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NEW INVESTIGATION OF THE MINERALISATION IN BURDELL GILL, CALDBECK FELLS,CUMBRIA

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Abundant green pharmacosiderite occurs in a goethite, cryptomelane and pyrolusite impregnated quartz vein ,or veins, close to the head of Burdell Gill. Smaller amounts of beudantite, barium pharmacosiderite, barite, carminite, lepidocrocite, parasymplesite, plumbogummite, rhodochrosite, romanechite, scorodite, switzerite, vivianite and wolframite also occur in these veins. A considerable number of mainly supergene phosphate minerals reported from the area by Kingsbury are almost certainly not from this site. Burdell Gill and several other arsenic bearing, manganese and iron oxide rich quartz veins in the area are probably related to a halo of low temperature mineralisation around the tungsten arsenic veins in Grainsgill. The presence of wolframite in one of the veins would lend support to this idea.

INTRODUCTION

Burdell Gill is best known for the bright green pharmacosiderite specimens that were recovered by the late J. Ingham,and others, in the late 1970's; however, very little useful mineralogical information has been published on the locality. The earliest reference to this locality is that of Greg and Lettsom (1858) who recorded pharmacosiderite from "Burdle Gill" and state "It has lately been found in small but very brilliant cubes on quartz and decomposing limnite, the crystals sometimes with an iridescent tarnish." They also recorded manganite from the site. Subsequently reference was made to the occurrence by Goodchild (1885) and by Davidson and Thomson (1951) but these authors did not provide much new information apart from the addition of "pyrolusite" by the latter.

It was not until the site was examined by Kingsbury and Hartley in the late 1950's (Kingsbury and Hartley, 1958; Hartley, 1984) that the complexity of the locality became apparent. They claimed, based on Kingsbury's specimens, to have found well-crystallised jarosite, beraunite, cacoxenite, dufrenite, scorodite, strengite and vivianite. Specimens of these minerals and rockbridgeite from this site are preserved in the Kingsbury Collection in the Natural History Museum, London. Unfortunately recent work on this material has cast serious doubt over the provenance of much of Kingsbury's material allegedly from Burdell Gill (G.Ryback, *personal communication*). This said, some of Kingsbury's more unusual finds have been confirmed in this study, although the material is much less impressive than the material in the Kingsbury Collection. The more recent books by Cooper & Stanley (1990) and Young (1987) summarised the early work.

Although there are numerous works on mining in the Caldbeck Fells [e.g,Postlethwaite(1913), Shaw(1970), Cooper and Stanley(1990)] there is no specific reference to mining in Burdell Gill. It is, however, worth noting the comment made by Goodchild (1885) relating to the green pharmacosiderite, which stated that it had "lately been found", suggesting some sort of prospecting was actively being pursued in the area. Many exploratory trials were driven about this time (the early 1850's) throughout the Caldbeck Fells. Kingsbury recorded his finds in the Caldbeck Fells on a 6" to 1mile Ordnance Survey map, on this map he refers to a trial in the upper most part of the eastern most tributary of the gill and a vein outcrop a little way below it. There is a strong issue of water from a grassy hollow at the site today and this may indicate the presence of a trial level. However, it is possible that it may simply be a washout structure in the loose head deposits caused by a spring issuing from the fracture which hosts the iron manganese mineralisation.

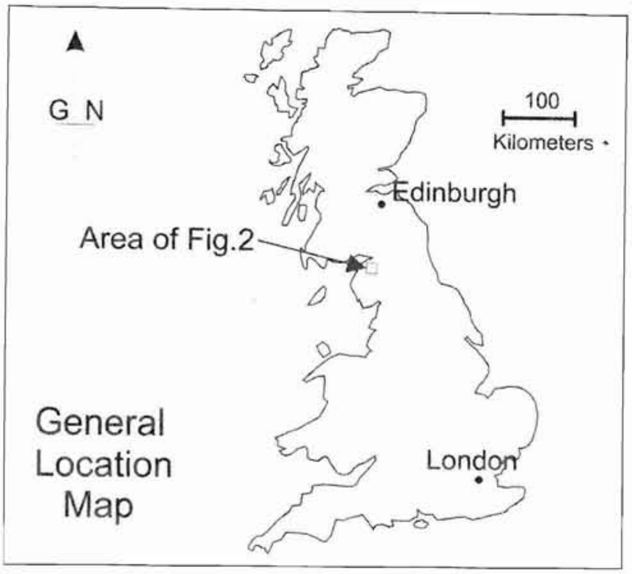

Figure 1.

LOCATION AND GEOLOGY

Burdell Gill is situated in the Caldbeck Fells, the northern most group of hills in the English Lake District *(Fig. 1)*. It is a small tributary of the River Caldew that flows southeast from high up on the southern flank of Coomb Height in the southern Caldbeck Fells. In its upper reaches Burdell Gill splits into numerous small, steep "V" shaped gullies, their profile caused by mantles of scree that obscure much of the *in situ* rock. It is now difficult to see most of the veins in place, although loose material is abundant in the screes and streambeds. Beyond the gullies an extensive blanket of thin peaty soil obscures the rock head. An outline geological map accompanying the 1976 stream sediment survey of the area around Carrock Mine (Appleton and Wadge, 1976) shows three, roughly parallel, iron manganese veins trending almost N-S across the head of the gill in the vicinity of NY 307 324. Mapping by one of the authors (TN) in 1979 revealed a more complex distribution of mostly barren iron-stained quartz veins, though some carry a little tourmaline and wolframite (marked "W" on *Fig. 2*). The iron manganese oxide mineralisation could not be seen *in situ* at that time.

The host rock in Burdell Gill consists largely of Ordovician greywackes and mudstones of the Skiddaw slates: these have been converted into cordierite hornfels by their proximity of the underlying Skiddaw granite. Near the head of the gill andalusite hornfels occur and Eastwood *et al* (1968) mentions small, somewhat altered, dyke-like bodies of fine grained, greenish igneous rock occurring in the Skiddaw slate in the upper part of Burdell and Wiley Gills. Rock outcrops often are noticeably bleached with black manganese-stained joint faces.

The manganese-rich veins themselves are no longer visible but, to judge from the debris in the gully bottoms, they consist of medium to coarse, granular to cellular, quartz carrying odd fragments of wall rock and selvages of iron manganese oxides. A fairly common form consists of euhedral bipyramidal quartz crystals, 1 to 2mm in size, supported by a fine-grained matrix of either pyrolusite or cryptomelane. The cavities and clefts are, more or less, filled with spongy to massive iron and manganese oxides. Where residual cavities remain in the oxide fill, botryoidal films of brown goethite or black manganese oxide (pyrolusite, romanechite and cryptomelane) occur. It is in these cavities that the pharmacosiderite, crystalline pyrolusite, velvety cryptomelane and other supergene minerals are found. Some of the goethite and cryptomelane exhibits evidence of having pseudomorphed a rhombohedral mineral, presumably a carbonate such as ankerite or siderite. No sulphides remain but pseudomorphs of goethite after, what were probably, tiny (1 to 2mm) pyrite and arsenopyrite crystals are sometimes encountered and a single specimen containing boxwork-like pseudomorphs of plumbogummite after 3mm grains of galena was also found. A little primary barite survives in some of this material; it occurs as either radiating laminar white aggregates to 20mm or as aggregates of randomly oriented white euhedral plates about 7mm across in cavities. Supergene barite occurs but the crystals are minute and glassy.

In addition to the manganiferous vein mineralisation there are present in the gill abundant blocks of pale grey to pale pink bleached mudstone that carry spherical to ellipsoid black manganese oxide nodules from about 5 to 20 mm in diameter. This material can be traced back to an outcrop high up in one of the central gullies of Burdell Gill and appears to be derived from a bedding -controlled zone of bleaching and alteration.

Appleton and Wadge (1976) state that "A grab sample from a N-S trending quartz manganese vein from the head of Burdell Gill contains 1200 ppm W..." (tungsten). This was presumably from one of the manganese veins they show on their

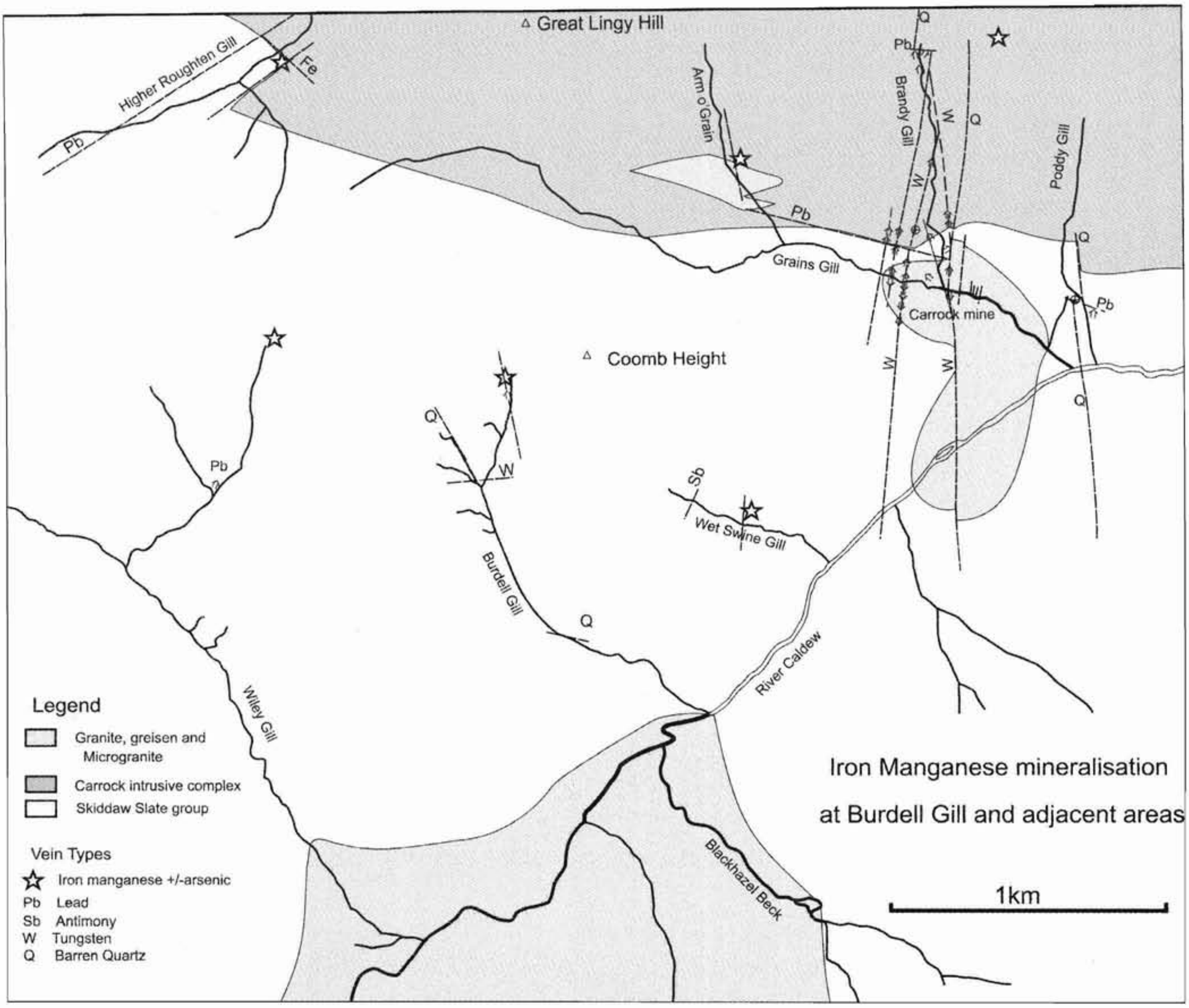

Figure 2.

map; however, no tungsten -bearing phase was identified. In this study wolframite was found in an E-W quartz- tourmaline vein lower down the gill but there is little associated manganese mineralisation. This vein dips to the south at about 70° and consists of about 200 to 300 mm of quartz that has been strong deformed into a series of overlapping en echalon quartz lenses separated by thin white-mica tourmaline membranes, the whole structure is heavily iron-stained. The lenses of coarse quartz contain irregular domains of fine -grained mosaic quartz, particularly along their margins, reminiscent of stress-induced recrystallisation. It also carries abundant chlorite, and a trace of residual arsenopyrite with associated supergene minerals; lepidocrocite, scorodite and jarosite.

Other veins in the gill are either weakly quartz-mineralised faults, trending 030°, or rather larger barren quartz veins trending roughly NW-SE (*Fig. 2*). The quartz in these latter veins resembles the quartz in the tungsten veins at Carrock mine, being very coarse and greasy with few cavities. Another style of mineralisation found as loose blocks in the stream, but not seen *in situ*, consists of pale, soft, bleached mudstone fragments cemented by thick selvages of cellular goethite and lepidocrocite that often carry epimorphs after a cubo-octahedral mineral, presumably pyrite. This material occurs in the same part of the gill as the pharmacosiderite bearing material but persists further up the gill, almost to the top.

THE MINERALS

The list of minerals described below includes only those minerals found by the authors. Reviews of the minerals not found by the authors (beraunite, cacoxenite, dufrenite, manganite, rockbridgeite and strengite) can be found in Cooper and Stanley (1990) and Young (1987). The manganese oxide mineral names were used rather indiscriminately in the past depending on the apparent physical nature of the material, so for example, psilomelane refers to a hard black fine-grained or colliform material. Manganese oxide minerals are notoriously difficult to identify, even today.

ARSENOPYRITE FeAsS

Although arsenopyrite must at one time have been an important component of the veins that now contain pharmacosiderite, no residual mineral has been found to the knowledge of the authors. Small amounts of residual arsenopyrite do however occur in the wolframite-bearing quartz vein.

BARIUM-PHARMACOSIDERITE
Ba $Fe_8 (AsO_4)_6 (OH)_8.14H_2O$

Yellow to orange-brown cubes to 1mm in size are much less common than the green pharmacosiderite crystals. EDAX analysis (M. Rothwell, *personal communication*) revealed major iron and arsenic and minor barium, suggesting that the mineral is the barium analogue. XRD reveals a small but distinctly different pattern to that of the green pharmacosiderite. The splitting of some peaks may indicate a loss of symmetry (D. Green, *personal communication*). The reduced Mn^{2+} and Fe^{2+} minerals are only associated with this type of pharmacosiderite and it is possible that it develops from normal pharmacosiderite by cation exchange in response to the barium released during the reduction of, say, a barian manganese oxide such as romanechite.

BARITE $BaSO_4$

Barite was reported on a specimen in the National Museum of Wales (Young 1987). It occurs most frequently as coarse white, radiating, primary aggregates in cellular quartz heavily impregnated with goethite and manganese oxides from the debris below the Fe/Mn vein and from float further down the gill. Less frequently, aggregates of small, randomly oriented, tabular white barite crystals occur in cavities in coarsely granular quartz with goethite films, acute rhomb shaped beudantite crystals and drusy plumbogummite. This latter material was found in float blocks from the middle reaches of the gill and may not have the same source as the previously described material. During the course of this work minute colourless, supergene, barite crystals less than 0.3mm in size were found. They occur as diverging aggregates of thin rhomb shaped tablets on films of brown iron oxide in debris from the Fe/Mn vein.

BEUDANTITE Pb $Fe_3(SO_4)(AsO_4)(OH)_6$

Beudantite is a rather uncommon mineral in Burdell Gill but occurs as sheaf-like aggregates of acute rhombohedra, or as minute discrete pseudo-octahedral crystals that are actually truncated rhombs which range in colour from yellow to dark brown. The structure was confirmed by XRD at the Natural History Museum, London using a D. Middleton specimen, and cited by Cooper and Stanley (1990). Occasionally it is associated with corroded mimetite and drusy red carminite on clinkery iron-stained quartz or as smooth, glassy, yellow spheres on an earthy manganese oxide or barite.

CARMINITE Pb $Fe_2(AsO_4)_2(OH)_2$

Carminite occurs very rarely as minute red acicular crystals associated with rhombs of beudantite on limonite, or as granular massive impregnations in quartz that are also generally associated with beudantite. The identity was confirmed by XRD at Manchester Museum (D. Green, *personal communication*). Small drusy red patches are occasionally found associated with beudantite and plumbogummite in fractures in barite and quartz from float in the middle reaches of the gill.

CRYPTOMELANE KMn_8O_{16}

A drusy black, capillary, manganese oxide forming velvety crusts less than 0.5 mm thick on pyrolusite or "psilomelane" has been identified as cryptomelane by XRD at the Natural History Museum, London. Cryptomelane is one of the most abundant supergene manganese oxide minerals and is probably a component of most compact "psilomelane" too. Further specimens afforded a slightly different XRD pattern (D. Green, *personal communication*) suggesting that some of it could be the sodium analogue manjiroite $(Na,K)Mn_8O_{16}$, but the composition would have to be checked to confirm the identity.

GOETHITE Fe O(OH)

Goethite is the most abundant supergene mineral in these veins. Much of it is massive and forms porous patches that fill voids in the quartz.

Where it lines open cavities it occurs as dark brown botryoidal films or as ochre-yellow velvety radiating aggregates or crusts. A very dark brown reniform crust that consists internally of radiating, orange brown, lustrous cleavages was confirmed as goethite by XRD (D. Green, *personal communication*). Goethite forms the substrate over which most of the other minerals are scattered apart from some of the "psilomelane". Very delicate golden yellow capillary crusts and pompon-like aggregates occur with plumbogummite in cellular quartz and resemble cacoxenite, however, EDAX analysis (D Green, *personal communication*) confirmed the iron oxide composition.

HEMATITE Fe_2O_3

Thin, dark maroon-red, earthy films of hematite, presumably supergene, occur with goethite as coatings on narrow fractures in the quartz in material from the Fe/Mn vein and with drusy orange red lepidocrocite from the tungsten vein. This material has not been analysed by XRD; however, EDAX revealed only iron (D. Green, *personal communication*) and the inertness of this material towards hydrochloric acid suggest that it is hematite rather than goethite or lepidocrocite.

JAROSITE $K Fe_3(SO_4)_2(OH)_6$

A light yellow microscopically crystalline powder is associated with lepidocrocite in fractures in quartz from the wolframite-bearing vein. Under the electron microscope it is seen to consist of minute six sided plates with alternately bevelled edges. EDAX analysis revealed major K, Fe and S but there is insufficient material for XRD analysis. Its composition and physical properties suggest that it is jarosite.

LEPIDOCROCITE $Fe O(OH)$

Lepidocrocite, a polymorph of goethite, has been confirmed by XRD at the Natural History Museum, London (G. Ryback, *personal comunication).* It occurs as minute scattered or drusy orange-red crystals in small (<5mm) cavities in quartz with goethite and structureless manganese oxide. Deep orange-red to orange-brown, thin velvety films lining cavities in cellular quartz are probably lepidocrocite too. In both of these habits it is associated with the pharmacosiderite assemblage. In the middle reaches of the gill a few blocks of pale pink bleached friable mudstone breccia cemented by up to 30 mm of cellular lepidocrocite have been found. Cavities in this cellular material may be lined with either lustrous dark reddish-brown to almost black botryoidal lepidocrocite or with lustrous drusy tabular brownish-red crystals, occasionally up to 1 mm or more in size though more typically 0.2 to 0.3mm. This material appears to be replacing pyrite in what was originally a pyrite-cemented breccia with very little quartz and is quite distinct from the arsenic/manganese mineralisation. Minutely drusy, bright orange-red, lepidocrocite also occurs in the wolframite-bearing quartz vein as selvages with corroded chlorite, earthy hematite and tourmaline. Here too, it is probably replacing pyrite.

MIMETITE $Pb_5 (AsO_4)_3Cl$

Tiny white pointed crystals on ferruginous quartz were identified as mimetite by R.S.W. Braithwaite of UMIST, Manchester, using infra-red spectroscopy; and this work revealed a virtually phosphate-free mimetite (Cooper and Stanley, 1990). We have found badly corroded prisms of white mimetite to about 0.5 mm in length associated with beudantite or with drusy carminite. Hollow epimorphs of brown iron oxide after mimetite are not infrequent. Hollow drusy epimorphs of beudantite after mimetite also occur occasionally.

