsequently believed that more of this ore might have been obtained, had it been considered to be worth working at the time of discovery, an adit was driven in 1893–94 eastwards into the cliff at Traie Vrish (National Grid Reference SC 214 774), 360 metres SE of The Niarbyl. Unfortunately, this exploration served only to prove that the orebody had been merely a small pocket, which had been entirely cut out in the previous workings (Lamplugh, 1903).

Specimens of stibnite may still be collected from the shore at Traie Vrish, and several sizeable waterworn boulders have been examined by the author. The small spoilheap at the foot of the cliff outside the flooded, but still open. adit is largely barren and consists mainly of fragments of shale with a little quartz, and carbonate veinstone. It should be noted that the small bay in which Traie Vrish lies is completely cut off at high tide, and

access can then only be made down a steep grass slope from the cliff-top path, descending at the southern end of the inlet.

Stibnite occurs here as coarsely crystallised grey metallic blades, associated with crystals of pyrite up to 5 mm across, in a grey quartz matrix. Masses up to several kilograms in weight and over 25 cm across have been collected. Isolated acicular microcrystals and strings of stibnite in quartz also occur, typically up to 2 mm in length and less than 0.1 mm across.

Valentinite occurs as distinctive colourless to white radiating acicular crystals and as spherical crystal aggregates up to 2 mm in diameter. It is associated with yellow-brown staining (antimony ochres?) and patches of a red mineral which are scattered throughout the quartz–stibnite vein material. At other British localities, similar red patches have been called kermesite, though in no case has the presence of kermesite been confirmed by subsequent XRD examination (Macpherson and Livingstone, 1982; Bevins *et al.*, 1988). It is clear from specimens examined that the vein was locally extremely rich in stibnite. but alteration to valentinite is restricted to small cavities and fracture surfaces.

Valentinite. the orthorhombic polymorph of Sb_2O_3. is one of the oxidation products of antimony ores, and was first listed from the British Isles by Hall (1868), at Glendinning mine, Dumfriesshire (see also Heddle, 1901). According to Collins (1871), valentinite "is said to have occurred in white, fibrous, and radiated masses, with other antimony ores, at Lee, near Callington" in Cornwall. Golley and Williams (1995) list five Cornish localities for valentinite and Young (1987) gives two localities in the Lake District, Cumbria. It is also recorded from Knipes mine, Ayrshire (Williams, 1965).

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ANTIMONIAN CLAUDETITE FROM WET SWINE GILL, CALDBECK FELLS, CUMBRIA, ENGLAND

C. Mike LEPPINGTON
1 Harrot Hill, Cockermouth, Cumbria, CA13 0BL

David I. GREEN
Manchester Museum, The University, Manchester M13 9PL

Claudetite, the monoclinic polymorph of As_2O_3, is a rare mineral which forms as a sublimation product near fumaroles in volcanic areas and during the supergene oxidation of arsenic-bearing mineral assemblages. Its artificial analogue is occasionally reported as a sublimation product following fires in coal or metal mines. The only British report of claudetite is from Huel Sparnon, Redruth, Cornwall (Hintze, 1904), but since no determinative data were provided, and the original specimens have not been located, this record is in need of confirmation (Macpherson, 1983; Golley and Williams, 1995).

The quartz–antimony vein at Wet Swine Gill (National Grid Rreference NY 3144 3215) in the Caldbeck Fells, Cumbria, was first described by Fortey *et al.* (1984). The vein contains an early antimony–iron–arsenic primary assemblage (comprising stibnite, berthierite and arsenopyrite) and a later antimony–lead assemblage (including zinkenite, fülöppite and semseyite) in massive white quartz. Supergene minerals, including bindheimite, senarmontite, stibiconite and sulphur, occur in small quartz-lined cavities and fractures within the vein. They generally form small inconspicuous crystals, although abundant yellow crusts of bindheimite were present at outcrop when the vein was discovered.

Claudetite occurs as colourless to white thin-tabular crystals up to 3 mm long (Fig. 1) and as foliated masses up to 5 mm across in cavities in vein-quartz. The crystals resemble gypsum in appearance, with a well developed cleavage on (010) and a similar monoclinic habit, but can

FIGURE 1. Claudetite, transparent monoclinic crystals up to 2.75 mm long, from Wet Swine Gill, Cumbria. Mike Leppington collection; photo by David Green

be distinguished by their resinous lustre. They are early in the supergene paragenesis and are commonly associated with transparent octahedral senarmontite and, rarely, with sulphur, both of which appear to be later than the claudetite.

Claudetite was identified by X-ray diffractometry at Manchester University (X-ray MANCH:XRD355). The X-ray identification was supported by a quantitative chemical analysis by energy dispersive X-ray spectroscopy, which gave a formula near $As_{1.2}Sb_{0.8}O_3$. The substitution of a large amount of antimony for arsenic

in claudetite has not been reported previously. The only published analysis of claudetite we have been able to locate, dating from 1903 and quoted in Palache *et al.* (1944) and Anthony *et al.* (1997), is very near to the ideal formula, As_2O_3. It is an average of two analyses made on specimens from Smolník, Slovakia, which were formed during a mine fire (and which should therefore be considered artificial). The genesis of the Slovakian specimens is clearly different to the specimens from Wet Swine Gill, which were formed by supergene oxidation, and a direct comparison is not useful.

Unlike the cubic polymorphs arsenolite and senarmontite, monoclinic claudetite, with a layer structure, and orthorhombic valentinite (Sb_2O_3), with a chain structure, are not isostructural (Bakakin and Godovikov, 1981). However, arsenic and antimony show a strong tendency for mutual substitution in compounds with highly electronegative elements such as oxygen or sulphur. In view of this and the abundant antimony mineralisation at Wet Swine Gill, the substitution of antimony for arsenic in claudetite is not particularly surprising.

A specimen of claudetite from Wet Swine Gill is preserved in the Manchester Museum collections (accession number MANCH:N13298).

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ATACAMITE, BOTALLACKITE AND CUMENGEITE FROM ABERSOCH, GWYNEDD, WALES

Ian DOSSETT

Coppice End, Cann Lane, Appleton, Warrington, Cheshire WA4 5NF

David I. GREEN

Manchester Museum, The University, Manchester M13 9PL

Atacamite, the orthorhombic polymorph of $Cu_2Cl(OH)_3$, is relatively rare in Britain, most occurrences of atacamite-like minerals having proved to be either paratacamite or the recently described monoclinic polymorph clinoatacamite (see Jambor *et al.*, 1996). Atacamite occurs in Cornwall at Penberthy Croft mine and Botallack mine (Golley and Williams, 1995), Newporth Beach (Dean *et al.*, 1983) and Loe Warren Zawn (Elton and Hooper, 1995). It has also been reported at several localities in the Caldbeck Fells, Cumbria (Cooper and Stanley, 1990), and in copper veins on the Solway Coast (Miller and Taylor, 1966) and the Rhinns of Galloway (Cameron and Lawson, 1979), Dumfries and Galloway.

Botallackite, a monoclinic polymorph of $Cu_2Cl(OH)_3$, occurs at a large number of Cornish localities (e.g. Golley and Williams, 1995), and has also been recorded from the Solway coast, Dumfries and Galloway (Macpherson and Livingstone, 1982), and from Halkyn in Clwyd (Bevins, 1994). The Welsh occurrence is in smelter slag, and does not represent a natural mineral according to the recent IMA definition (Nickel, 1995).

Cumengeite, $Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$, is rare in Britain. It was first recorded at Newporth Beach, Falmouth, Cornwall, where it occurs in a bornite-bearing quartz vein as equant blue crystals up to 4 mm across (Dean, 1982; Dean *et al.*, 1983). It has subsequently been reported at a handful of other localities on the coast of Cornwall where Pb–Cu veins crop out (Golley and Williams, 1995; Elton and Hooper, 1995).

Atacamite, botallackite and cumengeite occur in fractures in pebbles of hydrothermally brecciated Ordovician siltstone, containing quartz chalcopyrite–bornite veins, on the beach between Abersoch and Penrhyn Du, Gwynedd (around National Grid Reference SH 316 270). This is the first report of the three species in Wales. In common with many of the localities described previously, the minerals appear to have formed by supergene oxidation of primary copper and lead sulphides

in the presence of seawater. Atacamite is relatively common as a dark green encrustation of minute drusy crystals. Botallackite is rare, occurring as acicular to lath-like crystals up to 0.4 mm long, varying from deep emerald green to pale green. Cumengeite is also rare, occurring as light blue crusts which are composed of minute (<0.1 mm) bipyramidal crystals. The identifications of atacamite, botallackite and cumengeite are by X-ray diffractometry at Manchester University (X-rays MANCH:XRD368, XRD376 and XRD378).

Botallackite is the least thermodynamically stable of the polymorphs of $Cu_2Cl(OH)_3$, but experimental syntheses show that it forms as an intermediate metastable phase under most conditions where $Cu_2Cl(OH)_3$ is precipitated (Pollard *et al.*, 1989). For botallackite to form naturally, therefore, the solution from which it crystallises must dry out before its structure changes. This suggests a simple explanation for its occurrence at Abersoch, where copper-bearing pebbles would experience regular dry periods. The rarity of botallackite as compared to atacamite, and the altered appearance of many of the botallackite crystals, is also easy to understand in terms of its metastability.