ORTHOCLASE $KAlSi_3O_8$

Small pink millimetre sized crystals of feldspar occur embedded in quartz. By analogy with the nearby sites Arm o'Grain (Cooper and Stanley, 1990) and Upper Brandy Gill (TN specimen) this mineral is probably the orthoclase variety adularia.

PHARMACOSIDERITE $K Fe_4(AsO_4)_3(OH)_4.7H_2O$

Pharmacosiderite is the most abundant of the supergene arsenate or phosphate minerals at Burdell Gill. It occurs as drusy bright green to brownish- green glassy cube-shaped crystals to 2mm on edge. The crystals line cavities in the gossanous quartz-goethite-cryptomelane vein material or on botryoidal goethite. While most pharmacosiderite in Burdell Gill occurs as sharp green cubes it may also be pale to amber-yellow and occasionally exhibit small tetrahedral faces. Some of the cavities found in the 1970's were large enough to produce hand specimens. The mineral was first noted by Greg and Lettsom(1858) who commented on the frequent occurrence of a thin iridescent film that coated the crystals.

Pharmacosiderite is not only a mineral in its own right but has also given its name to a family of related arsenates containing a trivalent cation (usually Fe^{2+} or Al^{3+}), a large mono- or divalent cation (usually K^+ or Ba^{2+}) and a variable zeolitic water content. This family of minerals have zeolite-like framework structures.

The term "pharmacosiderite" refers to the potassium rich ferric arsenate member of the group. The situation is further complicated by the presence of numerous polymorphs (at least two cubic and two tetragonal) and it is not clear whether there is any relationship between composition and crystal symmetry.

PLUMBOGUMMITE
Pb $Al_3(PO_4)_2(OH,H_2O)_6$

Minute colourless drusy crystals (<50 microns) encrusting goethite-coated quartz were identified as plumbogummite by XRD at the Natural History Museum, London. EDAX analysis (D. Green, *personal communication*) of several specimens has confirmed the generally arsenate-free nature of the plumbogummite. This is an interesting observation since, on several specimens, it is associated with, and even replaces, mimetite. Plumbogummite may also occur as a microscopically drusy white frosted coating on larger beudantite crystals. There is no evidence of any tendency to form a solid solution between plumbogummite and beudantite or related ferric members of the group. A single specimen was found in which galena has been replaced by a hollow box-work of plumbogummite.

PYRITE FeS_2

Fresh pyrite was not found in any specimens examined by the authors but it was almost certainly a common component of several veins at one time. Tiny, 1 to 2 mm, cubes of goethite, presumably replacing pyrite, occur in the finer grained vein quartz associated with the pharmacosiderite. Slightly larger (2 to 4 mm) cavities in the wolframite-bearing vein, now lined with earthy hematite, botryoidal goethite and drusy lepidocrocite, are probably casts of pyrite crystals. Bleached mudstone breccia, cemented by thick layers of cellular lepidocrocite, occasionally contains hollow epimorphs, after cubo-octahedral crystals up to 5 mm across, presumably pyrite.

PYROLUSITE MnO_2

Although reported by Davidson and Thompson (1951) at this locality, it has not previously been confirmed by XRD. A specimen of "psilomelane" from the Kingsbury collection in the BM (NH), that was found to consist, in part, of pyrolusite is of uncertain origin. The mineral is common as hard crystalline black masses, containing quartz, or as tiny, brilliant, diamond-shaped orthorhombic tablets (XRD, D. Green, *personal communication*). The latter form is probably pseudomorphing manganite and may account for the earlier records of "manganite" from Burdell Gill.

RHODOCHROCITE $MnCO_3$

Rhodochrocite occurs very rarely as minute glassy crystals, usually less than 0.2mm, colourless to grey, or rarely pale pink, which are thinly scattered over joint faces and cavities in gossanous quartz. The crystals may be either rounded subhedral grains or sharp scalenohedra truncated by low angle rhombohedral faces. It is usually associated with orange-brown barium pharmacosiderite, perhaps indicating that this mineral formed, by reduction, from a barian manganese oxide mineral such as romanechite. It was identified by XRD, and analysed by EDAX (D. Green, *personal communication*); these techniques suggested a near end-member composition.

ROMANECHITE $(Ba,H_2O)_2Mn_5O_{10}$

Dull grey-black, dense to silky fibrous botryoidal romanechite occurs with granular to crystalline, metallic black, pyrolusite. It has been identified by XRD on material in the NHM (G Ryback, *personal communication*) and is probably a fairly abundant mineral amongst the black manganese oxides but its lack of any particular characteristic feature makes it easy to overlook. Occasionally romanechite occurs as small (2 mm) sheaves of lustrous black cleavages embedded in an unidentified, fine-grained, manganese oxide. Wet chemical analysis demonstrated that barium rich manganese oxide is fairly abundant, though less so than the potassium-rich material, and most of it is probably romanechite.

SCORODITE $FeAsO_4.2H_2O$

Minute pale yellow bladed aggregates, less than 0.1 mm, on iron-stained quartz were shown by XRD to be scorodite (D Green, *personal communication*). They appear to pseudomorphs after parasymplesite. Colourless to light grey drusy scorodite occurs with residual arsenopyrite in the wolframite-bearing quartz vein material from lower down Burdell Gill.

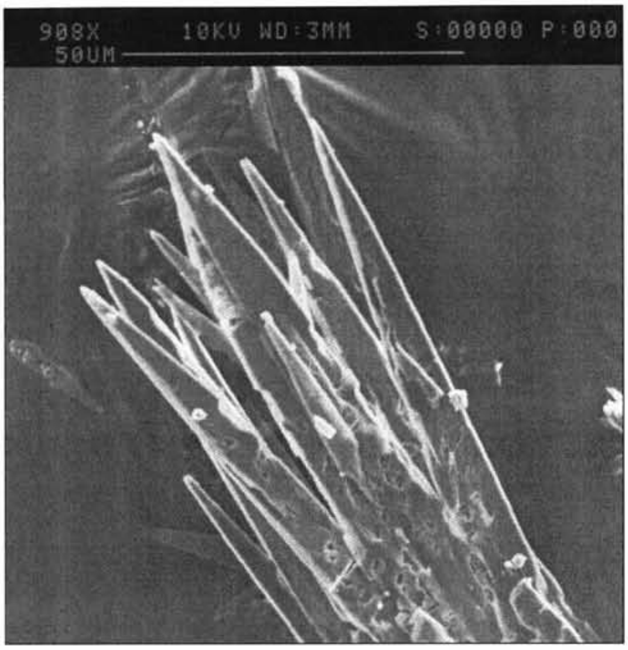

Figure 3. SEM image of switzerite from Burdell Gill (M. Rothwell)

SWITZERITE $Mn_3(PO_4.AsO_4)_2.2.7H_2O$

Switzerite from Burdell Gill is the first reported occurrence of this mineral in the British Isles. Switzerite and metaswitzerite typically occur in granite pegmatites as a late stage hydrothermal alteration product of minerals such as triphyllite and triplite. Switzerite rapidly dehydrates to metaswitzerite on exposure to the air.

At Burdell Gill, however, the mineral is a genuinely supergene phase occurring as small divergent sprays of colourless to very pale brown obliquely terminated blades *(Fig. 3)* or as a thin film of pale coloured fibrous material on hairline fracture surfaces in, rather porous, gossanous quartz associated with barium pharmacosiderite. Analysis carried out by EDAX (M. Rothwell, *personal communication*) revealed manganese, phosphorus and arsenic, suggesting a mixed arsenate and phosphate and the pale colour suggests an Mn^{2+} compound. X-ray diffraction revealed that the mineral was switzerite (D. Green, *personal communication*). There are small differences in the XRD pattern between Burdell Gill switzerite and that from elsewhere. These are probably due to the substitution of arsenic for phosphorous and the absence of iron. Switzerite normally dehydrates within hours of being exposed to the atmosphere but, although the X-rayed specimen had been collected almost a decade ago, the XRD pattern clearly indicated switzerite rather than meta-switzerite. In a redefinition of switzerite White, *et al.*, (1986) and Zanazzi, *et al.*, (1986) present evidence that it is the presence of iron that cause the rapid dehydration of switzerite to metaswitzerite. The Burdell Gill switzerite is essentially iron-free. However, it is unusually rich in arsenate, and it is possible that this contributes towards the stability of the mineral from this site. This possibility is supported by the fact that manganese arsenate can exist as manganese-hornessite, the higher eight-hydrate, $Mn_3(AsO_4)_2.8H_2O$, which is isostructural with vivianite and parasymplesite.

TOURMALINE Complex silicate group

Slender, pale grey-green to brown prisms with a rounded triangular cross-section, and 1 to 4mm in length, in quartz have been found *in situ* in the wolframite-bearing vein and in loose float blocks of vein quartz. The mineral has not been analysed but is thought to be a member of the complex tourmaline group of silicates-probably schorl.

VIVIANITE-PARASYMPLESITE
$Fe_3\ (PO_4)_2.8H_2O$-$Fe_3(AsO_4)_2.8H_2O$

Vivianite-parasymplesite was originally reported by Hartley(1984) on a specimen in the British Museum (NH) Kingsbury collection, however, this specimen may not be from Burdell Gill. The material found by one of the authors occurs as tiny, dark green to dark indigo-blue sheaves of, rather typical, obliquely terminated monoclinic blades to about 0.2 mm on gossanous quartz. XRD confirmed that the mineral is vivianite though the pattern differs slightly from the ideal. EDAX analysis conducted on additional specimens revealed a wide range of arsenic substitution and at least some appear to have As>P and are therefore parasymplesites. The vivianite is often associated with corroded barium pharmacosiderite from which it appears to have formed. The vivianite and parasymplesite appear to have been confined to the isolated float blocks that also carried the switzerite and rhodochrosite.

WOLFRAMITE $(Fe\ ,Mn)WO_4$

Tiny black cleavages of wolframite, up to 2mm in length and aggregates to 6mm, occur with pale greenish-brown tourmaline, chlorite and arsenopyrite in lenses of quartz. These are in a roughly east-west trending, south dipping, iron-stained shear zone in the upper central tributary of Burdell Gill. The zone is about 300mm wide. Wolframite has been previously found in-situ in the stream sediment from Burdell Gill (Appleton and Wadge, 1976).

DISCUSSION

The Mn-Fe-As type mineralisation in Burdell Gill is superficially similar to that found at several other localities scattered over the southern Caldbeck Fells ,and centred on the Grainsgill griesen outcrop. Manganese oxide-rich quartz occurs at the head of Wiley Gill and there is a lead trial on a manganese- rich quartz further south, about 1km from Burdell Gill. An arsenic-rich, manganiferous quartz vein is recorded by Appleton and Wadge (1976) as outcrops about half way up Wet Swine Gill, some 1km to the ESE. North of the Grainsgill griesen very similar pharmacosiderite-bearing romanechite cryptomelane quartz vein material occurs abundantly as float blocks in the peaty soil around the head of Brandy Gill. This material is also tungsten-bearing and occasionally carries traces of stolzite with pharmacosiderite, beudantite, carminite, mimetite and arseniosiderite (Cooper and Stanley, 1990). This material is believed to come from the northward continuation of the Carrock tungsten mineralisation but cannot be seen *in situ*. N-S trending stringers of arsenic bearing manganiferous quartz occur *in situ* at the head of Brandy Gill but they do not appear to contain ferric arsenate minerals. A 150 mm wide mimetite-bearing quartz manganese oxide vein with an E-W trend can also be seen at the very top of Brandy Gill. Other roughly N-S trending manganese oxide veins outcrop in Higher Roughten Gill, Arm o'Grain and Black Hazel Beck, at least the two former are arsenic bearing. Firman (1978) and Appleton and Wadge (1976) believed that at some of these structures are related to the tungsten arsenic mineralisation spatially associated with the Grainsgill griesen.

One feature, however, makes Burdell Gill unique and this is the presence of the lower valency iron and manganese minerals, vivianite, parasymplesite, switzerite and rhodochrosite. These Fe^{2+} and Mn^{2+} minerals are sensitive to oxidation and yet clearly encrust Fe^{3+} and Mn^{4+} oxides. They are, therefore, later than the iron manganese oxides of the initial supergene assemblage suggesting that, at least locally, the initial oxidation phase was followed by a phase of supergene reduction. Under these conditions pharmacosiderite could have given rise to vivianite and parasymplesite, and the cryptomelane, romanechite, etc., to rhodochrosite and switzerite. It is possible that the association of barium pharmacosiderite with the Mn2+ minerals is caused by cation exchange, a process that is well established in pharmacosiderite, the barium being released by romanechite during reduction.

One can only speculate on the likely cause of reduction but the extensive blanket of peat on this side of Coomb Heights could have saturated the ground beneath with water that was rich in organic matter and this could cause reducing conditions. The source of the phosphorus is enigmatic though the presence of plumbogummite would support a local source. A significant source of phosphorus is probably not a requirement for the formation of the small amounts of vivianite, given suitably stagnant condition, as traces of phosphorus are ubiquitous and the presence of vivianite in numerous modern river sediments, and other soils, bears witness to this.

ACKNOWLEDGEMENTS

The authors wish to thank all those colleagues who have helped this paper through its long gestation, in particular the late George Ryback (Natural History Museum, London) for his critical assistance on the manuscript and for the unpublished information and XRD data that he provided. We would also like to thank David Green (Manchester Museum) for numerous EDAX analyses and XRD confirmation of the minerals. The late Mike Rothwell also carried out a large amount of analytical work on material from Burdell Gill when the paper was still merely a distant dream. It is a great sadness that Mike Rothwell and George Ryback will not see the publication of this paper.

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SECONDARY MINERALS FROM THE CWMAVON VALLEY COPPER SMELTING SLAGS, GLAMORGAN, SOUTH WALES.

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A range of secondary minerals have been identified from copper smelting slags in the Aberavon, Glamorgan, area. A variety of unusual crystal forms of atacamite have been observed. Some of the slags are particularly rich in rare copper arsenate minerals including chalcophyllite, lavendulan and lindackerite.

INTRODUCTION

Materials from the metal- smelting slags attract the interest of amateur mineralogists because of their beauty and perfect form although, since 1995, slag materials are no longer recognised as minerals because they have been derived from man-made materials (Nickel and Nichols 1991). Laurion in Greece (Gelaude *et al.*,1996) is probably the most well-known source of slag minerals however, many other sites world-wide are known such as at Rammelsberg, Harz mountains, (Berg, 1990) and at Sclaigneaux, Belgium (De Nul, 1999). Several sites in the UK have yielded a wide range of interesting minerals, the majority derived from copper and lead smelting activities , (Braithwaite, *et al.*, 1993: Green, 1987). As far as the author is aware, no study of the secondary mineralisation within the slags from copper smelting sites from Wales has been published, apart from one cited occurrence of botallackite from a smelting site at Halkyn in Clwyd (Bevins, 1994). Whilst copper smelting in Wales can be dated back to the bronze age

(Craddock, 1990) it was not until the sixteenth century that it really became established. The Mines Royal Society was set up during the reign of Elizabeth the first. In 1584 they started the first copper smelting works in south Wales in the Vale of Neath (Trott, 1974). The abundance of local coal and the availability of copper ore from Cornwall in particular were the main reasons for establishing the non-ferrous industry in the region . By the early nineteenth century south Wales had become the largest centre for copper smelting in the world (Roberts, 1956). Lead, silver, zinc and nickel were also produced by smelting. Whilst the majority of the copper smelting activity took place along the bank of the river Tawe at Swansea several large copper smelters were in operation in the contiguous areas of Llanelli, Burry Port, Port Talbot and Cwmavon. A copper works was established at Cwmavon in 1835 [SS782927], the site chosen being at the foot of Mynydd Y Foel in close proximity to the iron works which were already in existence. The works was purchased by Rio Tinto company in 1884 who used imported Spanish copper ore from the Huelva district in southern Spain. Towards the end of the nineteenth century a more concentrated copper precipitate was imported which could be more economically refined. Eventually, for economic reasons, a new copper refinery was erected at Port Talbot docks, now the site of Corus steelworks, where new works were commenced in 1906. The copper works at Cwmavon were abandoned in that year (Phillips, 1934). Very little remains of the Cwmavon copper smelter. The course of the flue from the works can still be seen today rising to the summit of Mynydd Y Foel at 400 metres and is over 1.5km in length. Waste slag from the smelter and other smelters down the valley were used in road -making and for pier construction at Port Talbot and at Aberavon on the coast. Copper smelting slag is fairly abundant on the beach at Aberavon [SS750888].

THE COPPER SMELTING PROCESS

Whilst native copper and the oxide and carbonate ores were the earliest sources of copper metal they represent a very small proportion of the copper minerals present in the Earth's crust. The bulk of the copper produced in the world today comes from low-grade deposits of the sulphide mineral chalcopyriteis derived from ($CuFeS_2$). Prior to the development of the direct reduction process in the late nineteenth century the smelting of copper ores was a laborious multi-stage process. The Welsh process involved at least six roasting and fusion stages to yield the copper metal (Gowland, 1930). A sequence of separate operations to remove sulphur, arsenic and other undesirable impurities, involved the roasting of ores (oxidation), high temperature liquid/liquid separation of a copper-enriched matte of copper-iron sulphides and a slag containing the iron-oxide, mineral-associated rock with added fluxes. This was followed by a slow elimination of iron content, another oxidation of the copper sulphide to oxide, and a final reduction to yield copper metal. The main by-product of the smelting process was a black slag with a very high iron content. The solidified slag is predominantly fayalite (olivine) which is an intermediate phase in the FeO/SiO_2 system.

THE COPPER SLAG

Black fayalite-rich copper slag occurs in large quantities as on the beach around Aberavon. Most is massive, extremely hard and devoid of mineralisation but some smaller pieces, contain small cavities up to 20 mm in diameter near their outer surface which may be richly mineralised . Slag rich in copper metal , copper prills and copper matte are occasionally found.

MINERALOGY

Most of the minerals recorded below occur in small cavities < 10mm in diameter. They typically occur as euhedral crystals (1mm). Identifications were confirmed by X-ray diffraction (XRD), infra-red spectrophotometry (IR) or as stated.

ARAGONITE $CaCO_3$ IR

Aragonite occurs, commonly, as minute <1mm white to colourless spheres or fan shaped sprays composed of radiating acicular crystals. It is sometimes associated with azurite. Some of the acicular material turned out to be calcite as confirmed by I.R. and X.R.D.

ATACAMITE $Cu_2Cl(OH)_3$
IR and XRD (film no, 11987)

Atacamite is the most common of all the secondary minerals found at Aberavon beach. It occurs as green amorphous powdery masses filling vesicles in the slag and as dark green tabular crystals or as interlocking rosettes of thin plates *(Fig.1)*. It also occurs as sprays of slender prismatic needles but a most unusual morphology is as green triangles pseudomorphing calcite or possibly hydrocalcite *(Fig.2)*.

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

Azurite has been found on only two specimens so far and occurs as deep blue aggregates, usually associated with calcite or aragonite.

BROCHANTITE $Cu_4SO_4(OH)_6$IR
Brochanite is usually found in the ferruginous slags where it occurs as pale green lath-shaped platy crystals or , more typically as elongated fan-like groups with frayed terminations. Some crystals are blue-green in colour, which may be due to inclusions of the chemically similar Langite group of minerals

CALCITE $CaCO_3$ Visual and IR
Calcite occurs commonly in a variety of forms. It occurs as aggregates of interlocking rhomboids, white spherical mamilliary masses, interlocking plates or white acicular balls. Very rarely transparent triangular crystals have been found but the majority have been pseudomorphed by atacamite.

CHALCOPHYLLITE
$Cu18Al_2(AsO_4)_3(SO_4)_3 (OH)_{27}.33H_2O$
IR and XRD (film no.1979F)
Chalcophyllite occurs rarely as turquoise pseudo-hexagonal interlocking plates, mostly grouped in the form of rosettes *(Fig.3).* The crystals are generally transparent covering several square millimetres of matrix.

CONNELLITE $Cu_9 Cl_4 SO_4(OH)_{32}.3H_2O$
Visual and IR
Connellite is fairly abundant on the external surfaces of the slag as light-blue coatings. Occasional cavities, particularly in the black glassy slag, yield rich pockets of deep-blue hemispheres of acicular needles *(Fig.4).* Connellite is commonly associated with atacamite and cuprite.

COPPER Cu
Copper metal occurs as relic material from the smelting process. It takes the form of nodules weighing up to 200 g or thin sheets or twigs attached to slag or firebrick. Copper prills are locally abundant. The copper is commonly coated with cuprite crystals.

CUPRITE Cu_2O Visual
Cuprite occurs as wine-red cubes or octahedra with a brilliant lustre up to 0.3mm on edge *(Fig.5).* Rarely the acicular variety, chalcotrichite, occurs as felted mats *(Fig.6).* Most of the cuprite seems to be of post-smelting in origin. Occasionally it can be found growing on gypsum crystals and, in this association, it must be one of the last minerals to crystallise.

DEVILLINE $CaCu_4(SO_4)(OH)_6.3H_2O$
IR and XRD (film no.12007)
Devilline occurs as clusters of sky-blue lath-like crystals up to 0.5mm in length. They possess a characteristic pearly lustre *(Fig.7).*

GYPSUM $CaSO_4.2H_2O$ Visual and IR
Gypsum forms clear prismatic needles spanning cavities to 10 mm. Sprays and single crystals occur with characteristic oblique terminations. Gypsum is common amongst the more iron-rich slags.

LANGITE $Cu_4 (SO_4)(OH)_6.2H_2O$ Visual and IR
Langite occurs rarely as blue prismatic crystals and as pseudohexagonal twins. Occasionally reticulated aggregates occur.

LAVENDULAN $NaCaCu_5(AsO_4)_4Cl.5H_2O$
IR and XRD (film no. 12009)
Lavendulan occurs, rarely, as sky-blue aggregates of tabular crystals with a pearly lustre *(Fig.8).* Cavities up to 5 mm in diameter completely filled with lavendulan have been found. Spherical aggregates occur on lindackerite, its most common associate.

LINDACKERITE $H2Cu_5(AsO_4)_4.8\text{-}9H_2O$
XRD (film no.12010)
X-ray analysis of an apple-green mineral bears a close similarity to the mineral lindackerite, originally described from specimens coming from the Eliaas mines, Jachymov, Bohemia, Czech Republic (Ondrus *et al.*,1997). This appears to be the first reported occurrence as a slag mineral. It occurs as radiating aggregates of fine needles showing colour zoning- green to almost colourless, encrusting cavities within a particularly copper-rich slag *(Fig.9).* Lavendulan is the most commonly associated mineral.

MALACHITE $Cu_2CO_3(OH)_2$ Visual and IR
Malachite occurs as botryoidal light to dark green crusts coating the walls of the slag cavities. Small fan sprays of acicular needles can also occur.

PHOSGENITE $Pb_2CO_3Cl_2$ XRD (film no.12022)
Transparent to transluscent multi-faceted barrel-shaped phosgenite crystals showing growth zones and as long prismatic crystals with polyhedral terminations occur rarely as single isolated crystals or in small groups perched on

the slag surface (*Fig. 10*). One solitary crystal was found growing on atacamite. This was the only lead mineral identified so far.

UNKNOWNS.

Several phases still need to be identified: UN 1. Deep azure-blue rectangular plates and stacked sheets growing on calcite. They bears a close resemblance to pseudoboleite. UN2. Langite-group mineral; sky-blue prismatic needles *(Fig.11)*. UN3. Primrose-yellow ball-shaped aggregates of crystals associated with dark brown lustrous crystals of indeterminate form. UN4. Brown hexagonal rosettes -probably ferrihydrite or akaganeite *(Fig.12)*.

DISCUSSION

The slag at Aberavon beach is continually exposed to sea-water by rising and falling tides. At high tide the majority of the slag is completely submerged. Consequently the chemistry of some of the secondary minerals is due to the action of sea-water on copper-rich slag. Of the three polymorphs of $Cu_2Cl(OH)_3$, botallackite,clinoatacamite, and atacamite, only atacamite has been confirmed by XRD and IR analyses. The fourth known polymorph, paratacamite, which apparently requires zinc to stabilise its crystal lattice, (Jambor *et al.*, 1996) has not been detected. In the presence of high concentrations of sea-water, (sea-water is nominally 0.5 molar sodium chloride) the crystallisation of clinoatacamite is inhibited with atacamite being the more stable phase, (Hannington, 1993). Other workers have confirmed this observation (Pollard *et al.*,1989). The intriguing triangles of atacamite were perhaps formed by the action of copper-rich solutions, in the presence of sea-water, reacting with, and replacing, the trigonal crystals of calcite to yield atacamite. The original source of the calcite was probably the leaching of carbonate-rich solutions derived from beach sands in which there is a plentiful supply of calcareous seashells. Laboratory work has consistently shown that it is possible to synthesise atacamite by the action of dilute copper (II) chloride solution on calcium carbonate (Garrels and Stine, 1948,Sharkey and Lewin, 1971). Connellite is closely associated with atacamite. The presence of local concentrations of sulphate ions, probably derived from the decomposition of remote sulphides in the slag, leads to the preferential formation of connellite, whereas a depletion in chloride ion activity leads to the formation of brochantite and related basic sulphates. The suite of copper-arsenic secondary minerals associated with the slag probably reflects the use of copper arsenides, or possibly contaminants such as arsenopyrite, during the smelting process. The extreme rarity of secondary lead minerals also reflects the high grade of copper ore or concentrate smelted. Further work is underway to examine other slag localities in the Swansea area.

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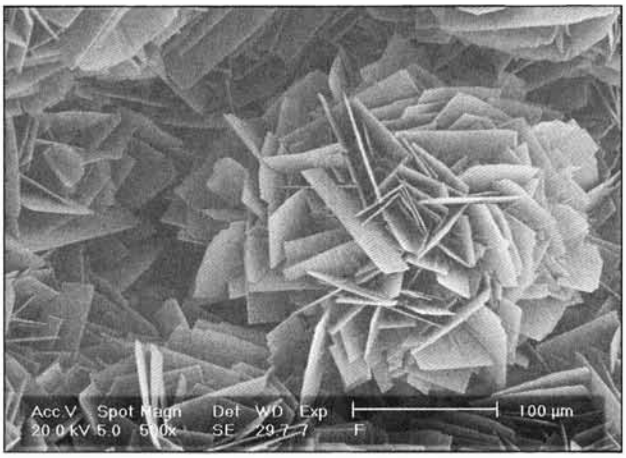


Figure 1. Interlocking platelets of atacamite. Magnification, x500. Field of view = 0.5mm.

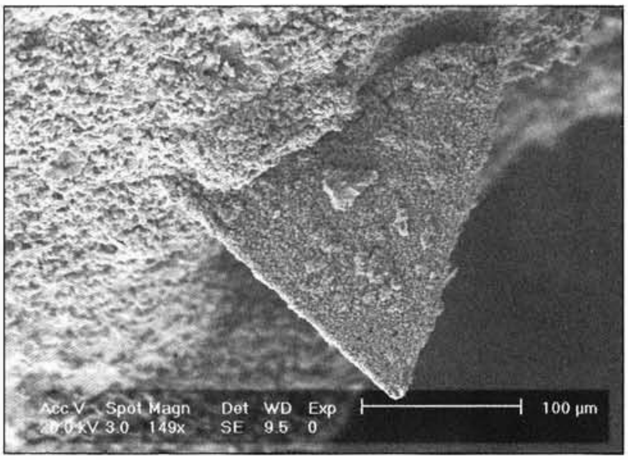


Figure 2. Atacamite pseudomorphing possibly calcite. The triangle is approximately 0.2mm on edge. Magnification,x149. Field of view = 0.5mm

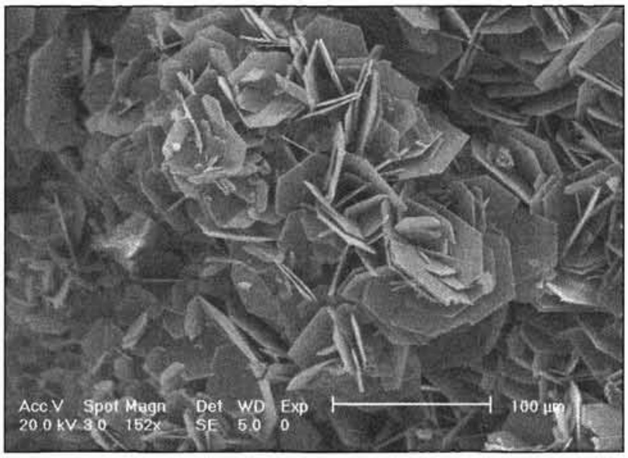


Figure 3. Pseudohexagonal interlocking plates of chalcophyllite. Magnification, x152. Field of view = 0.4mm.

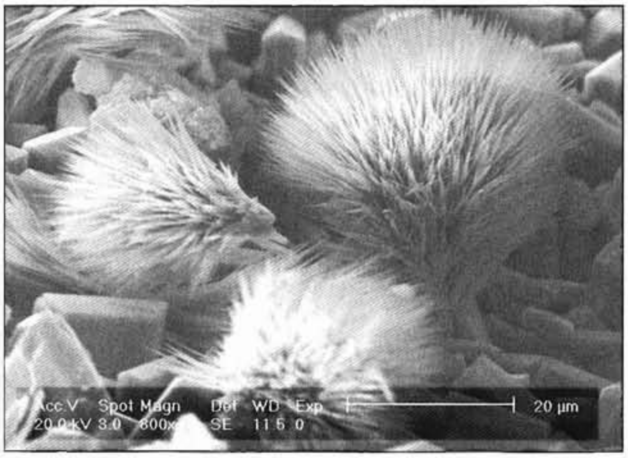


Figure 4. Acicular sprays of connellite on atacamite. Magnification,x800. Field of view = 0.08mm.

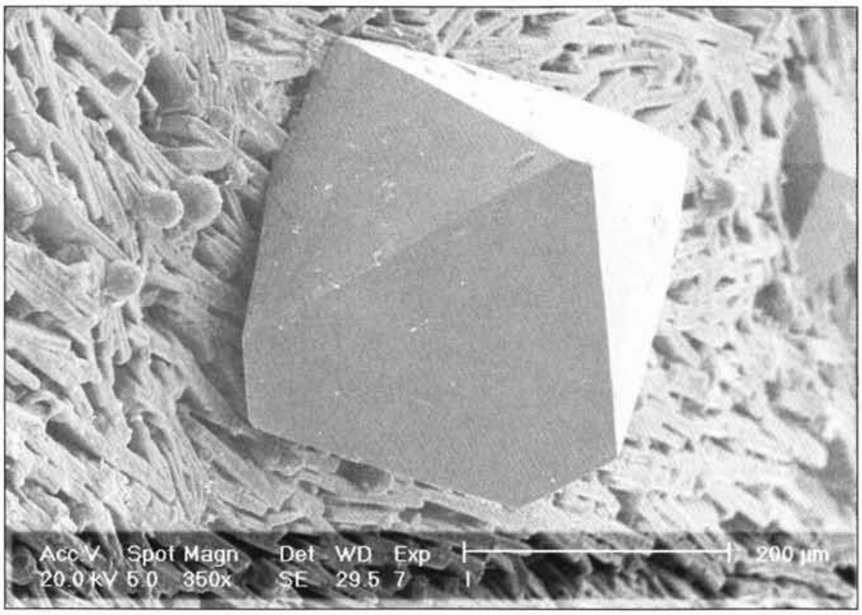


Figure 5. Octahedral crystal of cuprite on fayalite slag. Magnification,x350. Field of view = 0.6mm.

Figure 6. Chalcotrichite variety of cuprite with leaves of metallic copper. Magnification,x79. Field of view = 0.8mm.

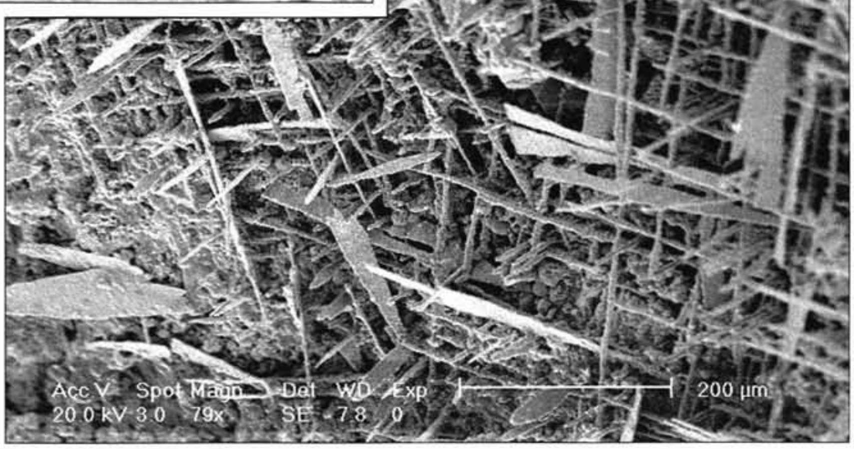
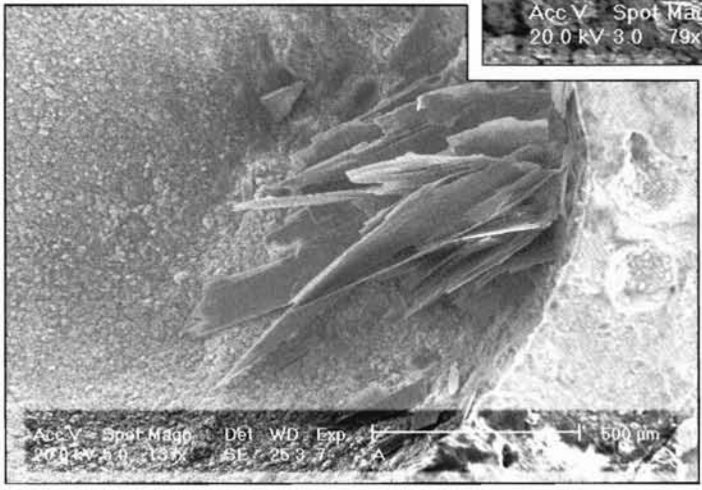


Figure 7. Thin lath-like plates of devilline in a slag vesicle. Magnification,x137. Field of view = 1.7mm.



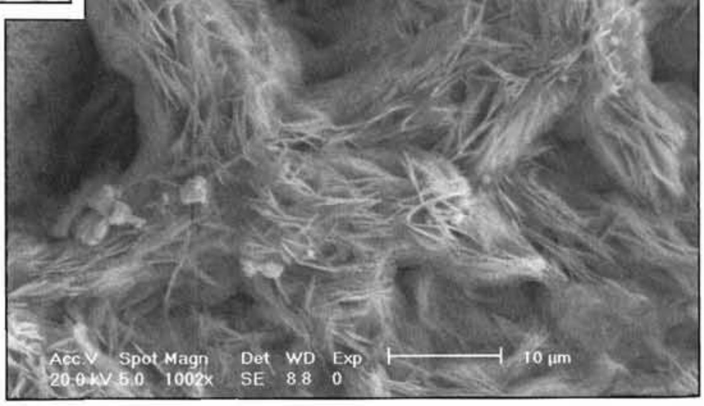


Figure 8. Thin interlocking plates of lavendulan. Magnification,x1002. Field of view = 0.06mm.

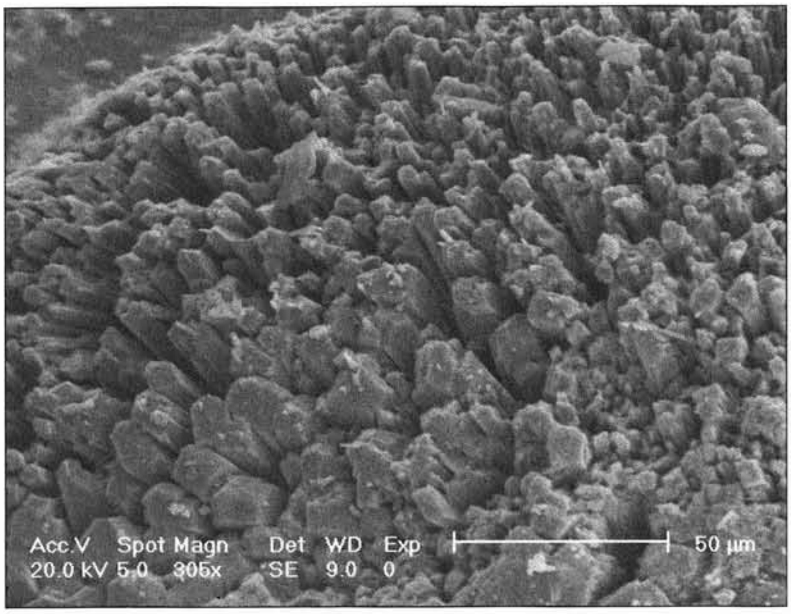


Figure 9. Radiating mass of lindackerite crystals. Magnification,x305. Field of view = 0.2mm.

Figure 10. Multi-faceted prisms of phosgenite. The central prism is 0.15mm in length. Magnification,x250. Field of view = 0.25mm.

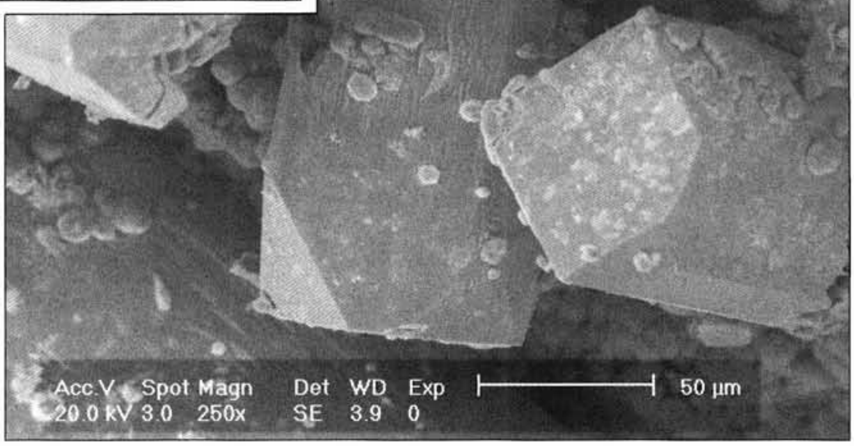
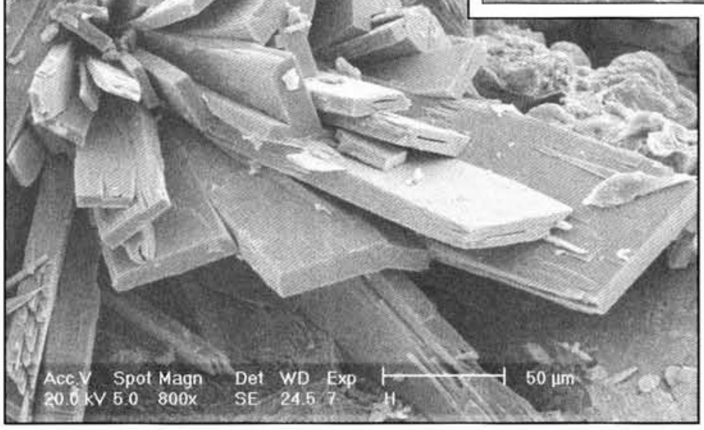


Figure 11. Prismatic plates of an unknown blue mineral. Magnification,x800. Field of view = 0.3mm.