Cumengeite requires a high concentration of chloride ions to form (Humphreys *et al.*, 1980). Its occurrence at Abersoch in the intertidal zone in association with other chloride-bearing phases is environmentally similar to the few other occurrences reported in Britain. The localities at Newporth Beach and Daymer Bay are also covered by seawater at high tide (Elton and Hooper, 1995).

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ANILITE, WITH BOTALLACKITE AND CLINOATACAMITE, FROM CASTLETOWN MINE, LOCHGILPHEAD, SCOTLAND

Roy E. STARKEY

15 Warwick Avenue, Bromsgrove, Worcestershire B60 2AH

Neil HUBBARD

30 Thirlmere Road, Barrow-upon-Soar, Leicestershire LE12 8QQ

Castletown mine was a small copper mine situated in the Dalradian metamorphic terrain on the east side of Loch Gilp, ~140 m west of Ballimore and ~3.5 km SSE of Lochgilphead, in Strathclyde Region. The vein was first worked a considerable time ago, and was opened up again in 1912 but had to be closed down owing to inability to cope with water ingress (Wilson, 1921). The vein averaged 6 feet (1.8 m) in width, and haded west at 70°, with an infilling of quartz, much of which was shattered and recemented by later growth of the same mineral. The ore was mainly cupriferous pyrite, with a little chalcopyrite and galena. (Wilson, 1921). The vein outcrop on the shore (National Grid Reference NR 874 846) shows massive white quartz ~2 m wide, running NE–SW for about 10 m. Patchy copper mineralisation is visible at the end closest to the shore, but appears to die away southwards. The following minerals have been identified on specimens collected from the vein outcrop.

Anilite, Cu_4S_7, occurs as silvery metallic masses up to 1cm across, intergrown with brassy chalcopyrite in quartz, and showing extensive alteration to green supergene copper minerals. Identification was by XRD (Manchester Museum film XRD424).

Botallackite, $Cu_2Cl(OH)_3$, occurs as felted masses of microcrystals up to 0.5 mm long covering areas up to 30 mm × 20 mm on iron-stained quartz, and also as larger

bladed transparent crystals, up to 3 mm long and 0.5 mm wide, commonly associated with dark golden-brown goethite and platy hematite. Botallackite was identified by XRD (Royal Museum of Scotland XRD Nos 4409, 4410).

Clinoatacamite, $Cu_2Cl(OH)_3$, forms dark green botryoidal crystal crusts and gemmy translucent bright green euhedral crystals and crystal aggregates up to 0.2 mm across, on sparkling colourless quartz. Identification was by IR; the spectrum matched that of authentic synthetic clinoatacamite kindly provided by Dr R.S.W. Braithwaite.

Connellite, $Cu_{19}Cl_4(SO_4)(OH)_{32}.3H_2O$, occurs as discrete dark blue spherical crystal aggregates up to 0.1 mm in diameter, on iron-stained cellular quartz, associated with transparent blades of botallackite and botryoidal crusts of dark green clinoatacamite. Connellite also forms thin coatings on quartz. Identification was by XRD (Royal Museum of Scotland XRD No. 4411).

Goethite, FeO(OH), is present as dark golden-brown acicular crystals up to 2.5 mm long, associated with hematite and botallackite; and hematite, Fe_2O_3. as individual dark red platy crystals and as crystal rosettes up to 0.5 mm across on white quartz.

This appears to be the first record of anilite from the British Isles. However, anilite may be overlooked since it is readily converted into digenite (Anthony et al. 1990) or djurleite (J.G. Francis, personal communication) by grinding for XRD analysis.

The suite of supergene copper chlorides at Castletown mine is analogous to that seen at other coastal copper vein localities around the British Isles; they are clearly formed by reaction between sea-water and copper sulphides. Atacamite has not so far been confirmed from Castletown mine. In Scotland, botallackite has been previously recorded from Southwick Cliffs, Solway Firth, Kirkcudbrightshire (Macpherson and Livingstone, 1982), while connellite is known from Southwick Cliffs (Miller and Taylor, 1966); Colvend mine, Kirkcudbrightshire (Moreton and Aspen, 1992); and Crammag Head, near Drummore, Wigtownshire (Cameron and Lawson, 1979).

Cameron and Lawson (1979) also record "paratacamite" from Barncorkrie Farm, near Drummore. In a recent study of $Cu_2Cl(OH)_3$ polymorphs, Jambor et al. (1996) have suggested that the rhombohedral paratacamite structure proper is stable only with small amounts of, e.g., Zn replacing the Cu, and have shown that the commonly used

Powder Diffraction File standard for paratacamite (card 25-1427) is that of a new monoclinic polymorph, named clinoatacamite, rather than paratacamite. The Drummore "paratacamite" had been identified by reference to the "paratacamite" XRD standard in the Natural History Museum, London, now identified as clinoatacamite (J.G. Francis, personal communication). Likewise, the "paratacamite" from Rhuba a'Mhill, Islay, Scotland (Green, 1988) is in fact clinoatacamite (D.I. Green, personal communication). Clinoatacamite is also known from Wha Taing, Burray, Orkney (N. Hubbard, unpublished).

Representative specimens from Castletown mine have been deposited in the collections of the Royal Museum of Scotland (NMS G 1991.13.1 and NMS G 1991.13.2).

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THAUMASITE FROM HIGH SEDLING MINE, WEARDALE, COUNTY DURHAM, AND FROM SHAP, CUMBRIA, ENGLAND

Brian YOUNG and Ewan K. HYSLOP

British Geological Survey, Murchison House, West Mains Road, Edinburgh EH9 3LA

Trevor F. BRIDGES

10 Springfield, Ovington, Northumberland NE42 6EH

Neil HUBBARD

30 Thirlmere Road, Barrow-upon-Soar, Leicestershire LE12 8QQ

The complex hydrated calcium silicate carbonate sulphate mineral thaumasite, $Ca_3[Si(OH)_6](CO_3)_2(SO_4).12H_2O$, has been reported from very few British localities but in a variety of parageneses. Embrey, in a footnote to Knill (1960), noted its occurrence, mixed with gypsum, in specimens collected by A.W.G. Kingsbury from a vein containing dickite, alunite and zunyite which cuts diorite at Embleton quarry, near Cockermouth, Cumbria. Thaumasite, accompanied by xonotlite, pectolite and gyrolite, was recorded from veins in serpentinite at Colla Firth, Shetland (Geological Survey, 1960). The mineral was decribed from weathered furnace slag at Dowlais Iron Works, near Merthyr Tydfil, Mid Glamorgan (Wilson, 1978) and was also noted by Young *et al.* (1985) in association with thenardite on an old specimen collected from a gypsum bed at Kirkby Thore, Cumbria. More recently the presence of thaumasite in a mineralised breccia, of possible post-mining origin, has been recorded by Ryback (in Bevins, 1994) at Glasdir mine, Dolgellau, Gwynedd. Reported here is the occurrence of thaumasite at two north of England localities.

At High Sedling mine, Cowshill, Weardale (National Grid Reference NY 8638 4099), thaumasite has been found as crusts of soft, white spherules up to 0.25 mm across, with a faint silky lustre, accompanied by dark brown 'limonitic' coatings on weathered, pale brown mudstone. Identification was by X-ray powder photography (BGS X-ray XE935). The mudstone fragments from which the thaumasite was collected were found as loose blocks in spoil from workings on Sedling vein. They are likely to have been derived from the beds between the Firestone and Low Grit Sills (Namurian), within a metre or so of the walls of the vein. A supergene origin for the thaumasite, similar to that at Glasdir mine, is likely.

At Shap Blue quarry, Shap, Cumbria (NY 564 106), a few rather blocky, hexagonal crystals of thaumasite up to

0.7 mm across encrust prehnite crystals which line small cavities in compact crystalline prehnite. Identification was by X-ray powder photography (Natural History Museum, London, X-ray 7643F). The prehnite occurs as segregations within garnet–epidote veins which cut hornfelsed and metasomatised rocks of the Borrowdale Volcanic Group (Ordovician) within the aureole of the Shap Granite (Young *et al.*, 1988). Several phases of mineralisation have been recognised at Shap Blue Quarry (Firman, 1957; 1978). Early garnet- and epidote-bearing assemblages are succeeded by assemblages which include quartz, calcite, chlorite, marcasite, magnetite, hematite, chlorite, hydrous mica, prehnite, etc. A later episode of hydrothermal mineralisation is indicated by the presence of abundant laumontite, pectolite, and rare apophyllite (Young *et al.*, 1988). Thaumasite appears to be a rare member of this assemblage.

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ENARGITE GROUP MINERALS FROM
SCALEBER BRIDGE, NORTH YORKSHIRE, ENGLAND

Robert A. IXER

School of Earth Sciences, University of Birmingham, Birmingham B15 2TT

Chris J. STANLEY

Department of Mineralogy, The Natural History Museum, Cromwell Rd., London SW7 5BD

The fahlerz minerals are complex sulphosalts that comprise the tetrahedrite group (tetrahedrite $Cu_{12}Sb_4S_{13}$ – tennantite $Cu_{12}As_4S_{13}$) and the enargite group (the orthorhombic mineral enargite Cu_3AsS_4 and the tetragonal minerals luzonite Cu_3AsS_4 – famatinite Cu_3SbS_4). They are of considerable mineralogical interest for their wide range of elemental substitutions and of archaeological significance as being the probable ores for the first metal alloys in the Early Bronze Age of Europe, namely the copper-arsenic bronzes. Finally, they have economic importance as potential silver-carriers in many base metal ores, or as indicator minerals for some types of gold ore; enargite, for example, is one of the characteristic minerals found in association with the acid-sulphate class of epigenetic gold deposits (Ixer and Pattrick, *in press*).