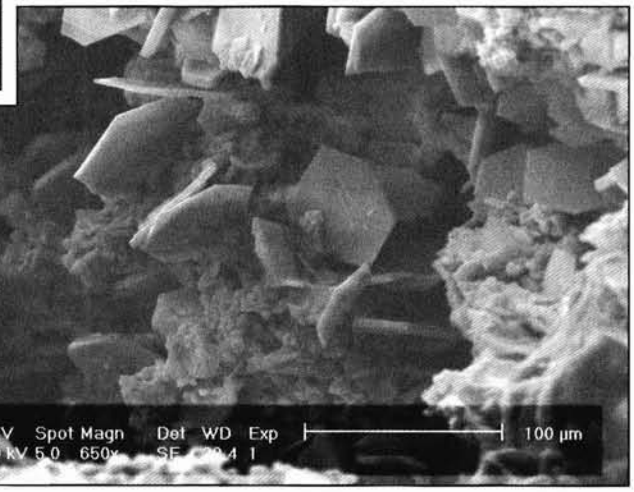


Figure 12. Unknown hexagonal plates in ferruginous slag. Magnification,x650. Field of view = 0.04mm.

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SYMPLESITE AND PARASYMPLESITE FROM CUMBRIA AND CORNWALL, ENGLAND

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INTRODUCTION

Symplesite and parasymplesite are dim-orphous monoclinic and triclinic iron (II) arsenates with idealised chemical formulae of $Fe^{2+}{}_3(AsO_4)_2.8H_2O$. Both minerals are relatively rare, typically being formed by supergene processes in the oxidation zones of arsenic-rich orebodies (Gaines *et al*, 1997).

In the British Isles, symplesite has been recorded at several localities the Lake District of Cumbria including Wanthwaite mine (Young., 1987); Nether Row Brow (Young *et al*, 1992), and Sandbeds Gill level (Thomson., 1997). Parasymplesite has been identified at Muckross mine, Co. Kerry, Ireland (Moreton *et al*., 1999), and Wet Swine Gill, Caldbeck Fells, Cumbria (Neall and Green, 2001). We report a number of addition discoveries of symplesite and parasymplesite in Cumbria and Cornwall

OCCURRENCES

Carrock mine in the Caldbeck Fells, Cumbria (NY 323 330) produced tungsten concentrates from high temperature wolframite-bearing quartz veins. A number of arsenic-bearing minerals including abundant primary arsenopyrite and the supergene species scorodite, arseniosiderite, olivenite and strengite have been recorded from the mine (Cooper and Stanley, 1990). Symplesite was identified by X-ray diffraction at Manchester Museum (X-ray reference number MANCH: XRD711) as poorly developed thin prismatic, sage green, crystals to 0.5 mm and in patches up to 1.5 mm across encrusting partly oxidised arsenopyrite. A small specimen (accession number N17113) is preserved in the Manchester Museum collection.

A diverse assemblage of supergene minerals including the arsenates erythrite and beudantite has been recorded from Tynebottom mine near Garrigill, Cumbria (NY 738 417) (Bridges and Young, 1998). The mine worked stratabound lead zinc orebodies in the Carboniferous limestone and sandstone of the Alston Block (Dunham, 1990). A dark green aggregate of poorly developed, somewhat rounded, bladed crystals to 1.0 mm on cellular limonitic quartz matrix with partly oxidised sulphides and etched carbonate was identified by XRD (reference numbers MANCH:XRD707 and XRD712) as an intergrowth of symplesite and parasymplesite. This, and similar specimens, are preserved in the collections of CML and TN.

Sandbeds Gill level is a small obscure copper trial in Skiddaw Slate at NY 2382 2896 on the western flank of Skiddaw, Keswick, Cumbria. A variety of supergene minerals occur in quartz veins containing chalcopyrite and galena. Symplesite, annabergite and erythrite were reported by Thomson (1997), and other arsenates including olivenite and parasymplesite have since been identified by XRD. Parasymplesite of end member composition occurs as minute steel blue to grey bladed crystals in cavities in vein quartz and, rarely, as radiating aggregates of deep blue to deep green prismatic blades. Pale blue to pale lilac crystals with compositions intermediate between parasymplesite, erythrite and annabergite (which are isostuctural) also occur. Some crystals are strongly colour zoned with pale- pink nickelian erythrite changing to a violet ferroan composition. At Sandbeds Gill level, parasymplesite is commonly pseudomorphed by white fine grained sodium-pharmacosiderite (identified by a combination of XRD and qualitative EDAX: XRD reference number MANCH:XRD688) and an amorphous red brown glassy phase. A suite of specimens from the locality is preserved in the TN collection.

Parasymplesite has been identified from Harriet's

Shaft Dump, Dolcoath mine, Camborne, Cornwall (SW 657 402). A specimen consisting of partially altered veinstone containing patches of a dark blue-green to deep forest-green fibrous mineral produced an X-ray pattern (XRD no. NMW:X-1275) consistent with parasymplesite. Spheres to 1 mm in diameter with a compact radiating fibrous internal structure occur in a matrix of finely crystalline primary siderite which cements small (generally <2mm) fragments of colloform-textured pyrite, arsenopyrite and occasional quartz. Siderite is present on the specimens as a bright yellow coating, which is almost certainly of recent supergene origin (XRD no. NMW:X-1274). Specimens are preserved in the Manchester Museum collection (MANCH: N16643) and at the National Museum of Wales.

DISCUSSION

Parasymplesite and symplesite are rare minerals that appear to have formed by recent (post-mining) supergene processes at most of the localities described above. The few symplesite specimens from Carrock mine were found with relict arsenopyrite on material collected from the dumps. At Dolcoath mine parasymplesite was almost certainly dump-formed and it is associated with recent supergene siderite (also an iron (II) mineral). At Tynebottom mine, most of the supergene arsenate mineralisation is post-mining in origin, as indicated by the abundant erythrite staining on the level walls. However, some specimens from Sandbeds Gill level were collected from *in situ* exposures, and are the product of natural weathering.

At Tynebottom mine, symplesite and parasymplesite crystallised at the edge of an area containing abundant post-mining iron (III) mineralisation, comprising highly limonitic cellular quartz, partly oxidised sulphides and etched carbonate. On the specimens collected to date, the iron (III) minerals are not in direct contact with parasymplesite or symplesite, although they are present on the same specimens. This suggests that the iron (II) arsenates crystallised from solution at the edge of a redox front in an area of reduced Eh, where iron (II) ions were stable.

Symplesite and parasymplesite are rare minerals at all of the localities described above. This is probably because solutions containing iron (II) are unstable with respect to iron (III) in the highly oxidising conditions encountered near the Earth's surface. Symplesite and parasymplesite are almost certainly unstable with respect to minerals such as scorodite and pharmacosiderite in highly oxidising conditions. The occurrence of sodium-pharmacosiderite pseudomorphs after parasymplesite at Sandbeds Gill level and of pseudomorphs of scorodite and pharmacosiderite after a mineral with a parasymplesite-like crystal habit at Burdell Gill and Sandbed mine, in the Caldbeck Fells supports this conjecture. In all of these cases, iron (II) arsenates have been pseudomorphed by iron (III) arsenates.

It seems likely that parasymplesite and symplesite are ephemeral minerals that form during the oxidation of arsenic-rich orebodies, only to be replaced by scorodite, pharmacosiderite and more stable iron (III) species as oxidation proceeds.

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TENNANTITE AND TYROLITE FROM THE COED Y BRENIN FOREST, NORTH WALES.

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The Coed y Brenin forest contains possibly the largest porphyry-type copper deposit in the British Isles with 200Mt of ore at a grade of 0.3% copper (Rich and Sharp, 1976; Miller, 1994) with the mineralisation disseminated throughout the host rock. This deposit shows characteristics of both the "diorite" and the " Lowell and Guilbert" models for porphyry copper (Allen, *et al.*, 1976), with a central mineralised core surrounded by zones showing propylitic and phyllic alteration. Principal copper minerals associated with this type of deposit are chalcopyrite, chalcocite, tennantite and enargite (Bevins and Mason, *personal communication)*.

Copper minerals previously reported from this deposit have been native copper, chalcopyrite, malachite, azurite, covellite, bornite and tetrahedrite (Rice and Sharp, 1976:Bevins, 1994).

We report here the findings of fieldwork in May 2000 where a forest road-cut (NGR SH 748 256) in the phyllic alteration zone exposed significant porphyry mineralisation. The outcrop consisted of a low bank with considerable seepage of groundwater along pronounced fracture planes.

In the sample collected, a silvery metallic mineral surrounded by an alteration halo of blueish-green crystalline was found disseminated throughout a pod-like area within a groundmass of intensely sericitised microtonalite. The patches of mineralisation were up to 1 by 4mm.

Examination by XRD (NHM film 11643F) suggested that the metallic mineral was tennnatite. A polished block (NMH P10002) was prepared for examination by reflected-light microscopy, and by microprobe analysis with an Hitachi S500 Scanning Electron Microscope and associated Link 200 Analytical Package.

Results from the microprobe analysis showed that the metallic mineral had a composition on copper, arsenic, iron and sulphur with a trace of antimony, which was consistent with the mineral being tennantite.

Tennantite, $(Cu, Fe)_{12} As_4S_{13}$, forms one end member of a series with tetrahedrite, $(Cu, Fe)_{12} Sb_4 S_{13}$, in which some of the copper may be substituted by iron. The tennantite grain, together with others in the block, showed a distinct alteration rim with much cracking. Further examination revealed that covellite and bornite were present whilst the infill of cracks contained high levels of copper, aluminium, arsenic and mercury.

XRD analysis (NHM film 11644F) showed the blueish-green alteration material to be a mixture of tyrolite, $CaCu_5 (AsO_4)_2 CO_3(OH)_4.6H_2O$, and malachite. It is suggested that these two minerals are a consequence of later weathering processes and not of the hydrothermal activity responsible for the formation of the deposit.

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THE SECONDARY MINERALOGY OF THE CLYDE PLATEAU LAVAS, SCOTLAND
PART 4. REILLY QUARRY

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Note. *Please address reprint requests for this article to the Editor*

Calcite, quartz and baryte mineralisation associated with minor amounts of sulphides and various silicates, including zeolites, occur in basalt lavas at Reilly quarry, Houston, Renfrewshire. The mineralisation differs from the more typical prehnite-rich assemblages that characterise the district and is probably related to a Permo-Carboniferous quartz-dolerite dyke that cuts across the quarry.

INTRODUCTION

Reilly quarry (National Grid Reference NS 419 695) is situated about 2.5 km NNE of Houston, Renfrewshire. It worked both the Lower Carboniferous Clyde Plateau lavas of Dinantian age and a Permo-Carboniferous quartz-dolerite dyke traversing the quarry *(Fig. 1)*. Although part of the quarry is now used as a landfill site, the remainder is still being worked for roadstone. Of the other localities described in this series (Meikle, 1989a, 1989b, 1990), Loanhead quarry lies 15 km SSW, Hartfield Moss 12.5 km south, and Boyleston quarry 12.5 km SE of Reilly quarry. Although the geology at these localities is broadly similar, the presence in Reilly quarry of the E-W trending Permo-Carboniferous quartz-dolerite dyke has resulted in a somewhat different suite of minerals from that adjacent to the NW-SE trending Tertiary tholeiite dyke at Loanhead quarry (Meikle, 1989b).

GEOLOGY AND MINERALOGY

The prominent, very broad, quartz-dolerite dyke of Permo-Carboniferous age (Macgregor and Macgregor, 1948), which trends here just south of west, runs more or less along the mid-section of the quarry *(Fig. 1)*. Such dykes are composed of basic feldspar, augite, hornblende, quartz and apatite, with occasional hematite and, quite often, abundant pyrite (Macgregor and Macgregor, 1948). The lavas are mainly macro-porphyritic olivine basalts of Markle type, both vesicular and amygdaloidal, and several flows can be seen in the quarry faces. Immediately north of the dyke the lava of the quarry face was noted to be highly altered, the result presumably of a hydrothermal aureole originating from the dyke. This altered lava is hereafter referred to as "botryoidal" because of the characteristic botryoidal surface appearance commonly noted where a number of unusual species occurred as reported below. A prominent, roughly ENE-WSW trending, vein of barite up to 50 cm wide at the quarry floor cuts the lavas approximately 40m north of the dyke.

The minerals described below were collected from the excavated area along the length of the north edge of the dyke and immediately north of this, as well as from the quarry face adjacent to the barite vein.

ALBITE, $NaAlSi_3O_8$

Brownish orange sub-millimetre crystals intergrown with tiny quartz crystals occur in small vesicles in altered lava. In the larger cavities it may be overgrown with calcite. In one vesicle, 12 mm across, these crystals formed fine leafy plates of albite overgrowing white orthoclase *(Fig.2)* and accompanied by chlorite. Both feldspars were identified by XRD and EDAX.

ANALCIME, $Na\,[AlSi_2O_6]\,.H_2O$

Colourless, semi-transparent, well-formed crystals of analcime (<3 mm) occur with blocky crystals of calcite and opaque pinkish-white platy aggregates of baryte, adjacent to the border of the dyke and the baryte vein. Small (<1.3 mm) opaque well-formed crystals frequently occur in the botryoidal lavas. The analcime was confirmed by visual examination and the well-developed crystal form.

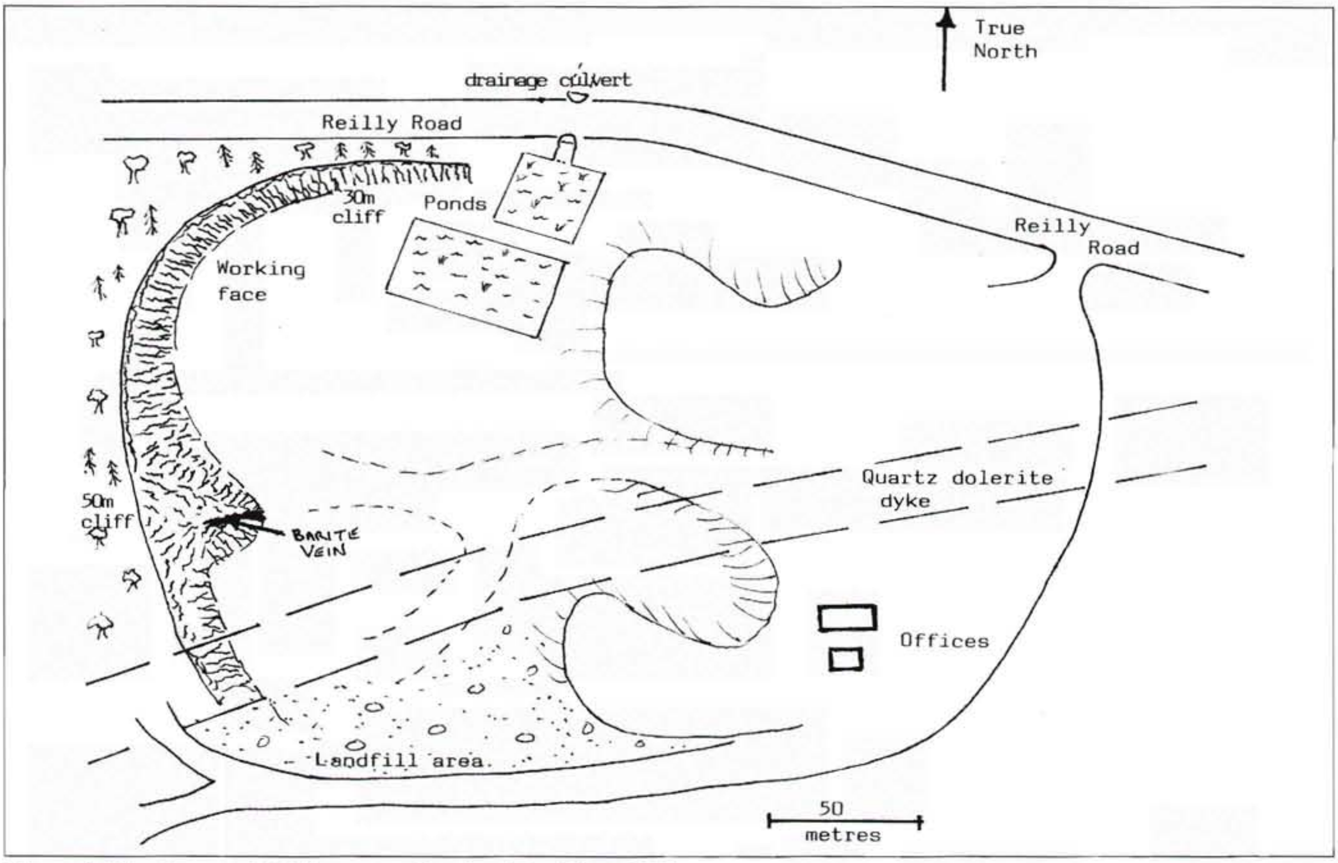

Figure 1. Sketch-map of Reilly quarry, Renfewshire (May, 1999).

ANDRADITE, $Ca_3Fe^{3+}_2(SiO_4)_3$

Small garnet crystals occur singly, associated with rhombic growths of calcite in the altered dolerite at the edge of the dyke; IR spectroscopy shows them to be andradite. They are generally well-formed, pale honey- to yellowish-brown in colour, 0.2–0.8 mm in size, and often form a margin with, or are embedded in, the calcite. Similar crystals, 1.5–2 mm in size, accompany epidote and small analcime crystals, occurring generally as single crystals embedded in the epidote, or closely grouped there in small pockets. Darker crystals noted occasionally in association with specular hematite are also andradite (IR identification).

BARYTE, $BaSO_4$

Secondary crystallisation of baryte occurs in the lava in close relationship to the edge of the dyke. This takes the unusual form of very fine cockscomb aggregates of pale pinkish-white, leaf-like platy crystals whose tapering terminations separate to show the cockscomb effect. The aggregates vary in size up to about 20 x 30 mm with individual plates to about 5 x 20 mm. The unusual features were not apparent at the baryte vein exposure, or in the vicinity of the quarry face. Despite the distance from the dyke it seems highly likely that hydrothermal activity took place in this general area and was responsible for the secondary mineralisation mentioned above. The vein is mainly opaque white and platy in character, bordered on both sides by veins of calcite reaching 10 cm in width. The vein is seen to narrow as it rises up the exposed face of the quarry, as do the bordering calcite veins. Individual barite crystals, up to about 5mm, occur frequently adjacent to, and often intergrown with, the calcite which displays well-crystallised joint surfaces *(Fig.3)*.

CALCITE, $CaCO_3$

Calcite occurs both as colourless, transparent, rhombohedral growths (<40mm), and as well-

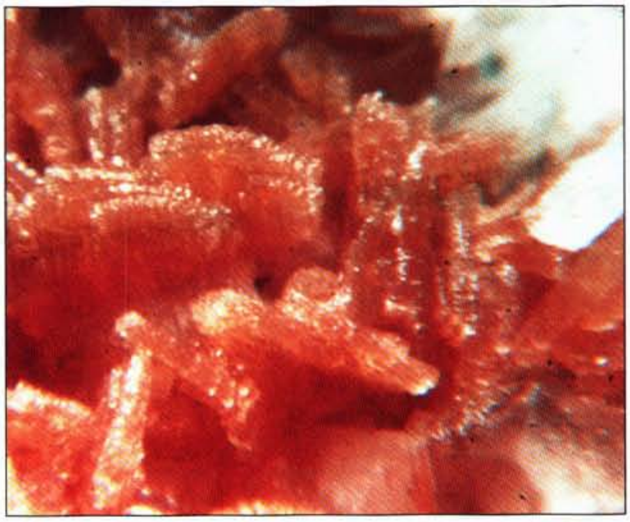

Figure 2. Albite, pink crystals (<0.5mm), with orthoclase.