Although the tetrahedrite group is widespread in the British Isles and reported from many different types of mineralisation this is not true for enargite group minerals, which have only been recorded from a few places and then often as minor alteration products of earlier minerals. Recently discovered examples include Alderley Edge, where optically zoned enargite group minerals together with spionkopite and covellite form 20 μm wide replacement rims about tennantite-bearing chalcopyrite, or are present as small inclusions in galena (Ixer and Budd, 1998), and at the yet to be described mineral occurrence at Dolyhir quarry near Kington in the Welsh Marches. Free-standing crystals of enargite occur in Gregory mine, Ashover in Derbyshire (Cooper, 1995), and primary minerals with an intermediate composition between luzonite and famatinite have been described from Clevedon, Avon (Ixer *et al.*, 1993; Ixer and Pattrick, *in press*), and Melbecks Moor, Askrigg (Vaughan and Ixer, 1980). The last three occurrences are all broadly associated with Mississippi Valley-style mineralisation in the Mendip, Derbyshire Dome and Askrigg Block orefields, respectively.

A new occurrence of fahlerz group minerals from Scaleber Bridge, ~3 km ESE of Settle, North Yorkshire, just south of the Askrigg Block orefield, is a further example of minor copper–arsenic–antimony mineralisation at the margins of British Mississippi Valley-style orefields. Here limestones including reef limestones of Late Asbian age lie to the south of the Middle Craven Fault just within the northern margin of the Craven Basin. Locally they have been dolomitised and

partially mineralised and so carry minor amounts of calcite, vuggy quartz, chalcopyrite, azurite and malachite (Dunham and Wilson, 1985). Heavily malachite-stained, coarse-grained, vuggy calcite crystals with visible sulphide inclusions were collected *in situ* from limestone outcrops close to Scaleber Bridge (National Grid Reference SD 842 626). One polished section of three calcite cleavage flakes, and a grain mount made of the insoluble residue from roughly crushed calcite dissolved in weak hydrochloric acid, were prepared. Routine petrographical investigation in reflected light using air and oil immersion lenses was followed by electron microprobe analyses of the largest enargite group mineral grains. EPMA analyses were performed on a Cameca SX50 using an accelerating voltage of 15 kV and with pure elements and FeS as standards.

Chalcopyrite, pyrite and marcasite are present as discrete mineral grains, or are intergrown with each other and with trace amounts of enargite group minerals and very rare tennantite to form inclusions up to 1 mm across that lie along internal growth zones in calcite. The majority of the sulphide grains have been altered to hydroxide and carbonate minerals.

Chalcopyrite is the most abundant sulphide with a grain size of up to 1 mm. It encloses 10–100 μm pentagonal dodecahedral crystals of pyrite, some showing a faint pink surface colour, plus 10–20 μm long laths of marcasite, mixed pyrite–marcasite aggregates up to 50 μm in width, and small (5 μm) grains of green tennantite. Many chalcopyrite grains have incomplete rims of pyrite and marcasite about them. Chalcopyrite alters to 1–10 μm long flecks of spionkopite or locally to 200 μm wide aggregates of 1-2 μm diameter spheres of cuprite, but mainly to banded limonite. Rhombic and lath-shaped crystals of malachite overgrow limonite pseudomorphs after chalcopyrite.

Pyrite is present as discrete, 10–200 μm diameter, crystals that lack the optical zoning associated with nickeloan pyrite (bravoite) that is so characteristic of similar assemblages described from the Askrigg Block and Peak District orefields (Ixer, 1986). Elsewhere, it forms fine-grained (1–2 μm) crystals in aggregates up to 100 μm across enclosed in a 10 μm wide rim of twinned marcasite. Indeed, poorly crystalline pyrite cores surrounded by radiating twinned marcasite are common. Marcasite also forms fine-grained aggregates up to 100 μm across. Both

TABLE I. Analyses of enargite group minerals from Scaleber Bridge compared with those from Clevedon (wt %).