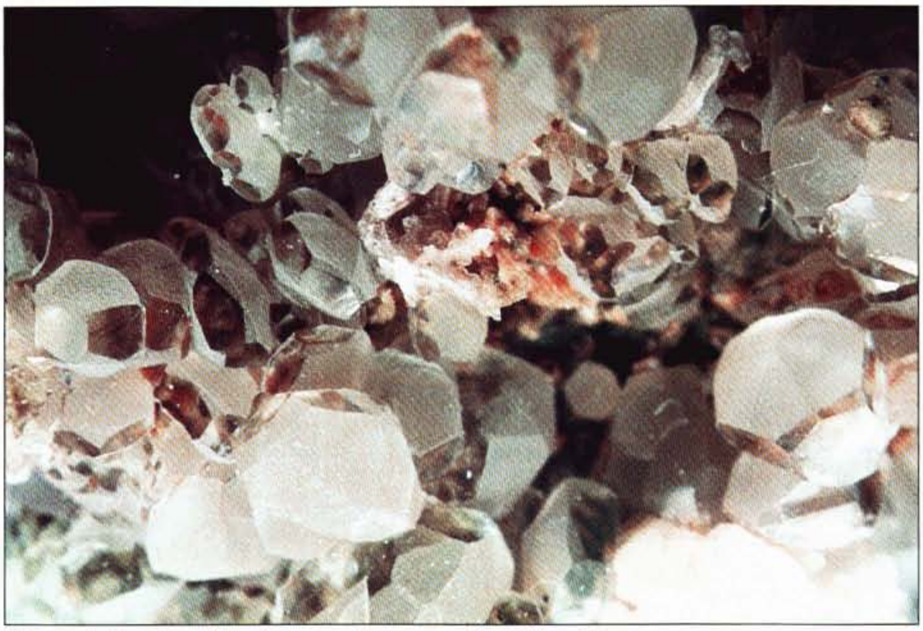

Figure 3. Baryte, pink platy crystal aggregate with calcite crystals on altered lavas. Width of field 18 mm.

formed crystals in close association with other species, at the edges of the quartz-dolerite dyke. The crystals are generally sharp, scalenohedral or pyramidal, prisms varying in size up to about 8 mm, and frequently accompany analcime or quartz crystals in cavities. Calcite also often accompanies stilbite in the highly altered botryoidal lavas, as transparent but multi-twinned crystals displaying many triangular, pyramidal terminations in parallel growth. On one specimen the calcite is of "nailhead" habit, i.e. flattened positive and negative rhombohedra with frosted faces, up to 3 mm across, on lustrous transparent stubby prisms up to 1 mm long *(Fig.4)*. Occasionally, small transparent scalenohedral faces cut the prism edges and rhombohedral faces to create bevels. The striking reflective difference between the faces makes these crystals very attractive. Occasionally the rhombohedral calcite is closely associated with garnet crystals and/or epidote crystal coatings on the dolerite, and is frequently coated, or stained, by included hematite. Calcite is the most abundant mineral at Reilly quarry.

CHLORITE

A chlorite occurs as dark-green bladed aggregates (<0.2 mm) in small vesicles, or as blackish-grey botryoidal aggregates lining, and sometimes filling, small cavities in altered lavas where they are often coated by a whitish later deposit. The species of chlorite has not been determined.

EPIDOTE, $Ca_2 Fe Al_2 (Si_2O_7)(SiO_4)(O,OH)_2$

Epidote occurs commonly on the altered dyke matrix as apple- to pistachio-green coatings and growths of small transparent platy crystals (up to 0.5 mm x 0.2 mm in size) that show either a square termination or, occasionally, the more common wedge. It is frequently associated, and intergrown, with small (<0.5 mm) opaque whitish crystals of analcime. It was identified by visual examination.

HEMATITE, Fe_2O_3

Hematite is relatively common in the alteration zones examined, but often occurs only as earthy coatings interspersing calcite and quartz crystallisations, or staining the matrix. It also forms inclusions in the calcite or, less frequently, the quartz crystals. Hematite was confirmed visually by both its crystal form and translucent blood red colour, as it occurred in the inclusions. Specular hematite also was noted in association with andradite as mentioned above.

NATROLITE, $Na_2 [Al_2Si_3O_{10}] 2H_2O$

Fan-shaped aggregates of opaque whitish crystals up to 30 x 1.5 mm in size have been identified by XRD and EDAX as natrolite. They are occasionally accompanied by dark lustrous chlorite.

PYRITE, FeS_2

This occurs as well-crystallised bright yellow coatings, up to 50 mm across, on unaltered dolerite; as irregular aggregates, up to 10 mm across, on the surface of altered dyke material; or

Figure 4. Calcite, doubly-terminated "nailhead" crystals up to 3 mm across, on altered lavas. Width of field 17.5 mm.

as single crystals and very small aggregates, sometimes accompanying calcite or impregnating the unaltered dolerite matrix.

QUARTZ, SiO_2

Quartz crystals are relatively common, second only to calcite in abundance. They appear to have been mainly formed during late, low-temperature, hydrothermal activity principally in the lavas adjacent to the dyke. Here they form stubby (doubly-terminated ? in parallel growth), colourless transparent crystals up to 3 mm long. Quartz also forms coatings of closely grown semi-transparent prisms (up to 0.3 x 0.1 mm) with short pyramidal terminations, covering quite large areas of altered lavas; they are frequently overgrown by small calcite crystals.

SPHALERITE, ZnS

Sphalerite occurs here as highly unusual multi-twinned spherical growths up to 2 mm across. They are semi-transparent, very pale-grey, and display highly lustrous triangular faces overall indicative of concentric growth. The spherules were found on only two specimens, associated with well-formed calcite crystals and creamy-pink cockscomb baryte. The spalerite was visually identified from lustre, colour and crystal form.

STILBITE, $(Ca_{0.5}, Na, K)_9[A_{19}Si_{27}O_{72}]\ 28H_2O$

A member of the stilbite series occurs in shallow cavities in the lavas adjacent to the dyke, associated with quartz and calcite. It forms random aggregates of small (<1.5 x 0.3 mm) of colourless, transparent, well-formed, doubly-terminated crystals. These are sometimes obliquely twinned or intergrown with each other. In addition larger crystals (up to 3 mm long), sometimes also doubly-terminated, form parallel aggregates of 3-4 individuals, each with typical wedge terminations. Identification came from this observation of the typical crystal form and wedge terminations, coupled with physical and chemical tests.

DISCUSSION

The suite of minerals identified at Reilly quarry differs somewhat from those found at Boyleston quarry, Loanhead quarry, and Hartfield Moss (Meikle, 1989a, 1989b, 1990). Thus prehnite is absent, as are the copper minerals and native silver which occur in small amounts at the other three localities. Andradite, pyrite and sphalerite are found at Reilly quarry but not at the other localities. Furthermore, the specimens generally seem to be scarcer and smaller. The extensive hydrothermal activity, which resulted in the distinctive mineral assemblages at the other localities, seems not to have taken place at Reilly quarry. Why this should be is unclear and, in the absence of data on the nature and origin of the fluids involved, it is not possible to draw firm conclusions. The field relationships of the minerals from Reilly quarry, as described herein, are consistent with formation during, and after, hydrothermal activity resulting from the intrusion of the dolerite dyke into the lavas. This appears to be different, and less extensive, to that experienced at the other localities cited above. Much of the mineralisation present can be related to the quartz-dolerite dyke, since many of the minerals described here are concentrated in the region of the intrusion.

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MINERALS FROM ORROCK QUARRY, FIFE REGION, SCOTLAND

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During the 1970s and 80s Orrock quarry, Fife, revealed two distinct types of mineralisation in Lower Carboniferous basalts in separate zones of the quarry. In the lower levels, fissures were filled with brecciated basalt and a variety of minerals, mainly calcite, prehnite, pectolite and apophyllite with minor natrolite. In the upper levels veins, and stockworks of veins, consisted primarily of calcite and quartz.

INTRODUCTION AND GEOLOGICAL BACKGROUND

Orrock quarry is a large working roadstone quarry on the west side of Orrock Hill, approximately 3 km NW of Burntisland, Fife Region, Scotland [NT216 887]. Orrock Hill is composed of a succession of basaltic rocks that belong to the Kinghorn Volcanic Formation of the Lower Carboniferous (Asbian) Bathgate Group. The rock types comprise a succession of microporphyritic olivine basalts, which include olivine-phyric and olivine-clinopyroxene-phyric types. Whereas many of the olivine basalts are interpreted as of sub-aerial origin, the presence of basaltic pillow lavas and basaltic hyaloclastites indicate a sub-aqueous origin for parts of the volcanic succession. Spectacular columnar jointing is characteristic of many of the basalts.

Detailed descriptions of the geology of the area include those by Francis (1961) and Browne *et al.*, (2000).

MINERALISATION

Joints and fractures within the basalts at Orrock quarry are commonly coated by a variety of minerals. Two discrete suites of mineralisation could be seen within the quarry during the 1970s and 80s, a lower zone in the lowest 50 m of the workings exhibiting a fracture containing abundant apophyllite, pectolite etc, and an upper zone in which the mineralisation consisted mainly of quartz and calcite.

In the lowest workings, one of these fracture fillings, partly exposed on the floor of the quarry in the early 1970s, comprised a NE-SW trending 'vein', which was 6 m high and locally up to 50 cm wide, composed principally of pectolite and apophyllite with smaller amounts of prehnite, natrolite and calcite. This was deduced from the remaining blocks of quarried material at the foot of the face: there was very little of the original vein in situ. Some of the remaining blocks consisted of fragments of altered basalt cemented with pectolite and other minerals. This basalt appeared rather altered, perhaps slightly chloritised. Other blocks, at the foot of the vein, showed a succession of layers of the three main constituents. These layers ranged from 2 mm to 10 mm thick, suggesting separate periods of deposition. Elsewhere, in the lower faces of the quarry, narrower fractures or joint fillings, typically up to 5 cm wide, were densely filled with pectolite.

Fractures in the upper part of the quarry exhibited veins and stockworks that were typically filled with calcite and quartz, substantial amounts of which were well crystallised (S.Moreton, *personal communication*).

All material collected from the upper level came from loose blocks and was not seen in situ, it was however evident that it came from the adjacent quarry face. It seems that there were several short periods of deposition as suggested by the different layers: buff-coloured calcite rhombohedra followed by colourless calcite, then quartz.

Brief descriptions of the minerals present in the two zones follow:

Lower levels of the quarry.

Most of the specimens mentioned came from loose blocks at the foot of the remaining vein.

APOPHYLLITE

Colourless, transparent crystals of apophyllite up to 10 mm across were common. These occurred as truncated tetragonal bipyramids with minor prismatic faces *(Fig.1)*. Heddle (1901), Plate LXXV, *Fig.12* No.435 described a similar habit from Storr, Isle of Skye. The apophyllite specimens from Orrock were identified by X-ray diffraction at the National Museum of Scotland (X-ray photograph No.608). Apophyllite crystals occurred scattered on prehnite, calcite or pectolite. Some were also found on a fine-grained, soft calcite (effervescence in acid and

Figure 1. Apophyllite on pectolite, Orrock quarry.

optical properties), un-attached to any other rock. In some instances apophyllite was found growing on the terminations of pectolite blades.

BARITE

A single, small (10x10x3 mm), barite crystal, tabular on (001) was collected from loose material on the NW side of the quarry floor, 20 m from the face and 50 m from the 'pectolite' vein. It could not be related to any other vein.

CALCITE

Crystalline white calcite, as layers up to 2-3 mm, was common as well as large, colourless, transparent cleavages up to 3 cm. Some of the calcite exhibited a pink tinge. A few, well formed, complex twinned rhombohedral crystals were found on prehnite.

CHALCOPYRITE

A few specimens of chalcopyrite, comprising small (1 mm) tetrahedra, associated with a group of very small, black, bladed hematite crystals, were found encrusting pectolite on calcite in the fissure fillings.

HEMATITE

A 2 mm mass of black hematite scales (0.05 mm) was found associated with chalcopyrite as described above. It was identified visually by habit and the steel blue appearance of some scales. In some cases, minute (0.3 mm) spherules of hematite encrusted the sides of the pectolite blades. Their identity was confirmed by X-ray Fluorescence Spectroscopy at the National Museums of Scotland.

NATROLITE

Aggregates of parallel crystals, up to 20 mm long and 0.3 mm across, were found sparingly in association with pectolite and apophyllite.

PECTOLITE

Pectolite was found to be comparatively common in joints and fissure fillings. Much of the mineral occurred as compact, rather tough, aggregates in veins up to a few centimetres wide. The wide vein yielded good examples of free standing blades, generally 2 x 0.8 x 0.02 mm in size, in masses up to 20 cm across *(Fig.2)*. Whereas the compact material appeared to be needles, the commonest free- standing crystals were thin blades. These were identified by their optical properties and confirmed by X-ray diffraction (photograph number 613) at the National Museum of Scotland. Some of the pectolite masses were encrusted with calcite or prehnite.

As noted above, there were often several layers of deposition. A typical example showed wall rock followed by 7 mm of compact pectolite, then a 30 mm calcite cleavage capped with 0.5 mm of prehnite. The next 2 mm of compact pectolite was covered with 3-5 mm of botryoidal prehnite. The free standing pectolite blades standing on this prehnite were themselves locally encrusted with a few small (0.1 mm) crystals of prehnite. These various layers were identified by their optical properties, as described by Fleischer, M. *et al.*, (1984). Occasionally fibrous pectolite was found as a thin coating on basalt wallrock.

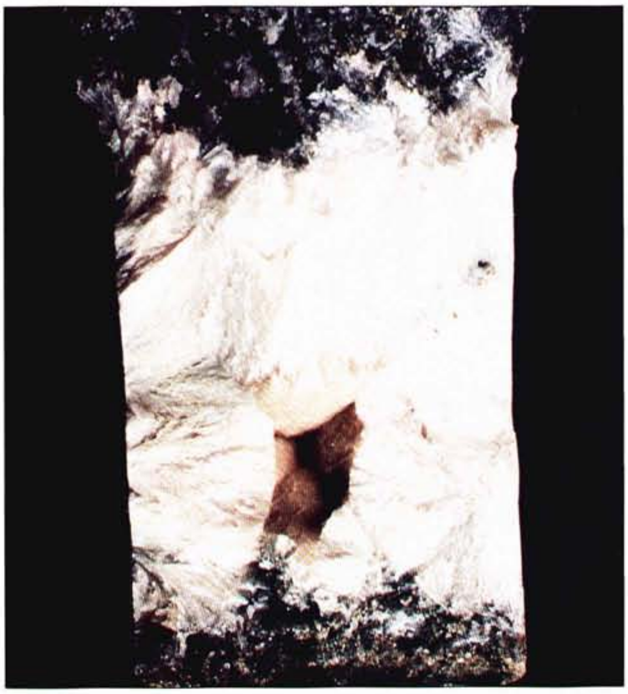

Figure 2. Pectolite in a 4 cm fissure, Orrock quarry

PREHNITE

Prehnite was commonly found as white, or very pale green, globular masses with crystal terminations. As mentioned above, minute, free standing, crystals of prehnite were found on the sides of pectolite blades. These were identified by their habit and optical properties, as described by Fleischer, *et al.*, (1984)

SPHALERITE

Two very small crystals of brown sphalerite, 1.2 mm across were found, between pectolite blades. One of these was identified by X-ray diffraction (photograph number 1176) at the National Museum of Scotland.

Upper levels of the quarry

CALCITE

On the upper level of the quarry, calcite was abundant as small (up to 10mm), buff-coloured rhombohedra. Larger crystals up to 50 mm across were also found (S.Moreton, *personal communication*). Small (up to 15 mm) translucent to transparent crystals, tabular on (0001) were also found and one of these showed even smaller (3 mm) crystals growing at right angles from a prism face and parallel to the incipient cleavage planes visible internally. A larger (3 cm) transparent crystal was a flattened rhombohedron.

Over some of the buff-coloured rhombohedra there were colourless, well formed complex twinned rhombohedra, up to 5 mm in size. Amongst these was a prismatic calcite with a complex termination.

GOETHITE

Sprays of goethite needles up to 2 mm in length were found both on buff-coloured calcite and on quartz crystals. Smaller sprays (<1 mm) were found enclosed within quartz.

HEMATITE

Small rosettes, up to 1 mm across, of black hematite scales were found either encrusting or within quartz. The hematite was identified visually.

MARCASITE and PYRITE

Thin, striated blades, up to 1 mm long, tentatively identified as marcasite, as well as pyrite cubes (0.5 mm), both tarnished to a dark hue, were found on both transparent and buff-coloured, rhombohedral calcite. Identification was visual.

QUARTZ

Quartz and calcite were both abundant amongst the boulders on the top bench. Three specimens of milky quartz crystals up to 15 cm long in groups up to 40 cm across were found. Only very small crystals were perfectly transparent. Amethystine crystals were fairly common, but never greater than 2 cm long, in masses up to 15 cm across. They varied from pale to medium purple. A quarryman reported finding an amethyst crystal slab up to 40 cm across. Locally, unattached, doubly terminated, quartz crystals up to 4 mm were found.

ACKNOWLEDGEMENTS

I would like to thank Dr.A.Livingstone of the National Museums of Scotland for various identifications by XRD. I am grateful to the then Orrock quarry manager, Mr J.Mckenna, and Wimpey Asphalt, the owners at that time, for permission to collect mineral specimens. I am also indebted to B.Young for help and useful suggestions.

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Note:

A.Livingstone, (2002). *Minerals of Scotland, Past and Present,* National Museums of Scotland Publishing Limited, p.126 mentions a large 'cairngorm' in the Heddle collection given to the NMS by Miss R.Orrock.

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CALCIUM ANALCIME FROM THE TOTHERICK AYRSHIRE, SCOTLAND: AN UNUSUAL CRYSTAL FORM WITH TRAPEZOIDAL FACES

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An unusual form of analcime from King's quarry, The Totherick, nr. Dunlop, Ayrshire has been analysed by XRD, XRF and thermal analysis. The analyses suggest that it is the first record of a natural calcium analcime.

INTRODUCTION

The zeolite analcime commonly occurs as well-defined icositetrahedral (trapezohedral) crystals. Heddle (1893), however, describes a curious form of analcime found by a Mr Robert Kidston FGS of Stirling at Earlsburn reservoir on Touchadam Moor near Stirling "just after the reservoir had been completed". Professor Heddle based his identification on "colour, lustre and transparency" and provided a rough sketch of the crystal, said to be less than "$^1/_4$ inch in length" and "of inexplicable form". He remarked that they resembled pseudomorphs of "dog tooth" calcite but that closer inspection showed them to be "acute four-sided pyramids". These pyramids were not merely crystals distorted "through the two pairs of lateral faces of the icositetrahedra being reduced to mere linear dimensions". They were likened to interpenetrating crystals rather than twins. A reproduction of Heddle's sketch is in *Fig. 1*.

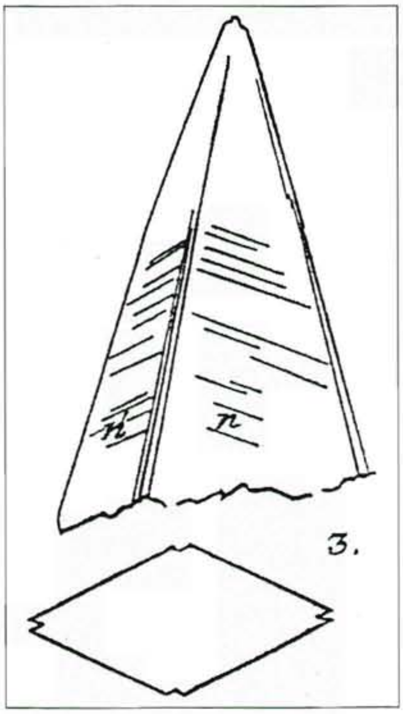

Figure 1. Pyramidal analcime, Heddle (1893).

Tschernich (1992a) noted analcime has been recorded as massive radiating columnar prisms that showed complex intergrowths of trapezohedra when terminations can be seen. A radiating analcime has been identified in the Antrim basalts (H. Foy, *personal communication*), and a "cubic" form occurs at Mont Saint-Hilaire, Quebec, Canada (Q.Wight, *personal communication*).

Figure 2. Pillared crystal (approx. 13mm high) from King's quarry, The Totherick, nr, Dunlop.

Tschernich (1992a) comments that non-icositetrahedral forms of analcime are very rare.