Nominally	Cu	Ag	Fe	Zn	Sb	As	S	Total	Formula
Famatinite	43.67	n.d.	0.05	0.03	17.20	7.81	30.39	99.15	$Cu_{2.90}(Sb_{0.60}As_{0.44})_{1.04}S_4$
Famatinite	44.66	0.07	n.d.	0.09	16.57	8.74	30.36	100.49	$Cu_{2.97}(Sb_{0.58}As_{0.49})_{1.07}S_4$
Luzonite	44.86	0.02	n.d.	0.08	14.63	9.67	30.70	99.96	$Cu_{2.95}(Sb_{0.50}As_{0.50})_{1.04}S_4$
Luzonite	44.87	0.09	0.10	n.d.	14.10	10.18	30.88	100.22	$Cu_{2.94}(Sb_{0.48}As_{0.56})_{1.04}S_4$
Luzonite	45.35	0.04	n.d.	0.09	14.05	10.11	30.57	100.21	$Cu_{2.99}(Sb_{0.48}As_{0.57})_{1.05}S_4$
Luzonite	45.20	0.02	n.d.	n.d.	12.92	10.68	30.77	99.59	$Cu_{2.96}(Sb_{0.44}As_{0.59})_{1.03}S_4$
Luzonite	45.43	0.15	0.10	n.d.	12.54	11.26	30.90	100.38	$Cu_{2.97}(Sb_{0.43}As_{0.62})_{1.05}S_4$
Luzonite	45.64	0.06	0.04	n.d.	11.61	12.11	31.17	100.63	$Cu_{2.96}(Sb_{0.39}As_{0.67})_{1.06}S_4$
Luzonite	43.90	0.11	0.05	0.07	15.19	9.41	30.30	99.03	$Cu_{2.92}(Sb_{0.53}As_{0.53})_{1.06}S_4$
Luzonite	45.50	n.d.	0.09	0.20	11.43	11.22	30.88	99.32	$Cu_{2.97}(Sb_{0.39}As_{0.62})_{1.01}S_4$
CL12 Enargite	46.56	0.09	0.41	0.00	10.69	11.54	30.71	100.00	$Cu_{3.06}Fe_{0.03}(Sb_{0.37}As_{0.64})_{1.01}S_4$
CL13 Enargite	47.02	0.07	0.36	0.00	7.83	14.04	30.81	100.13	$Cu_{3.08}Fe_{0.03}(Sb_{0.27}As_{0.78})_{1.05}S_4$
CL14 Enargite	47.33	0.02	0.36	0.06	8.09	14.15	31.21	100.22	$Cu_{3.06}Fe_{0.03}(Sb_{0.27}As_{0.78})_{1.05}S_4$

CL = Clevedon, Avon (analyses from Ixer *et al.*, 1993); the rest from Scaleber Bridge.
n.d. = not detected.

pyrite and marcasite alter to pale blue-grey limonite. Minor amounts of galena and sphalerite with orange internal reflections are present as discrete grains up to 100 μm in diameter.

Enargite group minerals, which include luzonite and famatinite, are present as isolated, brown-lilac, untwinned but highly anisotropic crystals up to 80 μm in length that are intergrown with minor amounts of chalcopyrite. Although microprobe analyses (Table I) show a range in compositions from luzonite $Cu_{2.98}(Sb_{0.39}As_{0.67})_{1.06}S_4$ to famatinite $Cu_{2.90}(Sb_{0.60}As_{0.44})_{1.04}S_4$, optical zoning is not seen.

There are few chemical analyses of British enargite group minerals. However, comparing the Scaleber examples and the partial analysis of stibioluzonite (= famatinite) from Melbecks Moor given in Vaughan and Ixer (1980) and those from Clevedon (Ixer *at al.*, 1993) show them all to have compositions that lie approximately half way between the end member minerals luzonite and famatinite. In more detail, the analyses in Table I show that the Scaleber minerals are richer in antimony but poorer in arsenic than those from Clevedon, that they have similar average silver and zinc contents, but that the Clevedon enargites are significantly richer in iron with an average of 0.38 wt % Fe compared to 0.04 wt % Fe for the Scaleber material.

Regional geochemical mapping of the North Pennine Orefield and its adjacent areas by the British Geological Survey (1992, 1996) shows that stream sediment samples close to the Craven Fault System have enhanced and interrelated concentrations of copper, antimony, arsenic and silver (plus some lead and zinc), suggesting the presence of a different sort of mineralisation from the main Mississippi Valley-style lead–zinc–baryte–fluorite mineralisation present within the Askrigg Block (British Geological Survey, 1996). Hence the presence of fahlerz minerals at Scaleber may not be an isolated topographical

curiosity but part of a wider mineralogical manifestation of this geochemical anomaly, and this in turn might possibly be related to the unique report of gold at James mine, Greenhow, which also lies close to the Craven Fault System (Dunham and Wilson, 1985; British Geological Survey, 1996).

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CD-ROM REVIEW

Discovering Geology: The Lake District. British Geological Survey, Keyworth, Nottingham, 1997. Price £39.95.