We have identified a pyramidal mineral (see *Fig.* 2) from King's quarry, The Totherick, nr. Dunlop, Ayrshire, NGR NS 4450 5100, and now in-filled. The material occurred in a large single boulder (1.5m x .75m) in a host rock that has been described as a trachyandesite of the Carboniferous Lavas. The crystals were striated, and were either clear or, more commonly, brown stained. The bases of the pyramids (*Fig.* 3) varied

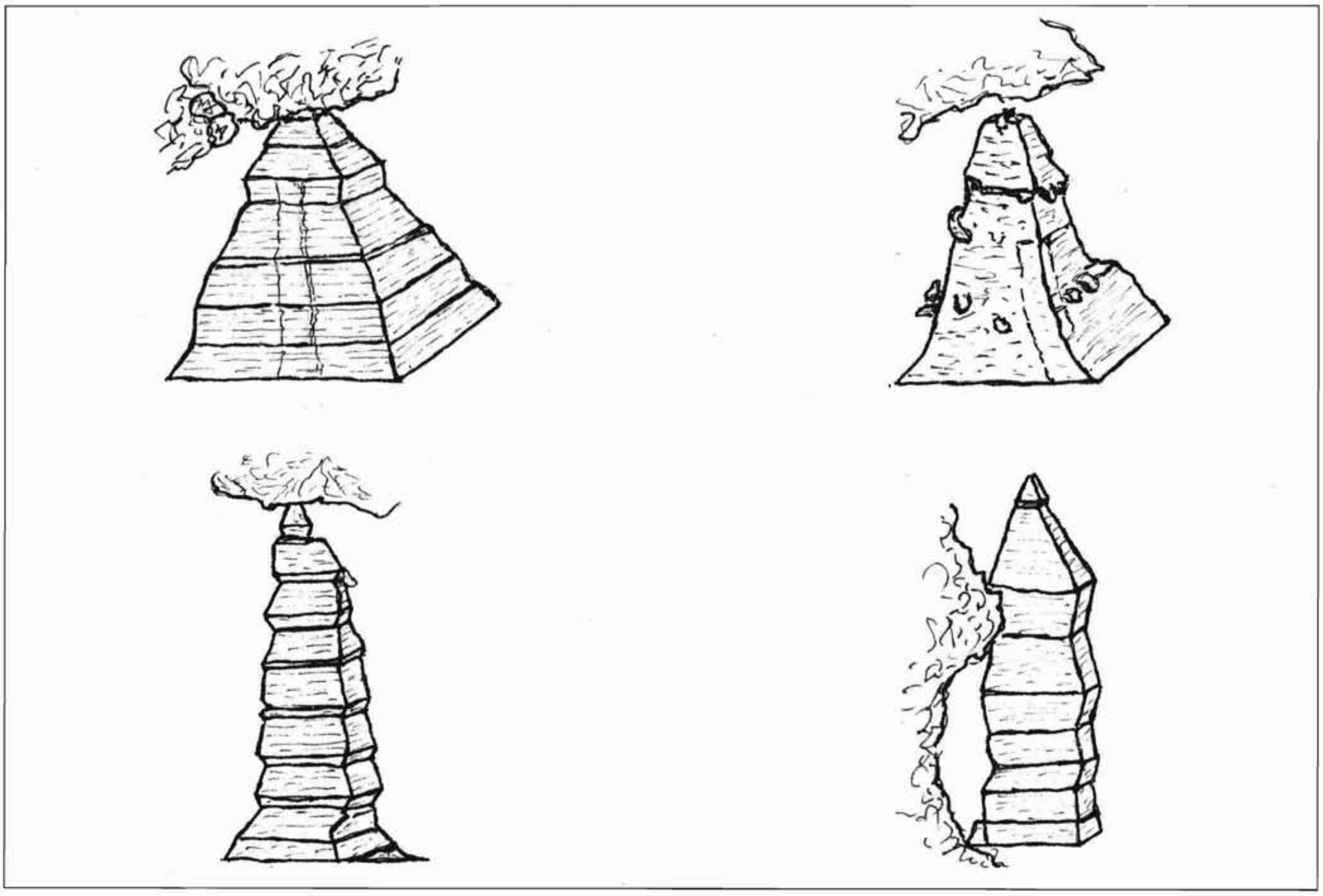

Figure 3. Sketch of crystals from King's quarry, scale approximately x 5

from 2-11mm and their heights were in the range 2-14mm. Some crystals resembled a concertina (*Fig. 3*). This paper identifies them as a calcium analcime.

EXPERIMENTAL

X-ray powder diffraction patterns were collected using a Phillips PW1710 with graphite monochromated Cu Ka X-rays. The diffractometer was interfaced with a microVAX3100 incorporating a full ICDD searchable database. X-ray fluorescence analysis used an ARL 8410 fitted with an end window rhodium X-ray tube and fully calibrated using 40 international standards. Differential thermogravimetric analysis was carried out using a Mettler TA 3000 system at a heating rate of 10K/min-1.

EXPERIMENTAL RESULTS AND DISCUSSION

The analyses gained from XRF are listed in Table I, which includes those carried out for comparison on a sample of icositetrahedral analcime collected from Barrhead quarry, Renfrewshire (NGR NS 4925 5975). Analysis of the Barrhead sample established the presence of both sodium and calcium. Published analyses of analcime indicate that this is a frequent occurrence (Gottardi and Galli, 1985a). The analytical data show that the Totherick mineral contains calcium but no sodium. The iron content is notably high.

Table I also contains an analysis for wairakite, a zeolite that is isostructural to analcime but has calcium as its major cation- often with very small sodium content (Tschernich, 1992b).

The elemental analysis suggests that the pyramidal crystals might be a form of wairakite, however the X-ray results (Table II) must also be taken into account.

These show that the Totherick material corresponds well to the literature values for analcime, with the shrinkage expected from the replacement of sodium by calcium. Differences were evident from the pattern obtained for a wairakite from Wairaki, New Zealand (Gottardi and Galli, 1985 b), especially the absence of the line at the maximum d-spacing of 6.82 Å.

Fig. 4 shows the differential thermogram of the pyramidal crystals. It can be seen that 3 mass losses have occurred. The one in the region of 200 C probably arises from the burning off of a small amount of organic material and that at c.530 C

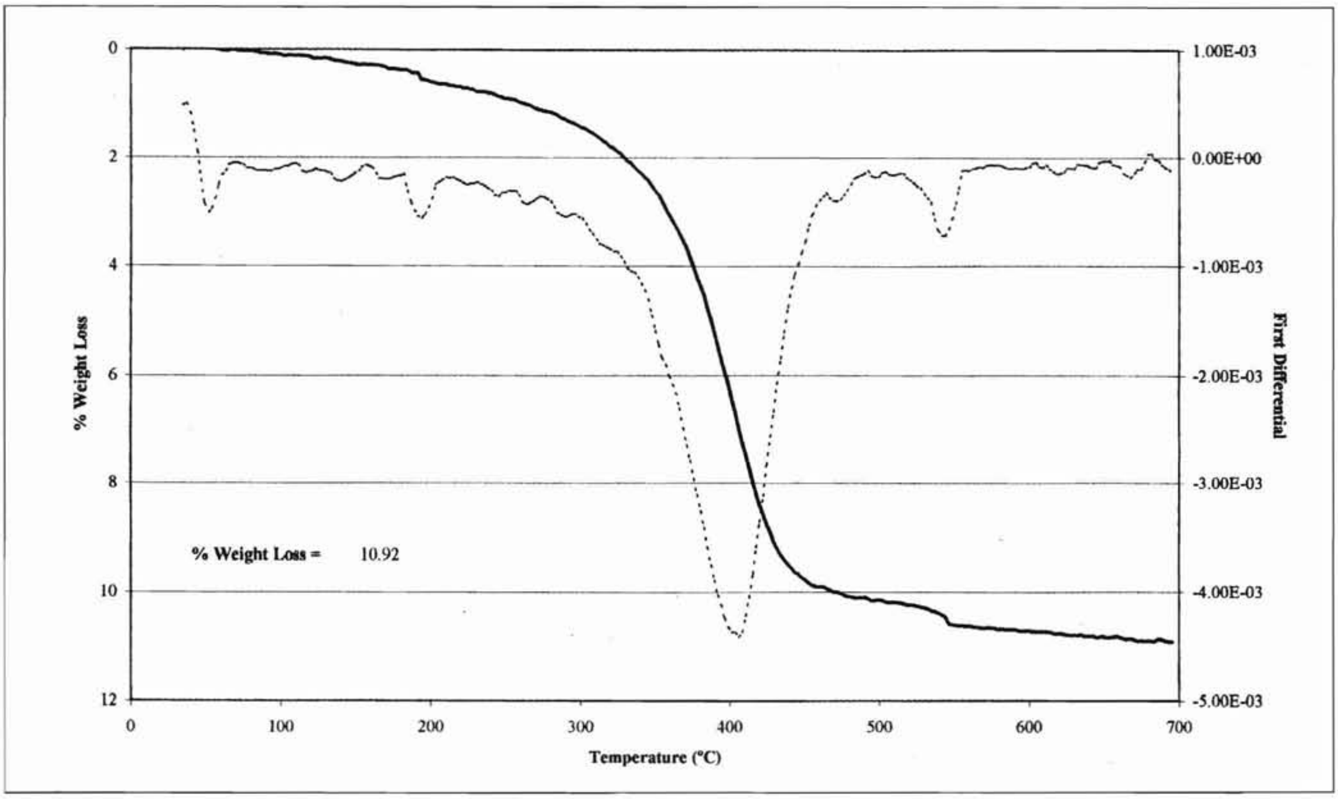

Figure 4. Differential thermogram of a pillared crystal.

from a calcite impurity. The mass change at close to 400 C is a typical zeolitic water loss.

Analcime loses its zeolitic water in a diagnostic single event (Dyer and Yusof, 1989) with a temperature maximum (Tmax) of around 370 C. Wairakite, on the other hand, displays 2 water loss peaks. The first of these is at a T max of c.350 C and the second is close to 500 C.

The thermal data also resembles that of the calcian analcime identified by Livingstone (1989) at Drynock, Isle of Skye in a reyerite-tobermorite amygdale assemblage in an olivine basalt.

Despite the high iron content revealed by elemental analysis of the pyramidal crystals no iron compounds were detected in the XRD studies. Iron is known to be capable of isomorphously substituting into zeolite aluminosilicate frameworks. Marco *et al.*, (1995) state that 96% of the iron content of a clinoptilolite from the Tasajeras deposit in Cuba is in the framework Synthetic zeolites with iron in their frameworks are well known (Szostak 1992). In addition Szostak (1992) records the existence of an "iron silicate pollucite". Pollucite, a caesium aluminosilicate is included in the most recent review of zeolite nomenclature because it also has the analcime framework (Coombs *et al.*, 1998).

The presence of some iron isomorphously substituted in the zeolite structure cannot be entirely ruled out for the Totherick analcime, but the clearly visible iron staining on many crystals, including those examined here, almost certainly accounts for the bulk of the measured high iron content

SUMMARY

The XRD, XRF and thermal analyses indicate that the Totherick material is a calcium-rich phase with the analcime structure. The presence of the calcium ion in such high concentration an analcime is surprising. Despite the well-studied cation exchange properties of this zeolite no evidence exists in the literature of the calcium cation being able to enter the zeolite structure, to any degree, as a consequence of exposure to calcium rich solutions. This suggests that the mineral may well be the first record of a naturally formed calcium analcime, as opposed to a wairakite. In this context Seki (1968) has pointed out that almost all attempts to synthesise wairakite have produced a calcium analcime.

The crystal habit of the Totherick analcime is unusual, but is unlike that described by Heddle (1893). The Totherick crystals (see *Figs 1* and *2*) are stacked truncated octahedra with trapezoidal faces that often (but not always) decrease in size to create a pyramidal form. The calcian-analcime noted by Livingstone (1989) is a porcellanous material.

ACKNOWLEDGEMENTS

The authors wish to dedicate this paper to the late Kemp Meikle, with thanks for drawing our attention to the Heddle record of pyramidal analcime. Jon Newton is thanked for carrying out the thermal analysis.

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Table I. Oxide contents (%) of analcimes and a wairakite

	analcime Barrhead	analcime Totherick	wairakite^1
SiO_2	55.9	54.0	55.9
Al_2O_3	29.0	25.5	23.0
Na_2O	4.3	-	1.1
CaO	1.4	4.4	11.7
Fe_2O_3	0.6	7.0	-
K_2O	-	-	0.2
H_2O	9.0	10.9	8.5
Total	100.2	101.8	100.4

1- Gottardi and Galli (1985a)

Table II. X-ray powder diffraction d spacings () for analcimes and a wairakite. Intensities (I/Io %) are in brackets.

analcime^1	analcime Totherick	wairakite^2
	6.82 (19)	5.61 (51)
5.59 (15)	5.57 (59)	4.86 (13)
4.85 (2)	4.83 (21) 3.66 (3)	3.63 (19)
3.44 (100)	3.42 (33)	3.41 (100)
2.93 (48)	2.92 (11)	2.94 (43)
	2.90 (40)	2.70 (15)
2.68 (100)	2.68 (14)	2.51 (13)
2.50 (4)	2.49 (20)	

1-Gottardi and Galli (1985b)

2-Steiner (1955)

Journal of the Russell Society, 8(1) 30-32 (2003).

CACOXENITE AND CRANDALLITE FROM PWLLDU BEACH, BISHOPSTON, GOWER, SWANSEA, SOUTH WALES: THE FIRST WELSH OCCURRENCE.

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Cacoxenite, $(Fe^{3+}, Al)_{25}(PO_4)_{17}O_6(OH)_{12}.17H_2O$, is a common accessory mineral, typically found in oxidised magnetite and "limonite" iron ores; in Fe, Mn-bearing novaculites (chert) and as a rare constituent of iron-rich sediments and soils (Anthony *et al.*, 2000). Widespread in small amounts, world-wide occurrences are numerous. The first recorded British material, noted by Ryback *et al.*, (1988), referred to specimens within the collections of the Natural History Museum, collected by Arthur Russell during 1943, from a stream bank opposite the old fort of Lismeenagh, Ballycormick, near Shanagolden, Co. Limerick, Ireland. Three further occurrences, mentioned by Ryback *et al.*, (1988), represent sites on the British mainland, all restricted to England including Burdell Gill in the Caldbeck Fells, Cumbria and two localities in Cornwall. Golley and Williams (1995) listed two further Cornish locations.

Crandallite, $CaAl_3 (PO_4)_2 (OH)_5.H_2O$, a secondary mineral that occurs in weathered phosphatic aluminous sedimentary rocks and carbonates; in phosphatic-rich nodules; from complex granite pegmatites and in amphibolite-grade metaquartzites (Anthony *et al.*, 2000) is somewhat rarer than cacoxenite in the British Isles. A short report detailing the identification of crandallite on a specimen from Wheal Jane, Cornwall, England (UKJMM, 1988) appears to be the only prior reference to this mineral within the British Isles. The short paragraph within "mineral notes" describes a large sample of amethystine quartz with green fluorite overgrowth - the fluorite cubes being coated with a brown crust of pyrite microcrystals set in a mineral identified at Camborne School of Mines as crandallite.

This paper reports the first occurrence of cacoxenite and crandallite from the principality of Wales, thus representing the first locality in the British Isles where the phosphate minerals wavellite, variscite, cacoxenite and crandallite occur together in close association.

At Pwlldu beach (National Grid Reference SS 576 870) cacoxenite is relatively common but easily overlooked, occurring as aggregates of very small (<0.3mm) tufted spheres and hemispheres of a yellow, gold or orange colour with a silky lustre. Clusters of spheres are frequently scattered over fracture and joint surfaces in chert, which occurs abundantly on this storm beach; and probably originates from the disused limestone quarry at Pwlldu Head, the geology of which has been described previously by Plant and Jones (2001). Identification of cacoxenite was made at the National Museums and Galleries of Wales using X-ray powder diffraction (X-ray no. NMW X1309) supported by electron probe microanalysis on a small specimen collected by one of the authors (AD). Diffraction spacing data (Table I) proved inconclusive, in part due to quartz contamination, though largely due to the unusual pattern that cacoxenite produces on X-ray film. The two strongest lines coincide with where the film is mounted within a Debye-Scherrer camera. This means that the diffraction lines are faint and partially overlap holes within the film. Further to this the majority of lines have an intensity of <10, being barely discernible on film. Elemental analysis (Table II), performed by electron probe microanalysis, provided additional information confirming the presence of significant iron, aluminium, phosphorus and oxygen, with minor silica due to quartz contamination. The relative proportions of the major elements are consistent with the formula for cacoxenite $[(Fe^{3+}, Al)_{25}(PO_4)_{17}O_6(OH)_{12}.17H_2O]$. The specimen analysed (NMW 2001.12G.M.1) consists of broken wavellite spheres to 25mm, partially overgrown by silky, yellow cacoxenite spherules to 0.2mm diameter. A mineral of a rusty orange/brown colour, almost completely covering some surfaces within chert blocks with minor residual cacoxenite, suggests that cacoxenite is chemically unstable and readily weathers to iron hydroxides.

TABLE I. X-ray powder diffraction data for cacoxenite.

Pwlldu beach, Bishopston, Gower, S. Wales. NMW X1309		Vanleer mine, Iron City Tennessee, U.S.A. PDF No. 14-331	
d_{obs}	I/I_0	d_{obs}	I/I_0
19.21	80	23.10	100
		13.90	6
12.10	100	11.90	100
		9.70	6
		9.10	14
		8.0	6
		6.91	10
		6.39	4
		6.05	2
		5.87	4
		5.54	4
		4.90	6
		4.59	2
		4.38	2
		4.16	4
		3.99	4
		3.84	4
		3.73	4
		3.63	<1
		3.46	<1
		3.43	2
		3.33	6
3.14	20	3.18	14
		3.11	4
		3.07	<1
		3.01	4
		2.93	4
		2.81	2
		2.77	4
		2.71	2
		2.66	2
		2.61	2
		2.56	2
		2.51	2
		2.44	2
		2.37	<1
		2.31	2
		2.26	2
		2.21	2
		2.16	2

TABLE II. Quantitative analytical results for uncoated powdered cacoxenite from Pwlldu beach. Analysed by electron probe microanalysis at the National Museums and Galleries of Wales.

Element	Atomic weight %
O	60.32
Fe	17.67
Al	11.44
P	8.69
Si	1.88
Total	100.00

This, the first record of cacoxenite from Wales, occurs in a setting with a close association to wavellite and variscite, which liberally cover some of the siliceous rock. The chert often consists of a radiolarian fauna, with silica in the form of white to blue chalcedony and quartz. Quartz is common with crystals often lining chalcedonic cavities within the chert; sometimes water clear but often with iron oxide inclusions. One brecciated mass of rottenstone, exhibits fractures infilled with wavellite, bi-pyramid red quartz and göethite pseudomorphs after pyrite cubes (AD specimen no. 345).

Wavellite has been noted to infill shell fragments within the limestone nodules. One example exhibits siliceous gastropod shells with green wavellite occupying the chamber cavities, presumably as a later phase of mineralisation (AD specimen no. 159).

Crandallite, $CaAl_3 (PO_4)_2 (OH)_5.H_2O$, appears less common than cacoxenite but is not easy to recognise in the field. It occurs as a creamy-white powdery coating upon limestone cherts and rottenstones, and is likely to be a weathering product of wavellite with which it is associated. Confirmation of crandallite was made at the National Museums and Galleries of Wales using X-ray powder diffraction (Table III) supported by electron probe microanalysis, on a specimen in the collection of Allan Dean (AD specimen no. 265).

TABLE III. X-ray powder diffraction data for crandallite.

Pwlldu beach, Bishopston, Gower, S. Wales. NMW X1334		Frederick County Virginia , U.S.A. PDF No. 25-119	
d_{obs}	I/I_0	d_{obs}	I/I_0
5.68	50	5.70	80
4.86	50	4.85	70
3.50	70	3.51	75
3.00	60	2.98	70
2.94	100	2.93	100
2.86	10	2.85	10
2.70	30	2.70	20
2.43	20	2.43	40
	2.26	10	
2.21	50	2.21	60
2.16	70	2.17	70
	1.99	10	
1.90	70	1.89	80
	1.84	10	
	1.80	10	
1.75	70	1.75	80
	1.69	10	
1.65	10	1.65	10
	1.63	10	
1.60	10	1.60	5
	1.55	10	
1.51	20	1.51	20
1.49	20	1.49	40
1.47	30	1.47	40
1.43	50	1.43	50
	1.39	10	
	1.37	10	
	1.36	10	
	1.34	20	
	1.32	20	
	1.29	50	

A suite of specimens from Pwlldu beach are housed in the mineral collection of the National Museums & Galleries of Wales. Included within this is part of the specimen confirmed as crandallite (AD no. 265) (NMGW 2002.23G.M.1) and the sample of cacoxenite used for identification (NMGW 2001.12G.M.1).

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The authors wish to extend thanks to Mr. M. P. Lambert (National Museums and Galleries of Wales) for assistance in using the Scanning Electron Microscope (SEM) for electron probe microanalysis.

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BRIANYOUNGITE FROM ELGAR MINE AND FRONGOCH MINE, CEREDIGION, WALES

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Brianyoungite ($Zn_{12}(CO_3,SO_4)(OH)_4$), is an uncommon zinc-bearing supergene mineral related to hydrozincite. It was first described from the Wellgill Cross vein in Brownley Hill mine, Nenthead, Cumbria, England (Livingstone and Champness, 1993) and has also been identified from the Middlecleugh First Sun vein, Smallcleugh mine in the same area. In both cases brianyoungite forms minute spherules composed of pointed lath-like crystals, which are typically intergrown with drusy gypsum crusts of post-mining origin (Bridges and Young, 1998).

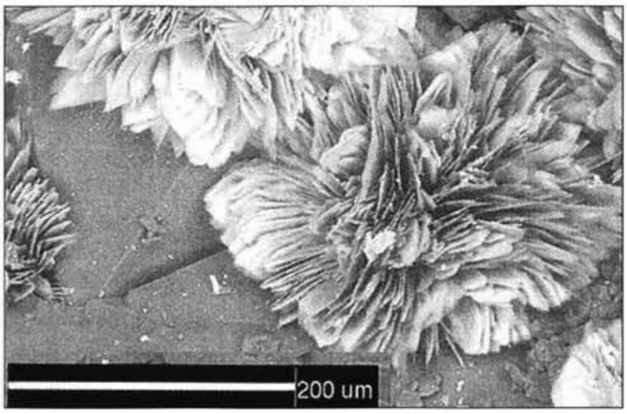

Figure 1. SEM image of brianyoungite rosettes on NMGW specimen 98.35G.M.973

In addition to the occurrences in Cumbria, brianyoungite has been identified at the Bastenberg mine, Ramsbeck, Germany and Vielle Montagne, Belgium (Livingstone and Champness, *op. cit.*); at Broken Hill, New South Wales, Australia (Birch, 1999); at the Tsumeb mine, Otavi, Namibia (determined by XRD at the University of Manchester), and at West Wheal Fortune, Ludgvan, Cornwall (determined by XRD at the University of Manchester).

Brianyoungite has recently been identified (XRD no. NMW X1268) on "A2" quartz-galena veinstone (Mason, 1994 & Mason, 1997) on National Museums and Galleries of Wales specimen no. 98.35G.M.973, which was collected in 1996 from the deep adit dumps of Elgar mine, Bow Street, Ceredigion (SN 662 860). Elgar mine is a small working on the westerly section of the Pb-Ag-Zn bearing Hafan Lode (Jones, 1922), which was investigated by one of the authors (JSM) as part of the NMGW Minescan project.

Rosettes of pearly white crystals up to 0.3 mm across were found during routine curation of ore specimens from Elgar mine (*Fig. 1*). Analysis by X-ray powder diffraction gave a pattern that was not consistent with any species in the museum's database. Electron probe microanalysis gave an indication of the chemical composition: the dominant elements were Zn and O, with minor S, C, Si and Al, but since the specimen was analysed whole and uncoated, Si and Al were almost certainly derived from the host rock. With a basic idea of the minerals composition it quickly became apparent that the XRD pattern was that of brianyoungite, (publication of which post-dated the most recent copy of the museums software). Comparison of the d-values with those determined for the type material produced a very good match (Table I).

Brianyoungite has also been identified at Frongoch mine, Devil's Bridge, Ceredigion (SN 722 744). Frongoch mine worked "Late Simple" or "A2" type Pb-Zn mineralisation on the WSW-ENE striking Frongoch Lode (Mason, *op. cit.*) and is well known to mineralogists for a diverse assemblage of lead, zinc and copper bearing supergene minerals, many of which appear to have formed by post-mining oxidation (Green *et al.*, 1996). Brianyoungite was identified by X-ray diffraction (XRD no. MANCH:XRD734) on specimen number MANCH:N17115. It occurs as spherulitic aggregates of pearly white lath like crystals up to 0.5 mm across in galena-rich matrix (*Fig. 2*).

The primary mineralisation in which brianyoungite crystallised at Frongoch mine and at Elgar mine belongs to the "A2" group of quartz

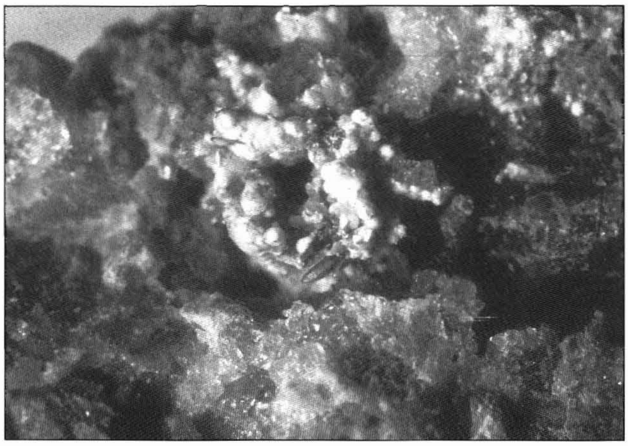

Figure 2. Brianyoungite spherules to 0.4 mm on specimen MANCH:N17115.

and galena bearing veinstones. At Elgar mine brianyoungite occurs on iron-stained quartz and galena, and at Frongoch it occurs with cerussite in galena-rich veinstone. Sphalerite is absent from the specimen examined to date, but in view of mobility of zinc this is perhaps not surprising. Brianyoungite tends to form relatively inconspicuous white crystals and is easily overlooked, it may be more common than the few published records suggest.

ACKNOWLEDGEMENTS

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Elgar mine, Bow Street, Ceredigion, Wales. NMW X1268		Brownley Hill mine, Nenthead, Cumbria, England (Livingstone and Champness, 1993).	
d_{obs}	I/I_0	d meas.Å	I/I_0
16.5	50	15.44	100
7.89	100	7.88	100
5.27	40	5.25	20
4.25	10	4.13	5
		3.94	5
3.14	30	3.13	10
		2.98	10
		2.91	10
2.79	10	2.80	10
2.72	70	2.71	40
2.68	40	2.66	10
2.58	40	2.58	20
		2.48	5
2.41	10	2.40	20
		2.34	5
2.27	10	2.25	10
		2.03	10
1.75	10	1.75	15
1.57	40	1.57	30
		1.55	10
		1.48	10
		1.35	10
		1.02	5

TABLE I. X-ray powder diffraction data for brianyoungite.

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WELL -FORMED CRYSTALS OF ERYTHRITE, WITH MERCURIAN SILVER, LAVENDULAN AND OTHER MINERALS FROM GORTDRUM MINE TIPPERARY, IRELAND

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Gortdrum mine, centred on Nat Grid. Ref. Ireland R 870 410, about 4 miles NNW of Tipperary, Ireland, was a large open-pit mine worked from 1967 to 1975. The open pit is now flooded, and the considerable area of dumps is being worked over for aggregate. The locality is known for its wide range of primary and supergene ore mineral species. It is particularly known for its mercury minerals, which are rare in the British Isles, and among which is gortdrumite $(Cu,Fe)_6\ Hg_2S_5$, a new species reported by Steed (1983) and named after the locality. Small but well-formed cinnabar crystals in ferroan dolomite veinlets are also well known (Ryback and Moreton, 1991). Epigenetic minerals of copper, iron, arsenic, mercury and minor bismuth are found here, in addition to cobalt minerals represented by cobaltite, and silver minerals represented by stromeyerite and "amalgam" (mercurian silver) (Morrissey *et al.*, 1971; Steed, 1975). Some uranium has also been recorded as colloform calcian uranite "pitchblende", brannerite and possible coffinite (Duane, 1988). The gangue minerals are calcite, quartz, baryte and ferroan dolomite (Morrissey *et al.*,1971;Steed, 1975). Crusts of secondary minerals are not uncommon, including malachite, azurite, tyrolite (Ryback and Moreton, 1991), and gypsum.

In 1998 the authors collected material from the dumps, including tyrolite, which infrared spectroscopy showed to contain both carbonate and sulphate. Among other species found were azurite in blades to 5mm, green microcrystalline crusts of brochantite (confirmed by infrared spectroscopy), pale green feathery crusts of devilline (identified by microchemical analysis), and small pale-pink radiating spherulites giving an infrared spectrum near to that of erythrite. In 1999 a return visit by one of us (J.I.W.) yielded a boulder rich in bornite, tennantite and chalcopyrite, and seamed with veinlets of ferroan dolomite with minor quartz.

Fracture surfaces of parts of this boulder are encrusted with well-formed crystals of erythrite, forming individual transparent well-terminated blades up to about 2mm long, and radiating clusters of similar blades, associated with malachite and minor microcrystalline azurite. The erythrite crystals gave an infrared spectrum typical of the species, and must be among the best specimens of this recorded from the British Isles. Some cavities, in parts richer in tennantite than bornite, are lined with colourful and attractive combinations of bright, colourless aragonite needles (to about 2mm) overlying tiny azurite crystals richly sprinkled on small ferroan crystals, with small patches of bright-red, powdery cinnabar. Part of the boulder also yielded bright-green fans of small tyrolite crystals. Some of the ferroan dolomite veinlets in more bornite -rich parts of the same boulder yielded variably merurian native silver (EDAX, and also see below). This forms inter-crystal cavity fillings and linings, occasionally dendritic, and thin cleavage fracture -filling sheets. Two selected grains of this silver, visually indistinguishable but one high and the other low in mercury, were quantitatively analysed by Mr D. Plant in the Department of Earth Sciences, University of Manchester, with a Cameca SX electron microprobe analyser using a 20 kV accelerating voltage and a beam current on 20 nA, the standards being silver and HgS. Five spot analyses on one grain gave weight % Hg values of 0.1% for 3 spots, 0.2% for one spot and 1.3% for another. Two spot analyses of the other grain gave 12.4 and 12.5 weight % Hg.

On a further visit, in October 2000, more erythrite was found, this time in pinkish-red, globular aggregates to 0.5mm, sometimes scattered and sometimes richly clustered, on a greyish quartz-rich matrix. Closely associated with this erythrite were thin, sky-blue crusts of lavendulan, occasionally in small spherules (to

0.2mm) typical of this species, and also sparse patches of posnjakite in blue-green blades to about 1mm. Both species were identified by infrared spectroscopy. Posnjakite has been reported from Ireland from Muckross mine, Killarney, Co. Kerry (Ryback and Moreton, 1993), with lavendulan (Moreton *et al.*, 1989). Good specimens of lavendulan have also been identified, using infrared spectroscopy, by the present authors, and again associated with erythrite, from a level on Seven Dial lode, Knockmahon, Co Waterford.

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The authors wish to thank Mr P. Rea for his permission to collect at the site, and Professor R. Pattrick and Mr D. Plant of the Department of Earth Sciences, University of Manchester, for EDAX and electron probe microanalysis.

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COTUNNITE FROM THE BEACH AT CLEVEDON, AVON, ENGLAND

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The rare mineral cotunnite, $PbCl_2$, has only been reported from two British localities.

Russell (1920) noted its presence on fused lead from the wreck of the fire-ship 'Firebrand' in Falmouth Harbour, Cornwall and Temple (1956) lists it from High Pirn mine and Hopeful vein, Leadhills-Wanlockhead Mining District, Scotland. A further occurrence of cotunnite is reported here from a pebble found on the beach at Clevedon, Avon.

The geology and mineralogy of the area have been described by previous authors (Starkey 1984 & 1986 and Ixer 1985). In the vicinity of Clevedon, the Upper Old Red Sandstone Portishead Beds, the Lower Carboniferous Black Rock Limestone, and the Lower Limestone Shale, are overlain unconformably by the Triassic Dolomitic Conglomerate. The Carboniferous rocks, together with a small area of Portishead Beds, are exposed along the coast south west of Clevedon between the pier and Blackstone Rocks. North-east of the pier, Dolomitic Conglomerate forms the cliffs. At Clevedon Pier [ST401 719] a roughly ENE-WSW trending fault, with an unknown southerly displacement, cuts the Dolomitic Conglomerate. The fault plane is exposed in the cliffs immediately east of the pier where it carries conspicuous pink to pale-cream baryte mineralisation. Several large boulders of baryte derived from this fault occur higher up the beach and there are numerous smaller rounded pebbles in the mud or the intertidal zone. Within the baryte are numerous cavities, usually quite small but locally up to 12cm across, commonly lined with small "cockscomb" baryte crystals.

Baryte is by far the most abundant mineral, but minor amounts of galena, sphalerite, chalcopyrite, pyrite, marcasite, aragonite and rarer tetrahedrite, tennantite and enargite (Ixer, 1985) are also present. Numerous species of supergene minerals occur in the cavities and include native copper and sulphur, cuprite, limonite, covelline, cerussite, malachite, azurite, aurichalcite, brochantite, phosgenite, (Starkey, 1984) and beudantite, (Starkey, 1986). The supergene minerals commonly form good euhedral crystals, but are usually quite small (less than 2mm).

The cotunnite, which was identified by X-ray diffraction, was in a single pebble in mud in the intertidal zone. The pebble contained an ovoid cavity approximately 25mm by 15mm, partly filled with corroded sphalerite and galena. The cavity was sealed from the seawater by a rim of baryte and crystalline masses of galena and cerussite. The sulphides and baryte within the cavity were partly covered with limonite and crusts of small (up to 1mm) phosgenite crystals, but several white to colourless needles of cotunnite up to 4mm long and 1mm across were found perched on the baryte and sulphides. The larger crystals tend to taper towards rounded terminations and often have a rhomboid cross-section, though in several cases this seems to be flattened.

Cotunnite and phosgenite at Clevedon occur in a very different situation to the oxychloride assemblages of the nearby Mendip Hills. The latter occur in joints and faults in the Carboniferous limestone in pockets rich in manganese and iron oxides and their presence is directly associated with manganiferous saline solutions (Symes and Embry, 1977). There are no manganese and iron oxide pockets at Clevedon and the chloride minerals have only been found in pebbles from the intertidal zone and not higher up the beach. It is therefore concluded that the cotunnite and phosgenite formed as the result of the oxidation of galena, the necessary chloride and carbonate ions being derived from seawater. Theoretically cotunnite would not be expected to form in a seawater environment. Based on the chemical model of seawater prepared by Garrels and Thompson (1962), the stable supergene lead mineral in seawater is cerussite. This is borne out by the frequency with which this mineral is found in cavities in the pebbles. However, in a nearly completely sealed cavity in a mineral of low solubility such as baryte, a slight lowering of seawater pH results in the stabilisation of phosgenite. Formation of a little cerussite would easily account for the necessary reduction in pH, by removal of carbonate ions from solution, although the presence of limonite in the cavity may suggest some acidification as the result of the oxidation of pyrite and/or marcasite. The high activity of sulphate ion in seawater, which is nearly saturated with gypsum, means that a further reduction in pH stabilises anglesite and not cotunnite. This is true even taking into account the fact that the temperature of the water in the Bristol Channel is well below that of the 25°C used in the Garrels and Thompson model. The most likely explanation for the formation of the cotunnite would seem to be that it formed when the cavity in question was in the splash zone. In this region, chloride ion activity could be increased by evaporation, while the solubility of gypsum would prevent sulphate ion activity increasing.

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

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Epimorphs of quartz after a cubic mineral, presumed to be fluorite, have long been known from the Northern Pennine Orefield. Wallace (1861, p143) states "In the Great Limestone stratum, a greater variety of minerals is mingled together in the veins than in any strata above. In the Nenthead mines, however, fluoride of calcium is rarely met in considerable quantities. At some former period it must have been plentifully deposited in the veins of the district, since casts of its crystals in quartz are by no means uncommon, even in veins where not the smallest particle of the substance can now be found". Specimens meeting Wallace's description occur in Smallcleugh mine, Nenthead (NY 788429) and one of us (HW) has found good examples in the Admiralty Concession Flat of Nentsberry Hagg's mine, Nenthead (NY 766450), a locality now dominated by barium minerals. Not infrequently, epimorphs occur in which there has been subsequent random regrowth of fluorite on the quartz. Good examples occurred at Cambokeels mine, Eastgate, Weardale (NY 985383). Rarely the overgrowth is perfectly aligned with the original structure. Since this is unlikely to occur by chance, it probably arises when a small piece of the original fluorite remained in a corner of the epimorph to orientate the new crystal growth. This is considered to be the best evidence that the original cubic mineral is indeed fluorite. Good examples occurred at Redburn mine, Rookhope, Weardale (NY 928432) and a particularly good example originated from Frazer's Hush mine, Rookhope, Weardale (NY 890444), (A.Rigby, *personal communication*).

It has recently become possible to access the Bounder End Cross vein from the Rampgill Horse Level [NY782435] and at the High Flat horizon of the Great Limestone excellent and interesting epimorphs of fluorite occur *in situ*. There is confusion in the literature on the precise location and name of the locality. The Vieille Montagne Zinc Co. working plan of the mine system, dated December 6th. 1922, shows the first major flats on the Rampgill vein as being on the Boundary Cross vein. Dunham (1990, p144) refers to these flats as being on the Bounder End Cross vein, the name also used by Wallace (1861, Plate IX, p102), so this name seems to have precedence. Once the Rampgill Horse Level passes the county boundary from Cumbria to Northumberland, the appropriate name for the workings is unclear. The earliest working from Northumberland was the Coalcleugh Level [NY 802452], driven above the Firestone Sill and well above the Rampgill Horse Level. Later, the Barneycraig Horse Level [NY804467] was driven under the Great Limestone and below the Rampgill Horse Level. Both seem to have operated as separate mines, presumably at different times. Vieille Montagne Zinc Co. appear to have worked both sides of the county boundary as Rampgill mine, though all three levels of the workings were connected at one time. In the absence of definite information, it seems best to consider the Bounder End Cross vein as part of Rampgill mine. Finally, the position of the county boundary underground is also unclear. Dunham (1990, p143) states that a shaft, which is referred to as 'Rampgill Shaft' on the Vieille Montagne plan, is 61m SW of the county boundary. The actual distance from the junction leading to the above shaft to an ore chute on the Bounder End Cross vein is 113m, and 7m beyond the ore chute is a slatted iron gate with padlock and chain, which would seem to mark the county boundary. The Vieille Montagne plan shows the county boundary as 89m SW of the shaft. There is, however, no doubt that the locality for the epimorphs is the High Flat horizon on the Bounder End Cross vein and, particularly, on a NE extension of the North String at the NW end of the flats.

In the North String the epimorphs line the inside of small fissures and cavities, generally of the order of 1m across and half this in height, in highly altered limestone. The cavities are partly coated

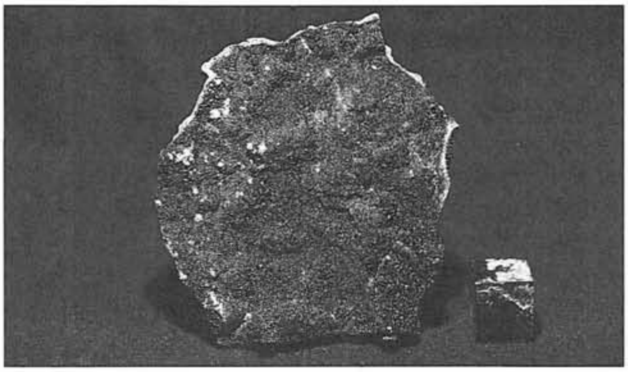

Figure 1. Upward facing surface of an epimorph, coated with siderite or ankerite crystals oxidised to limonite. The scale cube is 20mm on edge.

with sphalerite and the quartz epimorph sheets, which vary in thickness from 2 to 4mm, stand proud of this surface. The upward facing surfaces of the epimorphs are completely coated with large numbers (up to 500cm-2) of small saddle-shaped crystals of siderite, or possibly ankerite, which have oxidised to dark brown limonite (*Fig.1*). The undersides of the epimorphs have similar crystals, but far less numerous, scattered on the surface (*Fig.2*). These latter crystals are often orientated to one side of the crystals on which they grow. Other minerals associated with the epimorphs are sphalerite, fluorite and minor calcite. The sphalerite preceded the iron carbonate phase. The fluorite seems to have regrown before the iron carbonate phase in some cavities and after it in others. Often this late stage fluorite shows corrosion of the crystals. Calcite is the final phase.