The package is provided on a single CD-ROM, suitable for both Macintosh and IBM-compatible computers. The Home Menu page features 6 buttons: GEOCHEMISTRY, GEOPHYSICS, GEOLOGY AND MINES, SATELLITE IMAGES (LANDSAT), PHOTOGRAPHS, and REFERENCES, together with a relief map of the Lake District. Clicking on the "Locality" button on the map brings up a selection of place names showing their approximate position on the map. One might expect that clicking on each of these names would lead through to further data, or to a menu providing information about the chosen place, but there are no links and all one can do is toggle the names on and off.

GEOCHEMISTRY. Selecting the "Geochemistry" option from the Home Menu leads through to an elegant presentation of the *Geochemical Atlas of the Lake District* (see this Journal, vol. 5, p.130). Stream-sediment maps and supporting data are provided for 31 chemical elements, together with stream-water maps for uranium, conductivity, fluoride, bicarbonate and acidity. For each map one can call up statistical data, explanatory text, a locality overlay, overlays showing major faults and solid geology, information on sampling techniques, etc. This section is highly specialist and unlikely to be of much use to the majority of purchasers of the CD-ROM, unless of course they have purchased it primarily to have a digital version of the *Atlas*.

GEOPHYSICS. Two geophysical maps are included, the first showing Bouguer gravity anomalies and the second presenting aeromagnetic data. Both provide overlays and background text similar to those for the geochemical maps.

GEOLOGY AND MINES. This section is perhaps of most interest to the general user. Three options are available: Geology, Geological Column, and Mines and Minerals. Selecting "Geology" brings up a simplified geological map. Moving the cursor across the map calls up explanatory text panels naming the formation being pointed to. Three buttons are available on-screen: "Geological Column" reveals a coloured scrollable table listing geological periods and stratigraphic names; "Landmarks" calls up the now familiar place-names overlay; "Full Geology" leads to a more detailed geological map, with options to overlay faults, place names and a scrollable key to the map legend. A scrollable explanatory text panel gives a brief summary of the regional geology. "Hot links" are provided to text on such topics as intrusive igneous rocks, structure, and metamorphism, as well as sections on each geological period.

Clicking on "Mines and Minerals" brings up a simplified geological map bearing squares marking the positions of various mines, coupled with a scrollable index box listing mines alphabetically by name. Moving the cursor to a particular mine square on the map pops up basic information on the mine: the mine name, Grid Reference, years of operation, materials recorded (e.g. lead, zinc), and principal minerals (e.g. galena, sphalerite). The index covers around 90 mines spread across the Lake District and Northern Pennines. Selecting a mine by name from the index highlights the relevant square on the map, but this is not easy to distinguish on-screen. There is no facility to access the mine and mineral information in a table format, nor to print any reports from the data. Searching for information involves scrolling down the mine list, selecting a mine name, watching for the relevant square to be highlighted and then clicking on this to reveal the back-up information. Provision of an alternative route, e.g. by double-clicking on the mine name, would be a worthwhile improvement for future editions.

Text pages give additional details on mineralisation, covering topics such as basin margin mineralisation, hematite deposits of west and south Cumbria, and mineralisation in the Northern Pennine Orefield. There is a lot of good information here, in considerable depth, but no "hot links" are provided to the references cited, and this would have been a useful feature. The only way to follow up any given reference is to return to the main menu, click into "References", and scroll through the list.

A mixture of fonts is used for the mine information, with Force Crag and Barrow Mines being in normal style whereas Robin Hood Mine and Ruthwaite Mine are in italics. Apparently this is not to distinguish between, e.g., major and minor mines, and the reason for the different styles is unclear. The entry for Buckbarrow Beck lists "Bismuthite" (presumably bismuthinite), and for Shap Quarry monazite is listed amongst the principal minerals, which is stretching it a bit. Similarly, Ulpha Mine shows bismuthinite amongst its principal minerals why?

SATELLITE IMAGES (LANDSAT). The first screen shows a striking satellite image of the Lake District and adjacent areas. As with previous map screens, overlays are available showing place names and fault lines. One can zoom in and out on this screen and some of the detail in the image is quite fascinating. Clicking on the "Areas of Interest" button superimposes six frames highlighting the following areas: Skiddaw – Caldbeck Fells; Wigton Area – Glaciation; Sellafield – Esk Valley; Pennine Escarpment; Howgill Fells – Dent Fault; and Ambleside – Coniston. On selecting an area, a larger-scale image is presented, which can be rotated to provide views with north or south at the top of the screen. The harshly emphasised shadows make the images a little difficult to interpret but they do provide an interesting set of different landforms and features.