An area of flat mineralisation in the SE side of the Bounder End Cross vein (beyond the Horse Level) contains very similar epimorphs, except that the quartz is 10 to 15mm in thickness. Here fluorite is more abundant and galena is present. In addition to the epimorphs the flats contain large amounts of fractured rock and mineral, which seem to have spalled off from the roof. As in the North String, upward facing surfaces are generally covered in minute crystals of siderite or ankerite oxidised to limonite.

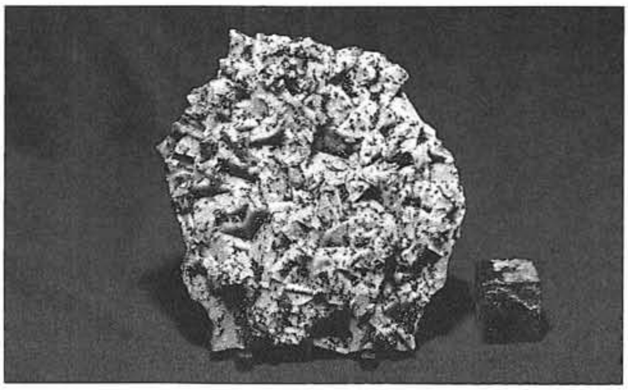

Figure 2. The downward facing side of the epimorph illustrated in Fig. 1.

The paragenesis of the deposits seems to be alteration of the limestone and cavity formation followed by deposition of sphalerite, and then fluorite, on the cavity walls. The fluorite was first overcoated with quartz , after which most of the original fluorite was dissolved by the mineralising fluids. Minor sphalerite followed and then, in some cavities, there was minor regrowth of fluorite. To account for the enormous number of siderite or ankerite crystals on the upward facing surfaces, it is suggested that the fluids in the cavities then became supersaturated with respect to siderite, or ankerite, and that a disturbance resulted in the formation of very large numbers of crystallites in the fluids. Movement of a fault could easily produce the required disturbance. Most of the crystallites settled on upward facing surfaces, but slow movement of the fluids in the cavities deposited some crystallites on downward facing surfaces with preferential settlement on the sides of some of the faces of the casts. The crystallites grew until the upward facing surfaces were totally covered with carbonate mineral. There was a final minor phase of fluorite deposition in some cavities, followed by oxidation of the iron carbonate to limonite. The corrosion of some of the fluorite crystals may have occurred prior to, or during, the oxidation stage. The minor calcite obviously formed quite late in the sequence and could even be supergene in origin.

Representative specimens of the epimorphs have been deposited in the collections of the Hancock Museum, Newcastle upon Tyne.

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Thanks are due to the members of NORPEX whose labours over many years have made access to the Bounder End Flats possible and to the North Pennines Heritage Trust whose members helped us in this work.

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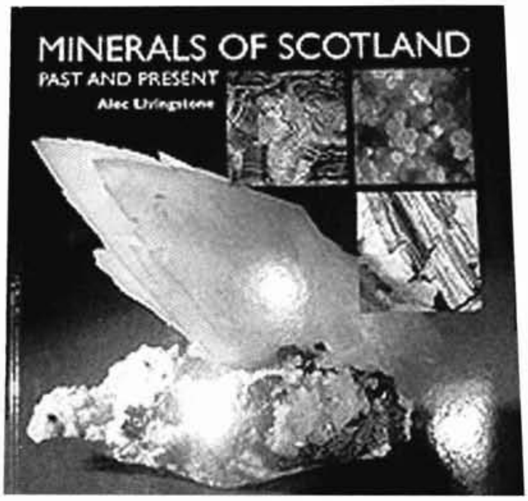
Book Review



Minerals of Scotland: Past and Present.
A. Livingstone,

Edinburgh (National Museums of Scotland Publishing Ltd.), 2002, xvi + 212 pp. Price £35.00. ISBN 1 901663 46 9.

This well-illustrated book is about minerals and the men who discovered, collected and studied them. It includes a list of the first documented reports of over five hundred mineral species native to Scotland (many of which were first found here). After a brief introduction to the geology of the country, there are fascinating and scholarly descriptions of the collectors and their collections. A coterie of Scots, many living and working around Edinburgh, contributed greatly to the early growth of mineralogy: the work of men such as Robert Ferguson, Robert Jameson, William Nicol, Thomas Allan, David Brewster and Matthew Forster Heddle is described, often accompanied by facsimile reproductions of pages from their mineral catalogues. Brief descriptions are given of University, Institutional and private mineral collections (including those of Thomas Edington and James Hutton), together with notes on some contemporary Scottish collectors, including Kemp Meikle, Gordon Sutherland and Alastair Mackay.

Some sixty of the minerals themselves are listed alphabetically and described in some detail (often illustrated by drawings of their morphology and/or colour photographs), with appropriate emphasis on such Scottish specialities as brewsterite, caledonite, corundum (var. sapphire) in the form of a megacryst (39 ct) in a camptonite and cut as the 'Saltire Sapphire' (9.7 ct), greenockite, harmotome, lanarkite, native silver and strontianite. This chapter is followed by an 'album' of 48 colour photographs of common or unusual Scottish minerals, ranging from analcime (6 cm crystal), apophyllite, elbaite, ilmenite, manganite, pectolite and prehnite to thomsonite and numerous other zeolites. The selection of mineral species for detailed descriptions together with their history and photographs, and of those chosen for separate inclusion in the 'album' appears to be arbitrary, though in the case of the 'album', the availability of suitable colour photographs may have had an influence.

The listing of the 552 mineral species recorded from Scotland and the listing of 29 species described first from here (including, in addition to those mentioned above, harkerite, mullite, pentlandite and tobermorite) are assigned to appendices; although Appendix 1 does not contain a key reference for each species. There is an extensive bibliography and a useful index.

In this work the author has painstakingly assembled information from museum archives, learned journals and estate papers, and has had the benefit of working in the National Museums of Scotland with all their rich historical collections. He has made good use of the availability of many excellent large colour photographs, enabling readers to savour some of the true aesthetic beauty of the minerals. The work gives somewhat more space to the history of the development of mineralogy as a science in Scotland and to the eminent collectors of the past than to the minerals themselves. But, nevertheless, it will be sought after eagerly by mineral collectors, both amateur and professional, both groups having contributed greatly to the development of mineralogy in Scotland. This book can only help to encourage further interest.

R.A. Howie

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GEARKSUTITE FROM THE OLD GANG MINES, SWALEDALE, NORTH YORKSHIRE, ENGLAND

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The uncommon alumino-fluoride mineral gearksutite is reported from the Old Gang mines, Swaledale, North Yorkshire. It forms white spherulitic masses composed of microscopic lath-like crystals associated with gypsum, allophane, serpierite and ktenasite in a mineral assemblage produced by post-mining oxidation on the wall of a mine level. This is the first British report of gearksutite, which is the second alumino-fluoride after prosopite to be identified from the Askrigg Block.

INTRODUCTION

The Old Gang mines in Swaledale, North Yorkshire were developed to exploit an extensive network of low temperature lead-bearing mineral veins hosted by Carboniferous limestone, chert and sandstone (Dunham and Wilson, 1985). Hard Level, at national grid reference NY 9712 0069, gave access to many of the richest veins at the level of the highly productive Main Limestone (Namurian). The Old Rake and Friarfold veins, which contained some of the most vertically and laterally continuous orebodies in the North Swaledale Belt were accessible via Hard Level, as was Lucky String where the mineralisation described below was found.

The lead-bearing veins of northern Swaledale are relatively simple mineralogically. The primary sulphides present include galena and sphalerite, with lesser amounts of pyrite and chalcopyrite, in a baryte-fluorite-calcite gangue with local witherite and strontianite. Supergene minerals including cerussite, malachite and smithsonite occur on the old mines tips and are sparingly developed *in situ* at the level of the Main Limestone on Old Rake vein (Mike Wood, *personal communication*, 1998).

GEARKSUTITE

Gearksutite, $CaAlF_4(OH).H_2O$, typically occurs as white nodular or earthy masses formed by the late-stage hydrothermal alteration of fluorine-bearing minerals (Bailey, 1980). It was first described by Hagemann (in Dana, 1868) from the famous cryolite deposit at Ivigtut, Greenland.

Gearksutite has subsequently been reported in a wide variety of geological environments. It occurs in fumerole deposits at Volcano, Lipari Islands, Italy (Bernauer, 1941); as a late stage mineral in miarolitic cavities in granite at Gjerdingen, near Oslo, Norway (Raade and Haug, 1982); in the evaporite deposits of the Inder region, Kazakhstan (Egorova, 1940); as a late-stage alteration product in a cryolite-bearing pegmatite at St. Peter's Dome, Colorado, USA (Cross and Hillebrand, 1882); in high temperature tin bearing veins at Colquiri mine, La Paz, Bolivia (Sugaki *et al.*, 1985); and in copper-rich veins at Veneziana mine, Veneto, Italy (Boscardin *et al.*, 1995). At all of these localities gearksutite occurs as earthy masses. Macroscopic crystals are known only from the Cleveland mine, Tasmania, Australia, where gearksutite occurs as millimetre-size crystals associated with other supergene fluorides, encrusting quartz and fluorite (Birch and Pring, 1990).

LOCALITY AND SPECIMEN DESCRIPTION

Gearksutite has been identified on specimens collected from Lucky String, the name given to the western section of the arcuate Alderson's vein, which strikes eastward from Dolphin's Shaft, near to the point where Hard Level cuts Old Rake vein in the Old Gang mines (Dunham and Wilson, 1985). Lucky String runs approximately parallel to Old Rake vein (the easterly continuation of which beyond Dolphin's Shaft is known as Reformer vein) for the first few metres of its course. The walls of the level at this point are encrusted in gypsum, with minor quantities blue and green copper minerals and abundant white spherulitic masses of what was subsequently identified as gearksutite (David

McCallum, *personal communication,* 2001).

Four samples collected from this area were submitted for identification at Manchester Museum in 2001 (accession numbers MANCH:N16536 to N16539). They comprised limestone wallrock fragments overgrown by thick crusts of gypsum (as crystals up to a few millimetres in length) on which pale blue and green copper minerals were sparsely crystallised. The most abundant copper mineral, which occurred as pale green aggregates of lath-like crystals up to about 1 mm in length but not more than 0.05 mm in thickness, was identified as ktenasite, $(Cu,Zn)_5(SO_4)_2(OH)_6.6H_2O$ (X-ray reference number MANCH:XRD644). Somewhat rarer aggregates of blue lath-like crystals proved to be serpierite, $Ca(Cu,Zn)_4(SO_4)_2(OH)_6.3H_2O$ (X-ray reference number MANCH:XRD704).

The gypsum and copper minerals were overgrown by white spherules up to about 0.5 mm across, commonly aggregated into spherulitic masses to 5 mm across, with no obvious crystal structure even when examined at high power under a stereomicroscope. Gypsum, allophane and the rare aluminofluoride mineral gearksutite were identified in these spherules by XRD and EDAX (X-ray reference numbers MANCH:XRD658 and XRD665).

DISCUSSION

Examination of the specimens indicates that the minerals must have formed by post-mining oxidation. Their presence as extensive crusts on the walls of a mine level allows no other explanation. This indicates a low temperature (ca. 10 C) hydrothermal origin, with crystallisation occurring over a period of not more than 100 years (Dunham and Wilson, 1985, indicate that Lucky String was developed between 1905 and 1908).

It seems likely that acid, metal-rich solutions percolating through the overlying orebody were neutralised when they encountered the limestone of the level wall producing abundant crusts of gypsum. The gypsum crusts eventually acted as a barrier, sealing the carbonate wallrock and allowing chemical conditions at the fluid-air interface to alter so that ktenasite and gearksutite could crystallise. Neither ktenasite nor gearksutite was ever found directly on the limestone wallrock, but only as overgrowths on gypsum crusts (David McCallum, *personal communication,* 2001).

Calcium and aluminium are abundant in the wallrock, and are readily mobile in acid oxidising environments. Fluorite is likely to have supplied the fluoride required for gearksutite to crystallise, as it is the only primary fluoride mineral in the orebody. In most of its occurrences, gearksutite is formed by hydrothermal alteration of fluorine-bearing minerals. The geological environment at Veneziana mine, Italy, where gearksutite occurs with the recent supergene species ramsbeckite and posnjakite (Boscardin *et al.,*1995) is directly comparable to that described here, and the occurrence at the Cleveland mine in Tasmania is also the result of late-stage low temperature hydrothermal alteration (Birch and Pring, 1990). Gearksutite has also been reported as a product of the supergene alteration of fluorite at the Voznesenskoe fluorite deposit in the Primorskoe region of Russia (Ziborova *et al.,*1986).

Examination of a number of gearksutite spherules under the scanning electron microscope shows that their surfaces are covered in pointed lath-like crystals up to about10mm in length. Qualitative analyses by energy dispersive X-ray spectroscopy showed Ca, Al, F and O to be the only elements present with an atomic number greater than 6. The powdery nature of the spherules and the fact that they also commonly contained allophane and gypsum made quantitative analyses impossible.

Gearksutite is the second alumino-fluoride mineral to be reported from the Askrigg Block of the Northern Pennine Orefield. The chemically similar species prosopite, $CaAl_2\,(F,OH)_8$, occurs at Coldstones quarry near Pateley Bridge as chalky or soft earthy masses in fluorite veinstone (Young *et al.,* 1997). In both cases the alumino-fluorides are late-stage supergene minerals.

Secondary fluoride minerals may be more common than hitherto suspected, and it would be worthwhile looking for them in any assemblage of supergene minerals derived from an orebody containing abundant primary fluorite. The alumino-fluorides are easily distinguished from carbonates, such as aragonite, hydrozincite and brianyoungite, with which they might otherwise be confused, by the application of dilute acid. The author has long suspected that there is a sampling bias among collectors that selects against inconspicuous white species.

ACKNOWLEDGEMENTS

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GARTRELLITE, A MINERAL NEW TO BRITAIN FROM LOW PIKE, CALDBECK FELLS, CUMBRIA, ENGLAND.

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Gartrellite is a member of the tsumcorite group of minerals, which have general formulae Me(1)Me(2)$_2$(XO$_4$)$_2$(OH,H$_2$O)$_2$, where Me(1) = Pb, Ca, Na, and partly Bi, Me(2) = Fe, Mn, Cu, Zn, Co, Ni and partly Al, and X = P, As, V, S. It was originally described from Ashburton Downs and Broken Hill, Australia with a complex formula which included significant sulphate and carbonate (Nickel *et al.*, 1989). Subsequent analyses of the type material resulted in a redefinition of the mineral with a considerably simplified ideal formula, $PbCuFe^{3+}(AsO_4)_2(OH)(H_2O)$ (Krause *et al.*, 1998). Zinc can substitute for copper in gartrellite and the zinc analogue, zinc-gartrellite, was described as a new mineral by Effenberger *et al.*, (2000). This placed an additional constraint on the chemical composition of gartrellite, which is defined such that zinc can substitute for copper at up to 40 mol%.

Gartrellite is a rare mineral that is typically found in the oxidation zones of lead- and copper-bearing mineral deposits. It typically occurs as greenish to brownish yellow crusts. Well-formed crystals are unknown and the absence of suitable crystals for structural analysis held up its publication as a new mineral species for many years. In addition to the co-type localities in Australia, gartrellite occurs at Tsumeb, Namibia; Gold Hill mine, Utah, USA, and several localities in Germany (Effenberger *et al.*, 2000).

Gartrellite has recently been identified in mine spoil derived from a trial adit on Low Pike vein at national grid reference NY 320 358 in the Caldbeck Fells, Cumbria. Little is known about this working, although the relatively small size of the dump indicates it was of little commercial importance. A quartz vein ca 0.75 m wide is exposed adjacent to the adit entrance and quartz veinstone and altered volcanic rock is present in the mine spoil. The geology, mineralogy and what little is known of the history of the working was summarised by Young *et al.*, (1990). A variety of supergene minerals including bayldonite, beudantite, brochantite, cornwallite, duftite, malachite, mimetite, mottramite, phillipsburgite and pseudomalachite occur in thin fractures in the quartz veinstone and surrounding wallrock (Cooper and Stanley, 1990; Young *et al.*, 1990).

Gartrellite occurs as yellow crusts coating fractures in quartz veinstone, covering areas up to several centimetres square. Some of these are simply smears without any obvious structure, but crusts composed of crude spherules up to about 0.1 mm across also occur. A single well-developed cleavage was evident in some of the spherules when they were examined under the scanning electron microscope, but nothing which could be unambiguously identified as a crystal face was observed even at the highest magnifications (>10,000x).

Gartrellite was identified by a combination of X-ray diffractometry (XRD) and qualitative energy dispersive X-ray analysis (EDAX). Identifications of tsumcorite group minerals by XRD alone are suspect because of close similarities in the patterns produced by different species. A specimen from Low Pike (accession number MANCH:N17114) matched the XRD pattern of type gartrellite from Australia well (Nickel *et al.*, 1989) and only Fe, Cu, Pb and As were detected by EDAX. In combination, these analyses rule out other members of the tsumcorite group, and particularly the closely similar mineral zincgartrellite.

Gartrellite is an inconspicuous mineral that may have been overlooked at other localities. Two properties that are useful as a guide for collectors in assessing suspect gartrellite specimens (for further analytical work) are the bright yellow colour of the powdered mineral and its solubility in dilute nitric acid. Most other supergene minerals containing iron (III) are insoluble and even greenish or brownish yellow gartrellite crusts powder to a bright ochre to mustard yellow colour.

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DG would like to thank the Manchester University Geology Department for access to analytical facilities.

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TYPESCRIPTS

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

The submitted material should normally contain original observations or experimental results relating to mineral occurrences in the British Isles, although other suitable topics maybe considered. Lull 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

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

Authors should present their material with clarity and conciseness. Results and discussion should not normally be intermingled. Identification of the less common minerals should be supported by sufficient proof (X-ray diffraction, analyses, etc.). It may not be necessary to reproduce such data in toll 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, 5T40 71).

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All figures should be numbered with consecutive Arabic numbers, and referred to in the text as Fig. I, 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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TERMINOLOGY

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 here this conflicts with Hey's Mineral Index (1993) or Mineralogical Magazine and Mineralogical Abstracts usage, the Editor will advise on the preferred nomenclature. Chemical nomenclature should conform to the rules of the International Union of Pure and Applied Chemistry. Crystal structure studies should be reported in the manner outlined by the International Union of Crystallography (Acta Crystallographica, **22,** 45 (1967)).

ABBREVIATIONS

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

The following abbreviations may be used without explanation:

XRD = X-ray diffraction
XRF = X-ray fluorescence analysis
EPMA = electron probe microanalysis (electron microscopy analysis)
EDX = energy dispersive analysis (same as EDA, EDAX, EDS)
SEM = scanning electron microscope or microscopy
TEM = transmission electron microscope or microscopy
IR = infrared
UV = ultraviolet
NCR = 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', 'h', etc. to the publication year.

A list of references in alphabetical order should form the last section of each paper. Some examples of the style used are given below; note that journal names are given in full. Papers in press may be included provided they have been accepted for publication and the journal name is given. Personal communications and unpublished work (except M.Sc. and Ph.D. theses), should not be included here but can be cited in the text, thus: (A. Brown, personal communication or personal communication, 1992), (B.C. Green, unpublished work). Likewise, references to Newsletters and similar publications will normally he cited in the text but not included in the reference list.

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