PHOTOGRAPHS. Sixty digital photographs are grouped under the headings Geomorphology, Minerals, Fossils, Rocks, and Palaeoenvironments. As the cursor passes over each photo title an arrow indicates the position of the locality on the map. Clicking on the title calls up the photographic image, and a pop-up scrollable caption box is available to provide explanatory information as required. No "hot links" are provided to keywords featured in the caption box and this means that following up any term which is unfamiliar to the user is a rather long winded business. Again, this would be a worthwhile enhancement for any future edition. The geomorphology images are generally very good and well selected, but some of the mineral photos are rather disappointing. The shots of chrysocolla, aragonite and hemimorphite are not worthy of inclusion, and there are many more attractive specimens of baryte from Frizington to replace the illustration from Greenside Mine. Two illustrations of "kidney ore" hematite out of a total of twelve pictures seems too much when there are so many other interesting mineral specimens from the area, and the absence of a fine fluorite from either Hilton or Weardale is a regrettable omission. The fossil and rock photographs are generally of a better standard, and the palaeoenvironments illustrations are typical of works of this type.

REFERENCES. Approximately 340 references are provided, covering a wide range of earth science and geochemical topics, but no cross-links to the references are provided from elsewhere in the CD-ROM. The choice of references is at times peculiar, and it looks as if this is simply the authors' list of references from a database, with no editing to make it relevant to the current project. For example, few users are likely to want to consult Balashov & Khitrov, "Composition of rare earths in the clastic material carried by the Volga River", or Karlin, "Palaeomagnetism, rock magnetism and diagenesis in hemi-pelagic sediments from the NE Pacific Ocean and the Gulf of California."

Finally, the Help and Information screen is something of a disappointment, as there is no on-disc Help facility to explain how to move around the CD-ROM, and nothing useful in the sleeve notes. The following options are available: CD-ROM, BGS, NERC, Copyright, Feedback Form, and References, but there is little here of value to the user.

This CD-ROM is a slightly odd blend of highly specialised and technical geochemical data, mixed up with basic geological information and photos. The mine and mineral data, in particular, are in a rather clumsy format and represent something of a missed opportunity for the BGS. The very wide audience claimed for the product in the accompanying leaflet is unrealistic and, inevitably, the compromises made mean that probably none of the target audiences are really served satisfactorily. The attempt to launch a product aimed at the fast-growing electronic publishing market has fallen somewhat short of a truly commercial standard. To have provided the Geochemical Atlas in digital format on its own would have been a worthy project and possibly well received by the earth science industry and the planning and environmental bodies. Similarly, a CD-ROM version of the *Glossary of the minerals of the Lake District and adjoining areas*, augmented by a good selection of colour illustrations, would have found a ready uptake amongst amateur geologists and mineralogists. The sketchy mineralogical listings and mine data are too thin to be of any worth to serious amateurs, and yet this group is probably one of the most likely to purchase the product. Educationalists will have to assess whether the blend of data contained on the CD ROM really serves their needs, and whether the rather awkward structure of the software will be too irritating. In comparison to the truly world class editorial and production standard of the mainstream BGS printed publications, this release is a pale shadow, and at a cover price of £39.95 cannot really be recommended.

Roy Starkey

JOURNAL OF THE RUSSELL SOCIETY

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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, which are usually invited, are also published occasionally.

FORMAT AND PRESENTATION

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Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, analyses, etc.). It may not be necessary to reproduce such data in full in the text, but they should be supplied to the Editor if required by the referees in the course of their assessment. For mineral occurrences of particular note (e.g. new occurrences in the British Isles or at a particular locality) authors are strongly encouraged to record the specimen number and the institution or collection where the specimen is lodged. National Grid References should be given for localities described in the text (the format is, e.g.: ST 4015 7185, ST 401 718, ST 40 71).

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

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Authors should adhere to the nomenclature and terminology of the International Mineralogical Association. The most recent *Glossary of Mineral Species* (at present the 7th edition, by Fleischer and Mandarino, 1995) can be used as a guide to mineral nomenclature, but where this conflicts with *Hey's Mineral Index* (1993) or *Mineralogical Magazine* and *Mineralogical Abstracts* usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (*Acta Crystallographica*, 22, 45 (1967)).

ABBREVIATIONS

Except for common non-scientific abbreviations and those for standard units of measurement, abbreviations should be spelt out in full at their first mention in the article, e.g. 'platinum group mineral (PGM)'. If used, 'n.d.' in tables must be defined ('not determined' or 'not detected'). The following abbreviations may be used without explanation:

XRD = X-ray diffraction
XRF = X-ray fluorescence analysis
EPMA = electron probe microanalysis (electron microprobe analysis)
EDX = energy dispersive analysis (same as EDA, EDAX, EDS)
SEM = scanning electron microscope or microscopy

TEM = transmission electron microscope or microscopy
IR   = infrared
UV   = ultraviolet
NGR = National Grid Reference

REFERENCES

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

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